Chalcogenide Sensitized Carbon Based TiO$_2$
Nanomaterial For Solar Driven Applications

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Abstract

The demand for renewable energy is growing because fossils fuels are depleting at a rapid pace. Solar energy an abundant green energy resource. Utilizing this resource in a smart manner can resolve energy-crisis related issues.

Sun light can be efficiently harvested using semiconductor based materials by utilizing photo-generated charges for numerous beneficial applications. The main goal of this thesis is to synthesize different nanostructures of TiO$_2$, develop a novel method of coupling and synthesizing chalcogenide nanocrystals with TiO$_2$ and to study the charge transportation effects of the various carbon allotropes in the chalcogenide nanocrystal sensitized TiO$_2$ nanostructure.

We have fabricated different nanostructures of TiO$_2$ as solar energy harvesting materials. Effects of the different phases of TiO$_2$ have also been studied. The anatase phase of TiO$_2$ is more photoactive than the rutile phase of TiO$_2$, and the higher dimension of the TiO$_2$ can increase the surface area of the material which can produce higher photocurrent.

Since TiO$_2$ only absorbs in the UV range; to increase the absorbance TiO$_2$ should be coupled to visible light absorbing materials. This dissertation presents a simple approach to synthesize and couple chalcogenide nanocrystals with TiO$_2$ nanostructure to form a heterostructured composite. An atmospheric pressure based, single precursor, one-pot approach has been developed and tested to assemble chalcogenide nanocrystal on the TiO$_2$ surface. Surface characterization using microscopy, X-ray diffraction, and elemental analysis indicates the formation of nanocrystals along the nanotube walls and inter-tubular spacing. Optical measurements indicate that the chalcogenide nanocrystals absorb in the visible region and demonstrate an increase in photocurrent in comparison to bare TiO$_2$ nanostructure. The CdS synthesized TiO$_2$ nanostructure produced the highest photocurrent as measured in the three electrode
system. We have also assembled the PbS nanocrystal sensitized photoanode using the one pot method.

Finally, the charge transportation effect of carbon allotropes has been studied. For this we assembled TiO$_2$ conductive carbon chalcogenide nanocomposite system. Surface and elemental characterization using electron microscopy, EDX (energy dispersive x-ray) and x-ray diffraction pattern, provide the insights into the assembly of the nanostructure. Optical absorbance, Photo chronometry, Linear sweep voltammetry, and electrochemical impedance analysis have been used to provide opto-electronic performance of the material. We have studied the loading effect of various carbon allotropes, [fullerene (C$_{60}$), reduced graphene oxide (RGO), carbon nanotubes (CNTs), and graphene quantum dots (GQDs)], loading effect of chalcogenide, and effect of nitrogen doping on the carbon allotropes to optimize the performance of the heterostructure.

This dissertation is expected to impact the materials synthesis strategies and assemble the nanostructures used in composite electrode driven applications in the area of photo electrochemistry, PV, solar-fuels, and other associated topics of energy storage and sensing.
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Citations to Previously Published Work

This dissertation has been prepared from the following published papers

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The Introduction and the conclusion chapter has been added for dissertation writing purpose.

The following published journal paper and patent were written during my PhD study but were not used in this dissertation

Vaidyanathan (Ravi) Subramanian, Pawan Pathak, and Satyajit Gupta, Chalcogenide materials, chalcogenide based materials and methods of using and making the same. (International publication number WO 2016/149281 A1)
Chapter 1

Introduction

Energy consumption has played a key role in modern civilization of human society. Most of the energy in the world is produced from fuels (gas, coal and oil) a non-renewable source of energy, which cause global warming and pollution.\[1\] Furthermore, due to the rapid growth of the global population, the current energy source is insufficient to meet increasing demand. This results the seeking of a greener solution through a use of renewable sources of energy. Wind solar and hydroelecpower are currently the most common source of renewable energy are being studied. \[2\]

Solar energy is one of the best solutions to this problem because it is a clean, sustainable, and huge energy source. Inside the core of a sun, a nuclear fusion reaction takes place by creating helium from four hydrogen nuclei. During the process, the sun emits solar radiation that resembles the blackbody radiation at 5777 K, as presented in Figure 1.1 \[3\]. The solar spectrum measured above earths atmosphere is called the air mass zero (AM_0) spectrum, and the solar spectrum measured on earths surface at the solar zenith angle of 48.19° is called the air mass 1.5 (AM_{1.5}) spectrum.\[4\] These standard spectra of the solar radiation above the atmosphere and at the surface of the earth is presented in Figure 1.1.

The amount of energy from the sun that strikes the earth is approximately 120,000
Figure 1.1: Solar spectrum above the atmosphere (AM$_0$), at the surface (AM$_{1.5}$) and 5778 blackbody radiation. Figure is reproduced from reference [3].
TW (Tera Watt) whereas the current energy need of the world is approximately 13 TW. [5] Therefore, solar energy is considered to be an ideal energy conversion process that can meet this requirement.[6]

1.1 Nanostructured TiO$_2$ Films

TiO$_2$ is one of the most widely employed wide bandgap semiconductor materials on account of its chemical inertness, non-photo corrosion, low cost, and non-toxicity. [7] Titanium dioxide has a broad range of applications in solar cells, photocatalysis, sensing, energy storage, and self-cleaning devices.[7] These applications are dependent on the phase morphology and the crystallographic structure of TiO$_2$. [8] TiO$_2$ thin film serves as the electron-conducting layer in semiconductor nanocrystal sensitized third generation solar energy harvesting materials. One of the important approaches to improve the efficiency of the material is to fabricate a well defined nano-architecture, which decreases the probability of electron recombination.[9] In this dissertation, we have fabricated three different nanostructures: rod, tube, and branched nano architecture.

The efficiency of the semiconductor nanocrystal sensitized solar material depends on the number of the semiconductor nanocrystals absorbed onto the surface of the TiO$_2$ electrode. Therefore, the second approach to increase the efficiency is to increase the total surface area available for sensitizing. We have for the first time fabricated 3D branched TiO$_2$ nano architecture using TiCl$_3$ treatment. Branched TiO$_2$ architecture has a much larger surface area available for sensitizing compared to 1D nanorod architecture. The second chapter in this dissertation deals mainly with the branched TiO$_2$ architecture and its multifunctional applications.

TiO$_2$ has three stable phases: rutile, anatase, and brookite. The phase of TiO$_2$ is shown in Figure 1.2. In chapter 5, we discuss the photoactivity of the rutile and
anatase phases of TiO$_2$. For this, we have synthesized TiO$_2$ rutile nano rod in ITO coated glass slides and TiO$_2$ rutile nano rod passivated with an anatase layer. Anatase has an indirect bandgap whereas rutile has a direct bandgap (presented in Figure 1.3). [10] In direct bandgap semiconductor the photogenerated electron-hole pair can recombine by generating the photons whereas, in indirect bandgap semiconductor electron-hole pair recombination process occur by emitting a phonon and the photon. [10] The anatase phase of TiO$_2$ is more photoactive than the rutile phase because of the difference in their electronic bandgap.

Figure 1.2: crystal structures of (a) anatase, (b) rutile and (c) brookite phase of TiO$_2$. Figure is reproduced from reference [10]
As shown in the spectrum presented in Figure 1.1, the sun emits wide range (300 - 2500 nm) of electromagnetic radiation. However, the wide bandgap of TiO$_2$ limits the light absorbance to UV radiation, which is only 4% of the sunlight falling on the earth’s surface. Because of this reason, solar energy conversion ability of TiO$_2$ by itself is limited. This problem can be overcome by integrating a suitable visible light sensitizer, such as semiconductor nanocrystals with TiO$_2$. This will help to converted the broad solar spectrum.
1.2 Semiconductor Nanocrystal

Semiconductor nanocrystals are crystalline semiconductors that range in the size from 1-10 nm. When the semiconductor material is reduced to a size smaller than its bohrs exciton radius, it is called quantum dot. In quantum dot energy confinement effect can be observed due to the limitation in kinetic energy and the magnitude of confined energy is given by equation 1.1

\[ E_{\text{confinement}} = \frac{\hbar^2 \pi^2}{2a^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) = \frac{\hbar^2 \pi^2}{2\mu a^2} \]  

(1.1)

Where \( m_e \) is the effective mass of the electron, 
\( m_h \) is the effective mass of the hole, 
\( \mu \) is the reduced mass of the exciton system, 
and \( a \) is the radius of the quantum dot.[11]

As indicated by equation 1.1 smaller size crystals have higher confinement energy that leads to the variation in material properties such as bandgap, photoluminance, and the extinction coefficient compared to the bulk material. Due to this exciting property, extensive research has been carried out on quantum dots in a wide range of the applications such as biological imaging, solar energy harvester, fuel cell, and light emitting devices.

Semiconductor quantum dot nanocrystals are simple to process via solution-based chemistry makes them ideal for use in photo driven electrode material. Thus, they have the potential to be an alternative to the high cost and process-intensive materials that are currently used in photovoltaic devices.[12] However, the cost effective, efficient coupling of low bandgap 0D chalcogenide nanocrystals with wide bandgap 1D oxide surface is a challenging task. Chapter 3 in this dissertation deals with an efficient method of coupling developed in our laboratory.
1.3 Carbon Allotrops

The charge recombination effect dominates in nanometer sized semiconductor particle and the charge separation can be greatly improved by using charge transporter. [13] With regards to the aforementioned points, carbon is a universal, inexpensive, and unique additive that can aid in charge separation and transport. Elemental carbon is found in nature both as diamond and graphite. These two forms have different physical and electronic properties due their unique elemental arrangements. The crystal structure and the properties of graphite and diamond are fully understood, diamond consist of sp$^3$- hybridized carbon atoms whereas graphite consists of sp$^2$- hybridized carbon atoms. [14]

Synthetic carbon allotropes like graphene, reduced graphene oxide, carbon nanotube, and fullerene have outstanding electronic and physical properties. Due to this, numerous applications in the field of nanoelectronics, sensors, catalysis, solar cell, supercapacitors, and batteries have been realized. Graphene is a two dimensional sheet of sp$^2$- hybridized carbon of few layers of the graphite. It has high electrical ($10^4$ S cm$^{-1}$) and thermal (3000 W mK$^{-1}$) conductivity. [15] Graphene quantum dot is the small fragment of graphene where electronic transport is confined. [16]

Fullerenes are hollow cage sp$^2$- hybridized molecule discovered in 1985. C$_{60}$ is the most symmetrical molecules and looks like a soccer ball. Fullerene is made of a combination of hexagons and pentagons (normally 12). The size of the fullerene depends on the number of hexagons present in the fullerene structure. Carbon nanotubes have a one-dimensional nano structure with electrical and thermal conductivities of $1.85 \times 10^3$ S cm$^{-1}$ and 6, 600 W mK$^{-1}$ respectively. On the basis of the atomic arrangement, carbon nanotube have arm chair, zigzag, and chiral structures. [17] Graphene oxide is formed by reducing the graphite powder. Hummers method is the most common method to form bulk quantities of the graphene oxide. Graphene oxide can be easily
dispersed in the aqueous medium and can be reduced through heat treatment.

One of the important processes that limit the efficiency of photoanodes is the recombination of the photogenerated electron-hole pairs. Therefore, both of the charge carriers must be transported to opposite electrodes before recombination. As mentioned above, carbon allotropes are good conductors. Consequently, we have incorporated the carbon allotropes in the photoanode to reduce the recombination of the electron-hole pairs. In Chapter 4, we have compared the charge transport effect of synthetic carbon allotropes (carbon nanotube, reduced graphene oxide, graphene quantum dots, and fullerene) on the photoelectrochemical activity of chalcogenide nanocrystal sensitized 1D TiO$_2$ nanorod. The schematic is presented in Figure 1.4.

1.4 Working Principle of Quantum Dot Synthesized Solar Cell

When a semiconductor is exposed to light that has energy greater than the energy of the bandgap, photons can excite electrons from the valence band to the conduction band. During this process, positively charged holes are generated in the valance band. These electron hole pairs are called excitons. The excited electron can combine with the hole due to the columbic interaction. As the photoexcited electron is injected from the small bandgap semiconductor it moves toward the widebandap semiconductor whereas, holes moves towards the semiconductor nanocrystals. Holes accumulated in the semiconductor nanocrystal are scavenged by the electrolyte. The sulfide/polysulfide ($S^{2-}/S^{n2-}$) electrolyte is the most commonly used redox electrolyte in the semiconductor nanocrystal sensitized solar cell. In this dissertation we have used sodium sulfide electrolyte. As the sulfide electrolyte increases the photo anode stability because of the formation of a cadmium sulfoselenide layer on the semicon-
Figure 1.4: Schematic showing different carbon allotropes used on the CdS sensitized TiO$_2$ nanorod.
Figure 1.5: The Figure represents the working mechanism of the quantum dot sensitized photo anode in two electrode cell. Figure is reproduced from reference [18]
ductor nanocrystal surface.
The schematic working mechanism is shown in Figure 1.5.

1.5 Goal of the Dissertation

The focus of this dissertation is to minimize the cost of the quantum dot nanocrystal sensitized photoanode by improving the performance of the material and developing a new fabricating process using a wet chemical approach. Three main points are addressed in this dissertation:

1) We have fabricated rod, tube, and tree nano-structures of TiO$_2$. A novel synthesis
method has been developed to grow branch TiO$_2$ nano structure.

2) A unique, simple, and cost effective method of coupling quantum dots to TiO$_2$ nano architecture has been developed.

3) We have studied the effect of employing different conducting carbon layer on the performance of semiconductor nanocrystal sensitized TiO$_2$ nanorod.
Chapter 2

TiO$_2$ Nanobranch

Abstract: A nature-inspired tree-like 3D hierarchical titania/ TiO$_2$ architecture-was prepared as a facile strategy to assemble reduced graphene oxide/RGO (a facile charge transporter) and cadmium sulfide/CdS (a visible light harvester) is presented for the first time. The core 3D TiO$_2$ heterostructure was prepared using a TiCl$_3$ mediated surface treatment of titania nanorods on fluorine-doped tin oxide (FTO) coated glass-slides. The performance of the 3D TiO$_2$, which varies as a function of the treatment time, was first examined to achieve optimal photoelectrochemical response. Subsequently, the architecture was tested for its (i) theoretical water-splitting potential and (ii) ability to immobilize chalcogenide nonocrystals (CdS) with and without RGO. The best applied bias to photoconversion efficiency (% ABPE) was noted to be 0.36% (?0.15 V vs Ag/AgCl) for the TiO$_2$ architecture. A 140% increase with CdS deposition on the branched TiO2 indicated the structures ability to effectively immobilize the chalcogenide. The effect of RGO on the photoelectrochemical response was explored and an optimum loading (1 mg.mL$^{-1}$) of RGO was noted to boost the photoresponse by an additional 150% compared to CdS-only photoanodes. Further, stability analysis performed over 3 h showed that the presence of RGO significantly delays CdS corrosion-driven deactivation. Finally, the fundamental insights...
on the impact of RGO in the 3D TiO\textsubscript{2}/RGO/CdS photoanode and its effect on the charge transportation mechanism were examined using electrochemical impedance spectroscopy.

### 2.1 Introduction

Chalcogenide-based nanocrystals are highly effective light harvesting agents and are hence used as a major component in photocatalysis, photovoltaics, and photoelectrochemical processes. [19] Employing them allows one to leverage the unique properties they offer such as quantization effects [20, 21, 22] (size dependent optical properties) and broad spectral bandwidth absorbance [22] (achieved by sequential assembly of varying sized nanocrystals). Their potential to aid in the realization of multiple-exciton generation is a yet-to-be-fully-tapped feature that can significantly impact light to energy conversion efficiency.[23] Further, their adaptability to numerous cost effective methods to integrate them with a large bandgap oxide surface (such as SILAR [24] or chemical linking[25] ), compatibility with metal nanoparticles [26] or conductive carbon (for accelerating redox kinetics and charge transport) are added benefits that make them leading candidates for consideration in light-driven applications.

Traditionally, the bare [27] or doped-chalcogenides [28] are immobilized on large bandgap and high surface area 0D oxides [29] such as TiO\textsubscript{2} or ZnO to i) enhance their distribution, ii) improve light absorbance, and iii) produce high magnitudes of photoelectrochemical responses. These responses occur by the well know mechanism of charge separation followed by hopping across the interface conduction bands of the chalcogenide to the oxide. One of the factors that critically influence this mechanism is the physical dimension of the underlying oxide. [30, 31] It is reported that 1D oxide films offer improved prospects for charge transport compared to the 0D films.[32, 33]
This is because, high density of interparticle grain boundaries, characteristic to a 0D particulate oxide film, is found to be significantly reduced in epitaxial grown 1D continuum of the oxide films. [34, 35] Comparative studies involving 0D and 1D oxides have shown that photocurrent magnitudes are several times higher with the 1D film. [36] Recently, three dimensional TiO$_2$ architectures have been reported in literature.[37, 38, 39] From an application standpoint, it was also recently reported that 3D oxide films consisting of 1D TiO$_2$ rods with microscopic outwardly radiating branches are far superior to unbranded 1D TiO$_2$ which in turn is superior to 0D structures.[40] Therefore, it remains to be seen how these physical features of the 3D oxides aid in improving PEC responses once the chalcogenides are immobilized on their surface.

Another aspect that impacts charge transport and is as noteworthy of consideration as light harvesting, is the role of additives that promotes the transportation of charges once they are photogenerated. Reduced graphene oxide (RGO) is a graphene-like conductive carbon additive that can accelerate the transport of the electrons once photogenerated because it has a charge mobility of 200,000 cm$^2$ V$^{-1}$ s$^{-1}$. [41, 42, 43] RGO has been used with promising results as a part of 0D oxide composites: 0D TiO$_2$ -dyes [44] or 0D ZnO-chalcogenides. [45] These results suggest that the integration of a 0D oxide with a facile charge transporter (RGO) and a light harvester can provide effective solar-to-electric conversion. With respect to 1D systems, we have recently demonstrated that 1D ZnO nanorods can be used as a substrate to immobilize CdS with RGO. [46] Scheme 2.1 shows the benefits of such an integration approach involving 1D ZnO.

The present work discusses a synthesis strategy for the designing of a unique tree-like 3D TiO$_2$ architecture that starts as a 1D TiO$_2$ with synthesis condition dependent ability to transform into tree-like 3D TiO$_2$. For the first time, the deposition
Figure 2.1: Notable benefits of the inclusion of reduced graphene oxide (RGO) in and oxide chalcogenide composite.
of chalcogenide CdS nanocrystals and reduced graphene oxide on this 3D branched TiO₂ architecture has been examined and a systematic study undertaken to characterize its optical, surface, and photoelectrochemical properties. The ensuing analysis shows that i) these 3D tree-like transformable architectures can be candidate photoanodes for photoelectrochemical water splitting reactions, ii) the cylindrical rod-like outgrowths favorably contribute to improving the deposition of the CdS, iii) the CdS presence on the 3D TiO₂ enhances the charge generation due to visible light activity of the CdS deposits, and iv) the RGO boosts the photoelectrochemical response of the TiO₂/CdS architecture, multifold by aiding the transport of the photogenerated electrons.

2.2 Experimental Section

2.2.1 Chemicals, Optical, surface, Photoelectrochemical, and Photocatalysis Studies

97% titanium (IV) isopropoxide, titanium (IV) butoxide, and cadmium nitrate [Cd(NO₃)₂] were obtained from Sigma Aldrich. Titanium (III) chloride was obtained from Across Organics. Sodium sulphide nonahydrate (Na₂S 9H₂O) was obtained from Alfa Aesar. 30% solution of hydrogen peroxide (H₂O₂) was purchased from Mallinckrod. Sodium nitrate (NaNO₃) and potassium permanganate (KMnO₄) were obtained from Fisher Scientific. Methanol (CH₃OH), concentrated hydrochloric acid (HCl), and concentrated sulfuric acid (H₂SO₄) were obtained from local suppliers and were used without further purification. Graphite flakes were purchased from Bay Carbon Inc. Deionized (D.I.) water was obtained from a Millipore lab water purification system.

The UV-visible absorbance studies were performed using a Shimadzu UV-2501PC.
spectrophotometer in absorbance mode, in the wavelength range of 300 nm-900 nm. Imaging of the samples (after thermal treatment of both the rod and branched structures TiO$_2$) was carried out using a Hitachi FESEM scanning electron microscopy (SEM) machine equipped with an oxford EDS analyzer. The TiO$_2$ structures deposited over FTO samples were coated with platinum prior to the examination. A JEOL 2100F high resolution transmission electron microscope (HRTEM) was used to examine the size of CdS deposits on TiO$_2$. The CdS was scrapped from the TiO$_2$ surface in a careful manner and then dispersed in ethanol by ultrasonication. From the dispersion, one drop was carefully deposited over carbon coated Copper grid, dried and used for TEM analysis. A Philips XRG 3100 X-ray diffractometer, operated at 35 KV was used to obtain the X-ray diffraction pattern and identify the phase of the material after each annealing step. The various TiO$_2$ structures on FTO, were directly mounted over the XRD instrument, while the CdS deposition was carried out over scratched glass slides.

The photoelectrochemical studies were carried out in a three-electrode system, using a quartz cell with Pt mesh as a counter electrode and a leak free Ag/AgCl (in 3M KCl) as the reference electrode. 0.1 M Na$_2$S in water was used as the electrolyte. In case of ABPE measurement of the TiO$_2$ based photoanodes, 1M KOH was used as an electrolyte. I-t characteristics were collected using an Autolab PGSTAT 30 electrochemical analyzer. The working electrode was irradiated with a 500W Newport Xenon lamp equipped with 0.5 M CuSO$_4$ solution as a far UV cutoff filter; this also attenuates the light intensity to $\sim$ 90 mW cm$^{-2}$. Impedance measurements were performed in a GAMRY setup, over the frequency range 0.01 to 105 Hz with 0.5 bias voltages. All the impedance measurements were carried out using the same electrochemical set-up described above, with 0.1 N Na$_2$SO$_4$ as an electrolyte and the obtained spectra were fitted to obtain equivalent circuits. The synthesis details are
discussed below.

2.2.2 Preparation of the Photoanode Samples

Preparation of the seed solution

FTO coated glass slides (supplied from Hartford Glass) were degreased by ultrasonication in DI water, isopropanol, and acetone separately (in that order) for 5 minutes each. A solution using 100 mL of ethyl alcohol and 10 mL of titanium (IV) butoxide was prepared for seeding the growth of the nanorods. [47] Each slide was spin coated with 10 drops (∼0.4 ml) of the seed solution over the conductive surface of the FTO slides at 2500 rpm for 30 s. The slides were then annealed at 500 °C for 30 minutes in air.

Synthesis of TiO₂ nanorods (rTiO₂) on the seeded FTO

TiO₂ nanorod arrays were grown over FTO substrates using a solvothermal approach. 60 mL of 6N hydrochloric acid was introduced in a Teflon-lined stainless steel autoclave of 100 mL capacity. 1 mL titanium-butoxide was added to this solution and stirred well to form a homogeneous mixture. Two spin coated FTO substrate were placed at an angle against the inner wall of the autoclave, with the conductive side facing towards the wall of Teflon liner. The autoclave was sealed and kept in an oven at a temperature of 180 °C for 6 h to facilitate the growth of the nanorods. Sufficient time was provided for the autoclave to cool to room temperature under natural convection. The FTO substrate was removed from the autoclave, washed in a mixture of methanol and D.I. water in the ratio of 1:1, dried in ambient air, and stored in dark.
Preparation of branched TiO$_2$ (bTiO$_2$)

TiO$_2$ branched architecture was grown over FTO slide with the TiO$_2$ nanorod prepared by the method outline above. 80 mL DI water was well mixed with 1 mL 12 N HCl. 1 mL of TiCl$_3$ was added to this solution drop wise to prepare a branch forming solution. Four FTO slides with TiO$_2$ nanorods were placed at an angle against the wall of the beaker, supporting each other at the base with the conductive side facing up, and containing the branch forming solution. The films were kept there for varying durations (1 to 4 h) at a temperature of 85 °C inside an oven, then rinsed thoroughly with ethanol. All the samples (rod and branched TiO$_2$), were subsequently annealed at 450 °C for 30 min in air, prior to further studies.

Deposition of CdS over TiO$_2$ nanorod with branched architecture by SILAR approach

The chalcogenide deposits were prepared using the SILAR approach. [48, 49] Clean FTO substrates deposited with TiO$_2$ from section 2.1.2 and 2.1.3 were exposed to a 0.5 M Cd(NO$_3$)$_2$ solution in (CH$_3$OH)/water mixture (1:1) for 2 min, where the Cd$^{2+}$ precursor adheres to the TiO$_2$ surface. This is followed by washing with D.I. water for 2 min. The samples were then immersed in 0.5 M Na$_2$S solution for 2 min, where the precursor ion reacts with S$^{2-}$. This was followed by cleaning the sample in D.I. water for 2 min. The steps were repeated again to increase the CdS deposits. The CdS deposited [as well as the graphene oxide or GO loaded FTO samples] were annealed at 350 °C for 3 h in ammonia atmosphere. The temperature of the oven was allowed to rise up to 350 °C at the rate of 2.2 °C per minute and kept constant for 3 h at that temperature. The contents were allowed to cool to room temperature at the rate of 2.2 °C per minute.
Synthesis of GO Using the Hummers Method

The Hummers method: The GO was synthesized using the Hummers method, [50] a technique involving an oxidative exfoliation of graphite sheets. Briefly, graphite powder and NaNO$_3$ was added to concentrated H$_2$SO$_4$ while maintaining the temperature of the mixture at 0 °C. KMnO$_4$ was slowly added to it under constant stirring condition and the temperature was allowed to raise up to 20 °C. The temperature of the bath was later increased to 40 °C and maintained for an hour. The solution becomes highly viscous and the resulting mixture was slowly diluted by adding D.I. water. The temperature of the bath was then increased to 95 °C and maintained for an hour. Subsequently, H$_2$O$_2$ solution was slowly added and the mixture was stirred. After one hour, it was filtered off and washed with warm water for several times until it becomes neutral. The recovered cake was dispersed in water and finally collected by centrifugation.

Graphene oxide coating The GO was dispersed in DI water in concentration of 0.5, 1, 2, and 3 mg mL$^{-1}$. For thorough mixing of GO in DI water, the solution was ultrasonicated for 1 h. The resulting suspension was coated over the conductive surface of branched FTO samples by a drop casting method. Then the samples were dried in air before CdS deposition by SILAR method. Thermal treatment to produce RGO was performed using the approach outlined in above section. For convenience, the rod-shaped TiO$_2$ and the branched TiO$_2$ are labelled as rTiO$_2$ and bTiO$_2$ respectively in the text and the figures.
2.3 Results

2.3.1 Surface, Optical, and Photoelectrochemical Responses of the Branched Architecture

Surface features of the TiO$_2$ structure as a function of TiCl$_3$ treatment time

All the SEM imaging were performed after thermal annealing as discussed in section 2.2.2. The exposure of the seeded film to an acidified solution of titanium (IV) butoxide under hydrothermal treatment leads to the epitaxial growth of several physically similar nanorods juxtaposed next to one another with inter-rod spacing and a rect-
angular cross-section as shown in the SEM image -Figure 2.2A (The view of a rTiO$_2$, indicating its length as $\sim$4 $\mu$m is shown in the inset of Figure 2.2A). After immersion of this rTiO$_2$ film in a TiCl$_3$ solution, a time dependent transformation of the rod is evident. The representative time resolved SEM images taken in an angle view shown in Figure 2.2B-E. at 1 h intervals indicate the evolution of the structure. In the first hour, particulate deposits were observed at the surface as shown in Figure 2.2B. These deposits change its form between $t$=1 h and 3 h. After 2 h, small and distinct microscopic branches appear all-over the walls of the TiO$_2$ trunk as shown in Figure 2.2C. Continued exposure to the TiCl$_3$ solution leads to a growth and densification of these branches (Figure 2.2D-E), indicating the evolution of the TiO$_2$ from a Figure 2.2D to a treelike 3D architecture.

After a 4 h exposure; the TiCl$_3$ solution was observed to become turbid and the TiO$_2$ trunk appears thinner. This observation could be attributable to the fissuring of the trunk, contributing to the formation of the smaller branches at an angle with the main trunk. This resulted in a decrease in the absorbance, observed in the UV-Vis analysis (Figure 2.4). Thus, the 1D TiO$_2$ transforming into a unique 3D treelike architecture by a time dependent evolution involving microscopic branches, is evident from the collage of images. The Figure 2.5) shows the XRD of the nanorods before and after the TiCl$_3$ treatment, indicating that the TiO$_2$ structures (rod and branched) are in tetragonal rutile phase. Oxidative, thermal treatment is required to transform the material from amorphous state. Following such treatment of both structures, the presence of the peaks characteristic to the crystalline TiO$_2$ are noted (JCPDS file # 76-1940).
Figure 2.3: Photoelectrochemical response of the bTiO$_2$ prepared over a duration of (a) 1, (b) 2, (c) 3, and (d) 4 h. The * indicates the value reported with a TiO$_2$ of a similar architecture in [37] (PEC conditions: CE, Pt; RE, Ag/AgCl; electrolyte, 1 M KOH).
Figure 2.4: The absorbance spectra of the rTiO$_2$ as a function of wavelength for different treatment times [after (a) 1 h, (b) 2 h, (c) 3 h, and 4 h] at 80 °C in the presence of a TiCl$_3$ solution.
Figure 2.5: The crystalline phase of the rod TiO$_2$ (rTiO$_2$) and the branched TiO$_2$ (bTiO$_2$) are examined using XRD over a 2$\theta$ range from 20$^\circ$ to 80$^\circ$. The XRD shows that both structures are in tetragonal rutile phase. A relative higher intensity peak at 2$\theta$=62.9$^\circ$ suggests that TiO$_2$ growth takes place along the 002 plane.
Optical properties of the TiO\textsubscript{2} architecture

The absorption spectra of the rod vs. branches are shown in the Figure 2.4. The optical response [onset at 413 nm and UV absorbance of TiO\textsubscript{2}] is along expected lines as noted elsewhere. The slight red shift of \(\sim 10\) nm (Figure 2.4c) in the absorbance coinciding with the branching is consistent with prior reported findings and is attributed to the directionality and the additional absorbance associated with the large aspect ratio rod. With an increase in the time for the TiCl\textsubscript{3} treatment, the absorbance onset remains the same while the overall absorbance increases up to 3 h. This increase in the overall UV absorbance is attributed to the increased TiO\textsubscript{2} content at the walls of the nanorod.

Photoelectrochemical responses of the TiO\textsubscript{2} under UV-vis illumination

J/V measurements - The performance of the 1D and 3D TiO\textsubscript{2}, were evaluated by using them as an electrode (photoanode) in a photoelectrochemical or PEC cell. J-V res responses were examined using 1 M KOH (Figure 2.3), under Xe lamp with CuSO\textsubscript{4} filter (energy output of \(\sim 90\) mW cm\textsuperscript{-2} (equivalent to AM 1.5 illumination). All the branched TiO\textsubscript{2} demonstrated a photoresponse as shown in the Figure 2.3. The J/V measurements of the samples in the absence of photoillumination were also performed as a control (2.6). A negligible photoresponse of the order of \(\sim 1-5\) \(\mu\text{Acm}^{-2}\) was noted; indicating that the current produced is because of photogenerated electrons. The photocurrent gradually increases with the surface treatment time, until 3 h. This observation is attributed to the photogenerated electrons produced by the UV absorbing TiO\textsubscript{2} distributed around the TiO\textsubscript{2} nanorod. The maximum photocurrent is obtained with the 3 h TiCl\textsubscript{3} treated bTiO\textsubscript{2} and it is 135 % higher than the rTiO\textsubscript{2} unexposed to the TiCl3 solution. Any further increase in the TiCl\textsubscript{3} treatment beyond 3 h was observed to be detrimental to photocurrent generation. This could
Figure 2.6: The photoelectrochemical response of the bTiO$_2$ prepared over a duration of (a) 1h, (b) 2h, (c) 3h, and (d) 4h measured in the absence of any photoillumination, performed as a control. This indicates a negligible photocurrent under dark condition. [PEC conditions: CE: Pt, RE: Ag/AgCl, Electrolyte: 1M KOH]
be correlated with the etching of TiO$_2$ as evident from the absorbance information presented in Figure 2.4.

Distinguishing features of the synthesis approach and the architecture - It should be noted that in a previous study a polymeric-sol method is used as a precursor to deposit a seed layer prior to growing the whiskers.[37] This method facilitates the formation of a 3D branched structure with long aspect ratio nanowiskers (more than twice the length of the whiskers noted in this work). That structure results in a photocurrent of 0.81 mA cm$^{-2}$ [at an applied bias of 0.8 V versus reversible hydrogen electrode (RHE)]. Since the only reference data reported is at 0.8V, this number is indicated as an asterix (*) in presented in Figure 2.3. In contrast, this study demonstrates the uses of a simpler approach that still is able to yield a similar photocurrent [0.80 $\pm$ 0.06 mA cm$^{-2}$ at an applied bias of 0.8 V, versus reversible hydrogen electrode (RHE)]. The distinctive aspects between our method and the ones reported in the literatures include: (1) the application of a simpler precursor (non-polymeric) solution to form the TiO$_2$ seeds over FTO slides, (2) only acidified TTIP (titanium isopropoxide) was used for the solvothermal growth as compared to a complex solution of potassium titanium oxalate in diethylene glycol (DEG) [52] (3) no separate seed layers were deposited at the rod surface to form the branches [37], and (4) the 3D bTiO$_2$ formed here demonstrates cylindrical rod-like deposits instead of whiskers.
Figure 2.7: Absorbance spectra of the (a) bTiO\textsubscript{2} prepared over 3 h exposed to Cd/S in a SILAR process over (b) 5 cycles, (c) 10 cycles, (d) 15 cycles, and (e) 20 cycles. The figure shows how the initial cycles aid in the steady increase in the optical density (at an arbitrary wavelength of 500 nm) and then tappers off after 15 cycles.
2.3.2 Optical, Surface, and Photoelectrochemical Responses of the Chalcogenide Sensitized Branched Architecture and the Role of RGO

Optical analysis of the CdS and RGO/CdS assemblies on rTiO$_2$ and bTiO$_2$

The electrostatic interactions between Cd$^{+2}$ and S$^{-2}$ at various available nucleating sites makes SILAR approach a simple and effective strategy to assemble chalcogenide deposits on intricate surfaces. The formation of the deposits on the branched architecture was monitored after every cycle. After $\sim$ 4-5 SILAR cycles, the formation of distinct yellow deposit, visible to the eye is noted, consistent with CdS formation.[53, 54] The onset absorbance is observed in this case at 536 nm. The increase in the absorbance indicates that the bTiO$_2$ and rTiO$_2$ surface participates as nucleating sites for the formation of these deposits. XRD analysis confirms that the SILAR deposits are of the CdS. The SILAR cycles for the CdS deposition over the bTiO$_2$ samples were optimized from UV-Vis analysis. For consistency the rTiO$_2$ was also exposed to the same number of SILAR cycles as the bTiO$_2$. It took 15 cycles for the bTiO$_2$ before the absorbance tapered (Figure 2.7). Any further increment in the SILAR cycle does not improves the absorbance indicating a maximization of the CdS loading. Interestingly, it can be noted, the absorbance of (e) at 350-500 nm goes down compared to (d). This is possibly due to the etching out of overloaded CdS particles from the vicinity of the solution-surface interface after a saturation limit of 15 SILAR cycles. Similar reduction in absorbance has been reported with wet chemically deposited CdS as reported elsewhere. [55]

The effects of RGO presence was first examined using absorbance measurements. The UV-Vis absorbance of the annealed TiO$_2$/CdS samples without RGO and with RGO is shown in Figure 2.8. The focus is more on the performance of bTiO$_2$ with
Figure 2.8: Absorbance spectra of the (a) rTiO$_2$, (b) bTiO$_2$ prepared over 3 h, (c) bTiO$_2$/CdS, and (d) bTiO$_2$/RGO/CdS (RGO: 1 mg mL$^{-1}$ and CdS 15 cycles).
RGO from this point since the rTiO$_2$ showed a lower performance (Figure 2.3) than the bTiO$_2$. Thermal treatment is one of the approaches to perform GO to RGO transformation. [56, 57] A red-shift is noted with the CdS films after the annealing of the samples at 350 °C. This effect is attributed to the increase in the CdS nanocrystal size afforded by the thermal treatment. [58] Interestingly, the absorbance of the RGO loaded samples was observed to be higher than CdS-only samples. The increased absorbance indicates that one can achieve greater CdS deposition and distribution, by leveraging additional site that become available by the RGO presence.

**Surface analysis of the composite assembly using SEM and (HR)TEM**

The distribution of the CdS on the bTiO$_2$ exposed for various duration was examined using SEM to determine the quality of the deposits. The Figure 2.9 shows the representative images of CdS on 2 h (Figure 2.9A) and 3 h (Figure 2.9B) bTiO$_2$. It can be generally noted that CdS formed by the SILAR treatment significantly alters the interstitial spaces in both 2 h (Figure 2.9C) and 3 h (Figure 2.9D) bTiO$_2$ samples. On comparing these images of CdS deposits with the corresponding bare 3D SEMs of TiO$_2$, an enhancement in the surface roughness, packing density, and topographical changes can be noted, irrespective of the nature of the branching. This indicates that the CdS can be successfully integrated with any form of 3D TiO$_2$ architecture using the SILAR approach. It is to be noted that the SEM image of the bTiO$_2$/CdS with RGO is similar to the 2.7D. This suggests that the RGO is well integrated into the 3D structure.

Further analysis of the deposits was performed using the HRTEM. The CdS nanocrystal size was estimated to be 6±1 nm [Figure 2.9 (E) and (F)]. The high resolution fast Fourier transformation (FFT) analysis of (Figure 2.9F) indicates a d-spacing value of 0.33 nm, corresponding to the 002 plane of the as synthesized CdS.
Figure 2.9: SEM images of the 3D structures (A) bTiO$_2$ (t = 2 h), (B) bTiO$_2$ (t = 3 h) before SILAR treatment, (C) bTiO$_2$ (t = 2 h)/CdS, (D) bTiO$_2$ (t = 3 h)/CdS using 15 SILAR cycles, while (E) and (F) show the HRTEM of the as-deposited CdS nanocrystals over bTiO$_2$ (after 15 SILAR cycles). The high resolution fast Fourier transformation (FFT) analysis of (F) indicates a d-spacing value of 0.33 nm, corresponding to the 002 plane of the as-synthesized CdS nanocrystals and the high resolution FFT pattern is shown in the inset of (F)
Figure 2.10: PEC responses showing the multiple on-off cycles using the (a) bTiO$_2$ prepared over 3 h, the CdS prepared by the SILAR approach on the bTiO$_2$ by exposing to (b) 5 cycles, (c) 10 cycles, (d) 15 cycles, (e) 20 cycles (PEC conditions: CE, Pt; RE, Ag/AgCl; electrolyte, 0.1 N Na$_2$S).
Figure 2.11: Comparative values of the stabilized peak current obtained in the PEC measurements of panel (a) with (A) CdS showing a 140% increase, (B) RGO/CdS showing an additional 150% increase, and (C) showing the overall increase of 500% because of the combined effect of CdS and RGO (PEC conditions: CE, Pt; RE, Ag/AgCl; electrolyte, 0.1 N Na₂S)
Figure 2.12: A) Shows the XRD diffraction pattern of the CdS nanocrystals, the peaks at 002, 110, and 112 corresponds to the wurtzite phase of CdS (JCPDF card # 77-2303) while (C), (D), and (E) shows the decoupled color distribution of CdS, Cd\(^{2+}\) and S\(^{-}\) respectively.

nanocrystals and the high resolution FFT pattern is shown in Figure (2.9F-insert). The X-Ray diffraction pattern of the film after the SILAR deposition is shown in Figure 2.12 indicating the formation of wurtzite phase of CdS (JCPDF card # 77-2303). The color mapping of the CdS [Figure 2.12 (B)] and the decoupling of the signals from elemental cadmium (Cd) and sulfur (S) are shown in the Figure 2.12 (C) and (D) respectively. The color mapping indicates the uniform distribution of CdS. Thus, the XRD, SEM, and the HRTEM analysis reveals that the CdS can be integrated across most available surfaces of the complex 3D TiO\(_2\) architecture both in the presence and absence of the RGO.
Photoelectrochemical responses of the CdS and RGO/CdS on the branched TiO$_2$

As indicated earlier, the branched TiO$_2$ demonstrated the highest current of 0.80±0.06 mA cm$^{-2}$ in 1 M KOH solution (as an electrolyte) at an applied bias of 0.8 V. Since, CdS is involved as a light harvesting agent, from a stability standpoint PEC data for photoelectrodes were examined using 0.1 N Na$_2$S solution. The effects of the CdS deposits formed after the 5th SILAR cycle showed an increase in the photocurrent beginning with $\sim$ 0.72 mA cm$^{-2}$. The maximum photocurrent was noted after 15 SILAR cycles at 1.2 mA cm$^{-2}$. It corresponds to the highest absorbance that the CdS/bTiO$_2$ demonstrated, indicating that the photocurrent is proportional to CdS content and a significant contribution to photocurrent occurs because of the CdS nanocrystal deposits around the bTiO$_2$. Chronoamperometry measurements indicating several on-off cycles are shown in Figure 2.10. The instantaneous current generation demonstrates the existence of a facile electronic contact between the bTiO$_2$ and CdS.

The addition of RGO with a 0D oxide is beneficial in multiple ways: positively enhances electron transport from a visible light harvester [59] or accelerate photocatalysis. [60] The beneficial effect of RGO inclusion is also noted with 1D systems. The integration of the RGO with the branched nanorod structure and CdS nanocrystals further enhances the photocurrent (RGO addition effect is shown in supporting information). The RGO loading was optimized by casting various concentrations of the precursor-GO solutions (0.5, 1, 2 and 3 mg mL$^{-1}$) on the branched TiO$_2$ as shown in the Figure 2.13. It is to be noted that the thermal treatment mediated conversion of GO to RGO was investigated in detail in our previous work using XPS and Raman studies.[43] The SILAR processes were however performed at the previously optimized 15 cycles. It was observed that, 1 mg mL$^{-1}$ produces the best photocurrent and any
Figure 2.13: The figure shows the photocurrent density of bTiO$_2$/RGO/CdS photoanodes as a function of RGO concentration varying from 0 to 3 mg ml$^{-1}$. The measurements were performed in a three electrode set-up, using 0.1 M Na$_2$S as an electrolyte.
further increase in the RGO addition decreases the photocurrent value. Under these optimized conditions, at $\sim 3$ mA cm$^{-2}$, a further $\sim 150\%$ higher photocurrent is noted with the bTiO$_2$/RGO/CdS compared to the bTiO$_2$/CdS as shown in Figure 2.11. This work shows a systematic comparison of the 3D bTiO$_2$ architecture with CdS deposits demonstrating a 140% increase in photocurrent while the addition of RGO boosts this to $\sim 500\%$. This highlights the benefits of the strategic assembly of these components on the bTiO$_2$.

Suitability of the TiO$_2$/RGO/CdS assembly as electrode for photoelectrocatalysis of water

(Phot)electrochemical processes can be applied to perform hydrogen evolution from pH adjusted water. The suitability of the 3D bTiO$_2$ architecture as a potential water splitting electrode can be determined using theoretical analysis of the PEC measurements. Applied bias to photo-electrochemical hydrogen generation efficiency (or ABPE) is a measure of the photoconversion efficiency for water oxidation. The ABPE is estimated using the following equation:

$$\eta = \frac{J_{ph} \times (1.23 - E_{RHE})}{P_{total}} \times 100\%$$  \hspace{1cm} (2.1)

where, the $E_{RHE}$ was calculate using the following equation:

$$E_{RHE} = E_{Ag/AgCl}^0 + E_{Ag/AgCl} + 0.059pH$$  \hspace{1cm} (2.2)

Here, $E_{Ag/AgCl}^0$ (0.1976 V at 25 oC) is the standard potential of the reference electrode (Ag/AgCl). $\eta$, $J_{ph}$ and $P_{total}$ are the efficiency, photocurrent density obtained under the applied bias ($E_{RHE}$ vs. reversible hydrogen electrode) and intensity of the incident light, respectively. The photoanode efficiency estimates are shown in Figure 2.15. The ABPE was observed to increase until the first 3 h of TiCl$_3$ treatment and
Figure 2.14: The applied bias photon-to-current efficiency (ABPE) versus applied potential values were determined for the photoanodes (a) bTiO$_2$/RGO/CdS and (b) bTiO$_2$/CdS. The measurements were performed using a three electrode set-up in the presence of 0.1 N Na$_2$S as an electrolyte.

decrease subsequently. The maximum ABPEs for 1 h, 2 h, 3 h and 4 h treatment time are 0.16 (at -0.05 V versus Ag/AgCl), 0.22 % (at -0.15 V versus Ag/AgCl), 0.36% (-0.15 V versus Ag/AgCl) and 0.26 % (at -0.15 V versus Ag/AgCl), respectively.

It is reported that TiO$_2$ - chalcogenide system can also be used for water splitting reactions to produce hydrogen.[66, 67] While a detailed study on this aspect will be a separate experiment topic, it would be worthwhile to perform a PEC analysis and determine the suitability of the CdS and RGO/CdS deposits for such an application. The on/off cycles of Figure 2.16 and the J/V data of Figure 2.17 indicate that the RGO presence consistently enhances the performance of the 3D bTiO$_2$/CdS. Applying
Figure 2.15: Estimated values of the applied bias photon-to-current efficiency or ABPE (using eq 2.2) for the (a) rTiO$_2$ and bTiO$_2$ prepared over a duration of (b) 1, (c) 2, (d) 3, and (e) 4 h.
Figure 2.16: (a) PEC responses showing the multiple On-Off cycles using the (a) rTiO$_2$, (b) bTiO$_2$ prepared over 3 h, (c) rTiO$_2$/CdS, (d) bTiO$_2$/CdS, and (e) bTiO$_2$/RGO/CdS (PEC conditions: CE, Pt; RE, Ag/AgCl; electrolyte, 0.1 N Na$_2$S).

The equations mentioned above, the maximum ABPE values of 1.8 % and 0.53 % respectively was obtained for the CdS deposited branched nanorod structure with and without RGO. This shows that ABPE improves $\sim$240%, when RGO is sandwiched in the photoanodes as indicated in the Figure 2.14. These preliminary insights set the stage for further systematic experimental analysis of the electrode to provide more information on this application of the 3D bTiO$_2$/RGO/CdS.
Figure 2.17: PEC responses showing J/V characteristics using the (a) rTiO$_2$, (b) bTiO$_2$ prepared over 3 h, (c) rTiO$_2$/CdS, (d) bTiO$_2$/CdS, and (e) bTiO$_2$/RGO/CdS (PEC conditions: CE, Pt; RE, Ag/AgCl; electrolyte, 0.1 N Na$_2$S.)
2.4 Discussions

The observation from the previous section indicates the i) benefits of the transformation of 1D rTiO$_2$ to a 3D bTiO$_2$ architecture, ii) compatibility of the 3D bTiO$_2$ with the CdS, and iii) the role of RGO in boosting the performance of the 3D bTiO$_2$/CdS composite. The following section provides additional insights into the fundamental photoelectrochemical processes that occur in this assembly as well as insights into the stability of the bTiO$_2$/RGO/CdS architecture.

2.4.1 Electrochemical Impedance Analysis

The standard (P)EC characterization techniques are generally focused on providing information on bulk characteristics. One needs to fully understand the internal functioning of the electrode for a complete picture of the mechanistic of the process, especially when it involves multiple components, as is the case in this architecture. Additional information can be obtained by observing electrochemical impedance spectroscopy for such particulate composite photoelectrodes.[68] Nyquist plot, Bode plot, and equivalent circuits of branch architecture with CdS and branch architecture with RGO and CdS are presented in Figure 2.18. The charge transfer resistance is proportional to the diameter of the arc of the Nyquist plot at constant bias voltage.[69] The complex impedance plane or Nyquist plot (Figure 2.18A) suggests that the charge transfer resistance is higher for the CdS-only sample in comparison to the sample sandwiched with RGO. This observation reiterates the results in the Figure 2.16 and 2.17 that the presence of RGO is favorable to charge transportation.

In the Bode plot (Figure 2.18 B, C), a logarithm scale representation to reveal the photoelectrode response at lower frequencies, is presented. From Figure 2.18B, it is observed that the branch architecture with CdS and RGO showed lower AC impedance than that of branch architecture with only CdS. Further, from the Bode
Figure 2.18: Collage shows the various results of the EIS analysis on the bTiO$_2$/CdS and bTiO$_2$/RGO/CdS: (a) Nyquist plot, Bode plots representing the variation in the magnitudes of (b) impedance with frequency, (c) phase angle with frequency, and (d) corresponding equivalent circuit of the heterostructures composite.
Figure 2.19: Time-dependent stability analysis of the electrode performed over a duration of 10000 s (≈2.8 h) under a continuous AM 1.5 illumination to evaluate the effects of RGO addition on the durability of the bTiO$_2$/RGO/CdS heterostructure.

Phase plot in Figure 2.18C, the characteristic frequency for the RGO loaded sample is nearly five times lower than the sample without RGO, suggesting that the electron lifetime of RGO loaded sample is five times higher than the sample without RGO. This analysis provides a perspective into how well the RGO aids in promoting the charge separation and prolonging the lifetime of the photogenerated electron and help complement the results observed in the comparative analyses of the electrodes in Figure 2.10 and 2.11.
2.4.2 Long Term Stability Analysis

From a practical application standpoint, it is important to understand the long-term performance of the electrodes as photoanodes. Particularly since CdS is involved as the photosensitizer, its corrosion is a well-known concern and several works have alluded to this challenge with CdS-based systems. [70, 71] The long-term stability of the CdS loaded samples vs RGO as an inter-layer was therefore analyzed by the photocurrent measurement under a constant UV-vis illumination as indicated in 2.19. This shows that RGO-interlayer exhibited a more beneficial role in stabilizing the photocurrent than CdS-only samples. In the case of CdS-only samples, 51% reduction in the photocurrent was observed, while in RGO loaded with CdS samples, only 6.5 % reduction was noted. Further, RGO-based samples retained its higher photoconversion efficiency over the complete 3 h duration of the test. The relative decrease in the photocurrent values observed in both the cases is due to photochemical bleaching of sulfide (S^-). Sulfide (S^-) photo-oxidizes to sulfate (SO_4^{2-}) species by the dissolved oxygen species present in the electrolyte solution.[72]

2.4.3 Beneficial Role of RGO in a 3D bTiO_2/RGO/CdS Architecture

The charge transportation mechanism in the bTiO_2/RGO/CdS electrode is shown in scheme 2.20. The beneficial role of RGO in the improvement of the PEC behavior of the photoanodes noted is (1) boosting in the photocurrent density by 3-fold, (2) shift in the apparent flat- and potential, and (3) significantly delaying the photocurrent decay for a prolonged period of illumination. The increase in the photocurrent is due to the effective electron shuttling capability of the RGO interlayer. This conductive carbon interlayer assists in the charge passage from the conduction-band electron of
Figure 2.20: Strategic Integration of the RGO (Conducting Medium) with CdS (a Representative Visible Light Harvester) over a Unique Pine-Tree-Like 3D TiO$_2$ Can Allow for an Efficient Charge Generation and Transport As Evident from a $\sim 500\%$ Increase in the Photoelectrochemical Response Which Can Be Favorably Leveraged in Application Such As PV or PEC Water Splitting.
CdS before recombination, into TiO$_2$ conduction band, by providing an affluent pathway and further charge holding capacity helps negative shift in flat-band potential. 1D architectures are perfectly capable host substrates for accommodating components in a multilayer assembly and beneficially leveraging the properties of each layer to deliver high photoelectrochemical responses. [73] This work shows that 3D surfaces are even better hosts if the charge transport layer and visible light harvesters can be synergistically integrated. Therefore, of further interest will be to examine if these benefits can be translated into application related to photo(electro)catalysis and photovoltaics with the possibility of realizing broad spectral absorbance.

2.5 Conclusions

The transformation of a 1D nanorod TiO$_2$ to a unique 3D tree-like branched TiO$_2$ architecture using a hydrothermal process is demonstrated. This 3D bTiO$_2$ functions as an effective substrate for the nucleation and growth of CdS with a high surface coverage. The integration of reduced graphene oxide with the bTiO$_2$/CdS, shown for the first time, leads to a dense, close-packed, and uniformly distributed bTiO$_2$/RGO/CdS. Extensive optical and photoelectrochemical studies have been systematically carried out on these electrodes to understanding the benefits of such a unique heterostructured assembly. Photocurrent values of 3, 1.2, and 1 mA cm$^{-2}$ have been respectively noted for the bTiO$_2$/RGO/CdS, bTiO$_2$/CdS, and rTiO$_2$/CdS. J/V results complemented by EIS analysis indicate 2 that the strategically placed RGO in the bTiO$_2$/RGO/CdS is successful and effective in promoting charge transport. Further, a reduction in the activity loss from 51% to 6% over a 3 h continuous illumination with RGO addition highlights the reliability of the architecture and proves the practicality of the RGO in delaying CdS destabilization. Thus, the work demonstrates that (i) branching of TiO$_2$ aids in improving PEC performance by offering more sites
for CdS deposition and (ii) successful integration of RGO with such a complex 3D TiO$_2$ allows for more efficient charge separation leading to further increase in the PEC performance.
Chapter 3

Chalcogenide Nanocrystal Deposition

Abstract:

This work presents a simple approach to the synthesis of CdS coatings on TiO$_2$ nanotubes (T_NTs) and to form a heterostructured composite. A non-pressure based, single precursor one-pot approach performed at a temperature of 160°C is used to assemble CdS on the TiO$_2$ surface. Surface characterization using microscopy, X-ray diffraction, and elemental analysis indicates the formation of dense hexagonal $<002>$ CdS nanocrystals along the nanotube walls and inter-tubular spacing. Optical measurements indicate that the CdS absorbs in the visible region and demonstrates a red shift with increased loading: up to 12 nm red shift is noted when the precursor concentration is increased from 0.1 - 3 mM. The 0D CdS/1D T_NT was also tested as an anode in a photoelectrochemical cell. The electrode produced the highest reported photocurrent of 9.3 mA cm$^{-2}$ under UV-visible illumination when compared with similar systems. The method may be used in assembling efficient photoanodes for multifunctional solar-driven processes.
3.1 Introduction

Hetero-structured optoelectronic materials (HOMs) are complex structures that consist of a unique combination of 0D or 1D high surface area substrate (e.g. oxide) and a visible light harvester (e.g. chalcogenide). [74, 75, 76, 77] In such HOMs, the intimate coupling of low bandgap chalcogenide nanocrystals with wide bandgap oxide surface to facilitate: i) broad band light absorbance, ii) facile charge separation/transportation, and iii) boost the photoanode efficiency, is a challenging task. The approaches to assemble such HOMs, that are known today, are either complex (involving multiple steps), require reagents that may be cumbersome to eliminate and risk reducing the HOM photoactivity (such as surfactants),[78] or have building components [29] that can prevent the formation of intimate electronic contact between the large and small bandgap oxide leading to suboptimal performance of the HOM. Simplifying the integration of oxide-chalcogenide to aid processability with minimal extraneous additive that are not participating in light-matter interactions will be transformational to assembling these materials for various applications. This work presents a simple approach to assemble a representative HOM consisting of a 1D oxide and a 0D chalcogenide nanocrystal.

Standalone chalcogenide synthesis can be achieved using a variety of approaches. For example, the reverse micelle method[79] requires the use of surfactant stabilized micro emulsions which need to be removed after the synthesis of the chalcogenide. Organic functional group (such as bi-functional linker-mercaptans) assisted synthesis, can aid with size control to improve optical response, but can interfere with charge transport.[22] Alternately, chalcogenide deposits may also be prepared directly on high surface area oxide films, for photoelectrochemical (PEC), Photovoltaic (PV), and photocatalytic(PC) applications. The popular successive ionic layer adsorption and reaction (SILAR) [80, 81, 82] approach requires several cycles of layer-by-layer
assembly approach to grow the cadmium sulfide (CdS) with a high absorbance coefficient. An electrochemical approach [83] requires the application of an external electric field and can limit the extent of deposit formation in highly intricate surface. Finally, solvothermal approaches can assist with uniform in-situ nucleation, growth, and coating of chalcogenides, but require a high pressure and time to achieve it.[35] In a recent study, an interesting self-assembly approach to deposit CdS on TiO$_2$ with small tube mouth has been reported. [84]

This work presents a facile atmospheric pressure-based hot solution dip-casting strategy to facilitate in-situ coupling of the CdS nanocrystals with titania (TiO$_2$) surface. The method demonstrated a uniform coverage of the CdS nanocrystals over the TiO$_2$ nanotube (T_NT) surface with the highest photocurrent compared to any other wet chemical approach reported to date using T_NT and chalcogenide-based systems. Earlier, we have shown various approaches to integrate chalcogenide with oxide substrates of 0D and 1D configuration.[46, 24] This approach to integrate a chalcogenide with a 1D oxide substrate is a simple wet chemical technique for this class of chalcogenide-based composites, especially considering the magnitude of the current that we are able to achieve. The unique aspect of this work include (i) using a one-pot approach with cadmium (Cd) and sulfur (S) from the same precursor, in order to nucleate, deposit, and grow CdS on 1D oxide with no extraneous additives, (ii) demonstrating the same or higher magnitudes of photocurrents compared to the values reported with other complex approaches, and (iii) improved stability of the photoresponse compared to composites formed using other techniques. This work also presents comparative results with T_NT/CdS prepared by the SILAR approach. [85, 86] SILAR approach was used as a benchmark comparison since this approach has been reported extensively and considered one of the low cost, reliable, and easily scalable method to CdX (X=S, Se, Te) formation on both 0D and 1D-oxide facades.
Figure 3.1: Schematic illustrating the deposition of the CdS nanocrystals on the TiO$_2$ nanotubes.

3.2 Experimental Section

3.2.1 Materials

Sodium diethyldithiocarbamate [($C_2H_5$)$_2$(NCS$_2$Na)], ammonium fluoride (NH$_4$F), cadmium sulfate (CdSO$_4$) (from Sigma Aldrich), oleylamine (Across Organics) titanium foil (Purity: 99.7%, 0.2 mm thick Strem Chemicals Inc), dichloromethane, ethylene glycol and ethanol were obtained from (local suppliers), deionized (D.I.) Water (Milli-pore lab water purification system) were used as received without further purification.
Figure 3.2: The photographs of the as-synthesized samples.
3.2.2 Synthesis Procedure

Titanium foil was used to prepare the titanium nanotubes (TNT) as described in our earlier studies. [87] Briefly, the titanium substrate was polished and ultrasonicated with DI water, isopropanol, and acetone separately for 5 minutes each. Fluorinated solution (0.5 % w/w) of ethylene glycol and DI water (10% w/w) was used as an electrolyte. Anodization was done in the two electrode system with platinum as the reference electrode using 40 V DC power supply for 2 to 16 h. Anodized samples were annealed at 450 °C for 2 h in air. Cadmium dithioarbamate Cd[(C$_2$H$_5$)$_2$NCS$_2$]$_2$ precursor was synthesized by mixing 0.1 M aqueous solution of CdSO$_4$ into 0.2 M aqueous solution of (C$_2$H$_5$)$_2$(NCS$_2$Na) for 3 h. The resulting solution immediately started precipitating. The white precipitate was then washed thoroughly with DI water and dried in oven for 6 hours at 50 °C. At first 30 mL of olylamine was heated at temperature 160 °C, and then TNT prepared at various anodization times were dipped in the olylamine solution. After 5 min, Cadmium dithioarbamate Cd[(C$_2$H$_5$)$_2$NCS$_2$]$_2$ precursor was synthesized by mixing 0.1 M aqueous solution of CdSO$_4$ into 0.2 M aqueous solution of [(C$_2$H$_5$)$_2$(NCS$_2$Na)] for 3 h. [88] The resulting solution remove organic ligand the sample was dipped into ethanol and dichloromethane separately for 8 h. To get better crystallinity, the sample was annealed at 350 °C for 3 h in nitrogen atmosphere. A schematic of the method is shown in the figure 3.1 and the photographs of TNT sample with various concentration of the Cd precursor is also provided in figure 3.2.

3.2.3 Characterization

The UV-visible absorbance studies were performed using a Shimadzu UV-2501PC spectrophotometer in the range of 300 nm-900 nm, in absorbance mode. Imaging of the samples was carried out using a Hitachi FESEM scanning electron microscopy.
Figure 3.3: (A) SEM image of bare T_NTs; inset: cross sectional view of the smooth T_NT surface, (B) SEM image of bare T_NTs with optimized CdS (prepared using 2 mM precursor); inset: cross sectional view of the T_NT/CdS surface, (C) TEM image of bare T_NTs with CdS deposited by the one-pot method on the T_NT surface, (D) TEM image of the as-deposited CdS on the T_NT surface indicating an average particle size of 10 ± 5 nm, (inset: FFT diffraction pattern).

(SEM) machine equipped with an oxford EDS analyzer. The cross-sectional morphology of the electrodes were observed by scratching the samples with a sharp object. A JEOL2100F high resolution transmission electron microscope (HR-TEM) was used to examine the size of CdS deposits on T_NT surface. A Philips XRG 3100 X-ray diffractometer, operated at 35 KV was used to obtain the X-ray diffraction pattern and identify the phase of the material after each annealing step, in the film form.
3.3 Results and Discussion

The scanning electron microscopy (SEM) image shown in figure 3.3A indicates cylindrical and well developed TiO$_2$ nanotube arrays, (T$_{NT}$) following anodization of Titanium (Ti) foil. The inset of figure 3.3A shows the cross-sectional view of the nanotube surface. The nanotubes are of 100 nm in diameter, with distinct interstitial spaces between the adjacent tubes. Post one-pot treatment, uniform coverage (coating thickness of 30 nm) can be observed all over the T$_{NT}$ as shown in Fig. 3.3B. The inset of figure 3.3B shows the cross-sectional view of the nanotube surface with the deposits. Additional cross-sectional SEM images of the bare nanotubes (Fig. 3.4 A) and with the deposits (Fig. 3.4 B,) show that the deposits are present along the mouth and the T$_{NT}$ walls while the nanotube mouth mostly remains open. This form of deposition is desirable as it can minimize clogging of the T$_{NT}$ mouth and improve photocurrent generation by maximizing electrolyte transport. It is noteworthy to mention that the approaches that use pre-formed nanoparticles with nanotubes risk significant clogging of the pore mouth. In this approach, the nanocrystals are formed on the oxide surface after diffusion of the precursor to the Ti sites followed by their nucleation and growth. The T$_{NT}$ with varying amount of deposits prepared using precursors of different concentrations are shown in figure 3.4 A-C.

Transmission electron microscopy (TEM) without and with high resolution imaging (HR-TEM) was performed on the HOM to determine the surface and composition of the materials. figure 3.3C shows the cross-section of a representative sample with the deposits. TEM images of the deposits at various magnifications are shown in Fig. 3.6 (A) and (B). The images confirm the observations made by SEM that the deposits formed are dense and continuous. They are distinctly evident along the walls attaching credence to the earlier hypothesis that the crystals are formed after the precursor diffuses along the interstitial spaces and nucleate on the surface. Fig. 3.3 D shows the
Figure 3.4: SEM images of the cross-sectional surface of (A) bare T_NT and (B) T_NT/CdS. [The CdS was prepared using a 2 mM precursor]

HR-TEM image of the deposits. The deposits are of 10 ± 5 nm in diameter. Further, they demonstrate crystallinity as evident from the fringe pattern in the HR-TEM image as well as the high resolution Fast Fourier Transformation (FFT) pattern in the inset of Fig. 3.3 D. These fringes can be indexed to the h002i plane enabling the identification of the deposits as CdS nano-crystals. The TEM image with additional d-spacing values is indicated in Fig. 3.7, and the FFT image is shown in Fig. 3.4 (B) These images indicate the polycrystallinity of CdS and confirm the deposits as the < 002 > plane of hexagonal CdS.

Additional comprehensive material characterization was achieved by performing color resolution mapping analysis of the elements. This specialized technique can provide insights into the distribution of the elemental cadmium (Cd), sulfur (S), and titanium (Ti). The decoupled colour mapping of the building block units in the HOM - Cd, S, and Ti - are shown in figure 3.8(A1 to A3). These images also indicate that
Figure 3.5: SEM images of T_NT samples with CdS deposits at various Cd- and S-precursor concentration of (A) 0.1 mM, (B) 1 mM, and (C) 3 mM.
Figure 3.6: TEM images of T_NT/CdS samples at various magnifications.

Figure 3.7: The (A) TEM image of T_NT/CdS with (B) high resolution FFT pattern, showing the d-spacing values. The 0.33 nm corresponds to 002 plane, 0.203 nm corresponds to <110> plane and 0.175 nm corresponds to <112> plane.
Figure 3.8: A1-A3) Cd, S, and Ti distribution on the T\_NT/CdS is evident from the color coding which indicates the spread of the different elements [images are best viewed in color]. (A4) The EDAX analysis of the deposited CdS over the T\_NT surface indicates the relative composition of the different elements on the T\_NT/CdS heterostructure.
Figure 3.9: (A) The XRD pattern of bare T.NT and CdS deposited T.NT prepared by the one-pot method. The polycrystalline nature of the film is evident from the signals. (B) The UV-visible absorbance spectrum of T.NT, deposited with CdS at various precursor concentrations. The presence of CdS shows a visible absorbance ranging between 516 nm and 528 nm.

The one-pot approach leads to homogeneous distribution of CdS. The color mapping analysis is a convincing cross verification of the microscope analysis in that the CdS is distributed along the cross-sectional length of nanotubes. Further, the energy dispersive x-ray spectroscopy (EDAX) analysis shown in figure 3.3 (A4) indicates the deposits are Cd-rich (Figure 3.3 (A4) Inset). This form of uniform and robust distribution is a prerequisite to any application. For example, if photoelectrochemical process is the primary objective, an excellent electronic contact between the two semiconductors is critical and will determine the magnitude of the photocurrent generated by HOM.

The surface and optical properties of the HOM architecture were analysed using X-ray diffraction (XRD) and UV-visible spectroscopy. The XRD pattern of the nanotube and nanotube with the deposits are shown in figure 3.9[A (a) and (b)] respectively. The indexing of the peaks to file # 21-1272 and file # 41-1049 of the
JCPDS database confirm that the nanotubes comprise of anatase TiO$_2$ and the deposits are hexagonal CdS. The absorbance spectra of T_NT with various Cd precursor concentrations are shown in Fig. 3.9B. The evidence of an onset at $\sim 515$ nm is consistent with the location where CdS nanocrystal absorbance should appear. The gradual red-shift in the absorbance value (516 nm-528 nm) with increased precursor concentration is indicative of the growth and densification of the CdS nanocrystals on the T_NT. Thus the SEM, HR-TEM, EDAX, color mapping, and absorbance results complement one another and confirm hexagonal type 0D CdS on the 1D TiO$_2$ nanotubes.

The photoelectrochemical responses of the HOMs were examined in a two and three electrode (with Reference Ag/AgCl) configuration. Chronoamperometry ($J/t$) measurements of the films are shown in figure 3.10 A. The results indicate that the UV-visible illumination leads to an instantaneous and reproducible response as evident from the several on-off cycles. The presence of CdS, prepared using a low precursor concentration of 0.1 mM shows a positive increase compared to the CdS-free T_NT. At 6.3 mA cm$^{-2}$, a maximum in the photocurrent is observe data CdS loading with 2 mM precursor concentration [an increase of 30-fold over the bare T_NT]. Any further increase in the CdS loading leads to reduction in the photocurrent.

The current density/voltage ($J/V$) analysis indicates the photocurrent response of the HOMs at various applied potentials Figure: 3.10 B. All the CdS deposited samples show higher photocurrent compared to the T_NT at any applied potential. Further, a negative shift in the apparent flat band potential (potential where the current becomes zero) with all the CdS deposits is noted, with the highest shift observed for the CdS deposits prepared using the 2 mM precursor. The negative shift is indicative of the charge generation, accumulation, and transport upon photo illumination in the HOM.

To evaluate the novelty and determine the limits of the HOM synthesis strat-
Figure 3.10: (A) J/t, and (B) J/V plot of CdS (prepared using various precursor concentrations) deposited on T_NT (prepared by anodization for 2h). The measurements were performed in a three-electrode quartz cell system with Pt mesh as a counter electrode and a leak-free Ag/AgCl (in 3M KCl) as the reference electrode, and 0.1 M Na₂S in water was used as the electrolyte. The working electrode was illuminated with a 500W Newport Xenon lamp equipped with 0.5 M CuSO₄ solution as a far UV cutoff filter. (C) Long term stability of the electrode over the duration of ~2 h under continuous AM 1.5 illumination (Inset) the energy band diagram with charge transportation mechanism. (D) J/t plot of CdS (2mM concentration) over T_NT (2, 8, 12, and 16h anodization time).
Table 3.1: Comparison of photocurrent values obtained using various other TiO$_2$/CdS systems under photo illuminated condition. The values reported are obtained from references [89], [90],[91], and [92].
egy, we performed a systematic and thorough literature survey of the 1D TiO$_2$ -0D QD systems and compared the photoactivity reported therein with our results. Fig. 3.1, shows the table listing the leading photocurrent results using 1D TiO$_2$ with chalcogenides to date. Ref. c and e uses T$_{NT}$/CdS, Na$_2$S electrolyte, and Ag/AgCl reference electrode. [Comparison limits: It is to be noted that the comparative information provided in the figure 3.1 is only meant as an indicator. This is because the test conditions in our experiments and those reported in the cited publications can vary. Therefore, to truly compare, the material should be i) synthesized under the same laboratory conditions and ii) tested with the same measurement system. Further, the electrolyte and surrounding environment should be maintained same.] There are few systems that show the photocurrent values similar to the magnitude reported here. On close examination of the approach used to synthesize the composites in the cited work, it may be noted that the approach presented here stands out along the following aspects: (i) this work has demonstrated a one-pot approach to form CdS nanocrystals at the 1D TiO$_2$ surface using a single-precursor as a simultaneous ?Cd? and ?S? source under atmospheric conditions, (ii) a point to be considered is the processing time. With the popular SILAR approach, depending upon the number of cycles employed, it can add up quickly and become a time consuming step while with the present process the removal of the organic ligand can take a long time (∼18 h). However, the time required for coupling is the lowest compared to the procedure used in the synthesis of the other composites. For example, it is 1/6$_{th}$ of the time required when compared to the sample that is reported to show a current-density of 6 mA cm$^{-2}$, and (iii) the CdS deposition appeared to be uniform and provided an intimate contact, which probably is the reason why our HOM demonstrates high photocurrent. It will be inferred from studies presented below that a better utilization of the CdS is the basis for this observation.
Figure 3.11: Collage of photoluminescence spectra and EIS of CdS deposits on T_NTs prepared with the SILAR and one-pot method. The figures present (A) photoluminescence spectra, (B) Nyquist plot, (C) Bode plots representing the variation in the magnitudes of impedance with frequency, and (D) phase angle with frequency.
Further, electrochemical measurements were conducted on T_NT/CdS to gather quantitative information on their performance. Figure 3.11 A shows the PL spectra of the T_NT/CdS prepared using the SILAR and the one-pot method ($\lambda_{ex} = 340$ nm). The two peaks around 520 and 560 nm is the resultant of the intermediate quenching between the CdS nanoparticle and T_NT.[93, 94] These peaks are caused by the radiative recombination of the electron-hole pairs between the interface of the CdS and T_NT. From the figure 8A the T_NT/CdS sample prepared using the one-pot approach exhibit a weaker peak intensity than the sample prepared using the SILAR approach. A lower quenching is attributed to better charge separation.[93]

Further, the electrochemical impedance spectra (EIS) were acquired to compare the performance of the CdS deposited on T_NT by the SILAR and the one-pot approach. Nyquist and Bode plots offer scientific reasoning through impedance measurements on the nature of electrical contact that exist in composite materials.[95] Specifically, the charge transfer resistance is proportional to the diameter of the arc of the Nyquist plot at constant bias voltage. The complex impedance plane or Nyquist plot (figure 3.11 B) suggest that the charge transfer resistance is higher for CdS deposited sample with SILAR approach than that prepared using the one-pot method. Figure 3.11 C and 3.11 D compares the results of the Bode impedance plot for the SILAR and the one-pot approach. Here as well, CdS deposited by the SILAR approach shows higher impedance than the deposits prepared by the one-pot approach. Further, from the Bode phase plot, quantitative information such as the average life time of the electron can be calculated using the following equation:

$$\tau = \frac{1}{2\pi f_p}$$

Where, $f_p$ is the characteristic frequency of the samples, related to electrochemical reaction at TiO$_2$/CdS and the electrolyte interface. The SILAR coupled sample has the electron life time of 94 ms and that of one-pot is 516 ms which indicates that
electron transfer process to TiO$_2$ channel and the flow of the electron from conduction band of CdS to TiO$_2$ is more effective in the one-pot synthesized HOM compared with the SILAR method. Thus, PL, Nyquist, and Bode analysis indicates that the one-pot approach enable establishing a strong contact between T_NT and CdS lowering the recombination of the photo-induced electron-hole pairs in the HOM.

A logical question then arises: *What will be the change in the photocurrent with respect to change in the anodization time?* To answer this question, the anodization was performed for a duration of 2-16 h. As indicated in figure 3.10 D, a T_NT sample anodized for 12 h demonstrated the best photocurrent when compared to T_NT anodized for 2h, 8h, 12h, and 16h. These results are attributable to greater CdS deposit formation over T_NT of increased length. Any further increase in the anodization time beyond 12 h makes T_NT more unstable due to delamination of some of the tubes from its base. Due to this CdS deposition is flaky and the photocurrent is decreased. The j/t and j/V responses of the 12 h anodized samples are shown in the Figs. 5A and 5B, since this condition is considered optimal for the system.

To the best of our knowledge, the current of 9.3 mA.cm$^{-2}$, demonstrated with the 12 h anodized sample here, is a significant improvement when specifically compared with systems involving 3-electrodes, Na$_2$S redox couple, and CdS as the sensitizer using accepted protocols published elsewhere. A sub-set of the compared references uses the T_NT/CdS, Na$_2$S electrolyte, and Ag/AgCl reference electrode. On another related note, it is known that CdS is prone to corrosion and hence its stability is of critical importance to any performance evaluation. Therefore, chronoamperometry measurements were performed to evaluate the HOM stability. The photocurrent magnitude was noted to reduce under continuous illumination by only 40 % over a period of 1 h. The results of a comparison with SILAR approach is given in Figure 3.12 C. A 50% decrease in the photocurrent was observed for SILAR samples in
spite of the photocurrent starting at a lower value. While this result is a promising step in the right direction, it also indicates room for improvement in stabilizing the T\(_{\text{NT}}\)/CdS response and highlights the potential of the one-pot approach to help realize competitively stable HOMs.

### 3.4 Conclusions

A one-pot approach to assemble a T\(_{\text{NT}}\)/CdS nanostructured composite is presented. SEM, (HR) TEM, XRD, and color mapping provide a detailed insight into the assembly and structure of the nanocomposite. At 9.3 mA cm\(^2\) the photocurrent value is the best achieved using this one-pot methodology. Using PL and EIS studies, the scientific reasoning for the improvement is determined as the existence of an excellent electronic contact between the T\(_{\text{NT}}\) and CdS. The results should lay the foundation for designing and developing other HOMs involving several combinations of nanocrystals, such as CdX (X = Se, Te). Further, multiple nanocrystals can be coupled to realize rainbow absorbance as indicated in the schematic of Fig. 3.12. The presented approach could be adapted to realizing such an assembly in an easier, effective, and cost-competitive manner. Obviously, key parameters such as tube dimensions, spacing, matching of appropriate energetics (such as conduction band levels of the nanocrystals) have to be examined for optimal photoanode performance. This approach is expected to impact the materials synthesis strategies used in composite electrode driven applications in the area of photoelectrochemistry, PV, solar-fuels and other allied topics of energy storage and sensing.
Figure 3.12:  (A) J/t and (B) J/V plot of T NTs deposited with CdS over T NTs anodized for 12 h, measured in a three-electrode system, using a quartz cell with Pt mesh as a counter electrode and a leak free Ag/AgCl (in 3 M KCl) as the reference electrode. 0.1 M Na₂S in water was used as the electrolyte. The working electrode was illuminated with a 500 W Newport xenon arc lamp equipped with 0.5 M CuSO₄ solution as a far UV cut-off filter, (C) the table shows the photocurrent values of the T NT/CdS illuminated for 1 h. Note the CdS deposit is prepared between 2 and 12 h (see text for details), and (D) hypothesis for the fabrication of a photoanode with a rainbow architecture.
Chapter 4

Charge Transportation Using Carbon Allotropes

Abstract:

The assembly of a large-bandgap one-dimensional (1D) oxide-conductive carbon-chalcogenide nanocomposite and its surface, optical, and photoelectrochemical properties are presented. Microscopy, surface analysis, and optical spectroscopy results are reported to provide insights into the assembly of the nanostructure. We have investigated (i) how the various carbon allotropes ($C_{60}$), reduced graphene oxide (RGO), carbon nanotubes (CNTs), and graphene quantum dots (GQDs) can be integrated at the interface of the 1D TiO$_2$ and zero-dimensional (0D) CdS nanocrystals; (ii) the carbon allotrope and CdS loading effects; (iii) the impact of the carbon allotrope presence on 0D CdS nanocrystals; and (iv) how they promote light absorbance. Subsequently, the functioning of the integrated nano-structured assembly in a photoelectrochemical cell has been systematically investigated. These studies include (i) chronoamperometry, (ii) impedance measurements or EIS, and (iii) linear sweep voltammetry. The results indicate that the presence of a GQD interface shows the most enhancement in
the photoelectrochemical properties. The optimized photocurrent values were respec-
tively noted to be 2.8, 2.2, 1.9, and 1.6 mA cm$^{-2}$, indicating $J_{\text{GRD}} > J_{\text{RGO}} > J_{\text{CNT}} > J_{\text{fullerene}}$. Furthermore, the annealing conditions have indicated that ammonia treat-
ment leads to an increase in the photoelectrochemical responses when using any form
of the carbon allotropes.

4.1 Introduction

Light-driven applications such as photocatalytic clean fuel production, [96] electricity
generation,[97] and environmental remediation [98, 99] involve utilizing photoactive
oxides as a major component. Oxides as the material of choice arise from the fact that
they demonstrate multi-functionality, can be assembled as particulate films on sub-
strates using a variety of cost-effective wet chemical and chamber-based processes,
and demonstrate wide ranging pH stability. [100, 101, 102] The assembly of 1D
oxide as films as opposed to 0D oxide films allows for a reduction in grain bound-
aries promoting epitaxial charge transport. [98, 103] This benefit has been one of
the basis for the study of 1D oxides with forms such as nanotubes, nanorods, and
nanowires. [104, 105, 106, 82] The application of these oxides in combination with
other photoactive materials such colored dyes (in DSSC), QDs (QDSCs), and metals
(Photocatalysis) has also been successfully demonstrated. [107, 108, 109, 110]

Since efficient photo-driven processes require leveraging visible light, chalcogenides
as visible light harvesting agents are of immense interest. [111, 112, 113, 114] They
display several unique properties such as i) size dependent optical absorbance (driven
mainly by quantization effects), [115, 116] ii) improved light-to-electrical energy con-
version (boosted by multiple exciton generation), [117] and iii) compatibility to wide
ranging applications (PV and solar fuel production). [118] The chalcogenides can
facilitate light absorbance across the visible and infrared thus covering a significant
range of the low energy bandwidth in the solar spectrum improving the overall efficiency of the nanocomposite. \[119\] The study of chalcogenides with oxides has been well documented; establishing this area as one of continued interest. \[120, 121, 122, 123\]

Of relevance to the aforementioned materials, carbon is a universal, inexpensive, and unique additive that can aid in charge separation and transport. Its properties have been leveraged in light-driven processes such as solar energy conversion as well as other energy related applications such as in fuel cells. Allotropic forms of carbon that have generally been examined are fullerene (C60 and its analogues), \[124, 125\] carbon nanotubes (single- / multi-walled), \[126, 127\] and graphenes (including reduced graphene oxides). \[128, 129, 130, 131, 132\] From a solar energy conversion standpoint, all of these carbon allotropes have demonstrated improvement in photoelectrochemical responses.\[133, 134, 135\] In the context of this discussion, they have been tested with oxides and chalcogenides as well albeit, the focus has primarily been towards its integration with 0D oxides.

Recently, we have shown that 1D oxide-chalcogenide can be coupled using reduced graphene oxide to assemble a unique heterostructure that demonstrate multifunctionality. \[136, 137\] As indicated in scheme 1, the RGO, in the form of a screen, offers a host of benefits in the domain of charge separation and transport. We have shown a proof-of-concept of such a heterostructure assembly using the popular ZnO in the 1D form. The architecture is photostable and demonstrates photovoltaic, photoelectrochemical, and photocatalytic properties. However, the role of the oxide phases (anatase and rutile) on the effects of charge transport in 1D is yet to be fully understood. Additionally, the questions that arise are: can all of the carbon allotropes be integrated to form a stable heterostructure using 1D oxide and chalcogenide. And if so, which one of these allotropic forms is the most suitable for promoting charge
transport for this architecture. This work focuses on answering these questions using CdS as the representative chalcogenide prepared using the SILAR approach.

4.2 Materials and Method

4.2.1 Chemicals

Titanium (IV) butoxide, and cadmium nitrate \([\text{Cd(NO}_3\text{)}_2]\) were obtained from Sigma Aldrich. Sodium sulfide nanohydrate \((\text{Na}_2\text{S}, 9\text{H}_2\text{O})\), fullerene \((\text{C}_{60})\), and carbon nanotube \((\text{CNT})\) were obtained from Alfa Aesar. Methanol \((\text{CH}_3\text{OH})\), concentrated hydrochloric acid \((\text{HCl})\), was obtained from local suppliers and was used without further purification. Graphite flakes were purchased from Bay Carbon Inc. \((\text{SP}-1)\). Deionized \((\text{D.I.})\) water was obtained from an in-house Millipore lab water purification system. Optical characterization of the materials was performed using a Shimadzu UV-2501PC spectrophotometer in the range of 300 nm-800 nm. The morphologies and microstructures of the samples were probed using a Hitachi FESEM scanning electron microscopy \((\text{SEM})\) equipped with an oxford EDS analyzer. The SEM samples were coated with platinum prior to the examination. TEM images of the samples were taken at 100 KV using a JEOL 2100F high resolution transmission electron microscope \((\text{HRTEM})\) JEOL100 and were used to examine the size distribution of the particles. X-ray diffraction measurements were performed using a Philips XRG 3100 X-ray diffractometer, operated at 35 KV to identify the phase of the material after thermal treatment of the samples.
4.2.2 Surface Passivation of Rutile TiO$_2$ Nanorods with Anatase Layer

The approach used for the synthesis of the rutile TiO$_2$ nanorod (aTiO$_2$) is described elsewhere. [138, 139] Anatase TiO$_2$ layer was deposited over the TNR using the following procedure. A 2M HCl was mixed with titanium (IV) butoxide to prepare a precursor solution. 0.5 ml of the precursor solution was added to 100 ml of 0.025 M HCl solution. Two FTO slides with TiO$_2$ nanorods were placed at an angle against the wall of the beaker, supporting each other at the base with the conductive side facing up. The beaker was kept for an hour at a temperature of 90$^\circ$C inside an oven. After cooling to room temperature, the sample was washed in DI water and dried in air. The samples were subsequently annealed at 350$^\circ$C for an hour in air.

4.2.3 Preparation of Graphene Oxide or GO and Graphene Quantum Dots or GQD

Step 1 The 8 g of graphite powder obtained from Bay carbon was kept with a solution of concentrated H$_2$SO$_4$ (30 mL), K$_2$S$_2$O$_8$ (10 g), and P$_2$O$_5$ (10 g) at 80$^\circ$C. The resultant dark mixture was thermally isolated and allowed to cool to room temperature. The mixture was then carefully diluted, washed, and filtered with distilled water to neutralize the solution. The product was later dried at ambient temperature over 24 hours. Step 2 This pre-oxidized graphite was kept in a cold (0$^\circ$C) concentrated H$_2$SO$_4$ (184 mL). NaNO$_3$ (4 g) and KMnO$_4$ (24 g) was added gradually to this mixture under constant stirring. The temperature of the mixture was kept below 10$^\circ$C and stirred for 1 hour. Later the temperature was allowed to increase to 35 $^\circ$C ($\pm$3$^\circ$C) and then maintained under stirring for 6 h. It was later kept overnight. Subsequently, adding distilled water (368 mL), led to a temperature rise to over 90$^\circ$C. 15 minutes later
the reaction was terminated by adding a large amount of distilled water (1120 mL) and 30 % H₂O₂ solution (20 mL). The resulting bright yellow colored mixture was filtered and washed with 1:10 HCl solution (1000 mL) in order to remove the metal ions. The mixture was further washed with a large amount of distilled water. The GO product was suspended in distilled water to yield a brown, 2 % dispersion, which was subjected to dialysis to completely remove metal ions and acids (7 days, changed DI-water every ~12 hours). Step 3 GO was dissolved in DMF with the concentration of 270 mg/10 ml. The solution was ultrasonicated for 30 minutes. Then the solution was transferred to a 100 ml Teflon-lined autoclave and heated at 200°C for 5 h. After this reaction, the reactors were cooled to room temperature. The brown transparent suspension and black precipitate were washed in the DI water and the solid samples were obtained by evaporating the solvents using a rotary evaporator. The residue was purified by column chromatography over silica gel using water as eluent to provide the desired product.

4.2.4 Coating of Allotropic Forms of Different Carbon

Single walled carbon nanotube was dispersed in the dimethylformamide solution with the concentration of 1 mg/ml. The fullerene was dispersed in the toluene solution with the concentration of 1 mg/ml and RGO was dispersed in water with the concentration of 1 mg/ml. While, GQD was obtained with a concentration of 0.6 mg/ml after synthesis (synthesis details given in supporting information). The carbon materials dispersed in solution were ultrasonicated for 1 h for thorough mixing of the sample and then coated on the 1D oxide with a brush.
4.2.5 Deposition of Chalcogenide

The SILAR approach was used for the deposition of the CdS on the 1D oxide - carbon. The FTO substrates deposited with 1D oxide and coated with carbon were immersed in the 0.5 M Cd(NO$_3$)$_2$ solution in CH$_3$OH/water mixture (1:1) for 2 min, where the Cd$^{2+}$ ions adhere on the substrate surface. This was followed by washing with DI water for 2 min to prevent homogeneous precipitation. The samples were then immersed in 0.5 M Na$_2$S solution for 2 min, where the precursor ions react with S$^{2-}$. This was followed by cleaning the sample in DI water for 2 min. The steps were repeated to grow subsequent layers via multiple cycles. After the SILAR deposition, the samples were annealed at 350°C for 3 h either in nitrogen or ammonia atmosphere.

4.2.6 Photoelectrochemical (PEC) Characterization

All the PEC measurements were performed using Autolab potentiostat (PGSTAT 302). [140] A Newport 500 W Xe lamp was used as the light source with a 0.5 M CuSO$_4$ solution as a far UV-cutoff filter to reduce the light intensity to $\sim$90 mW/cm$^2$ (equivalent to AM 1.5 illumination). [141] The three electrode experiments were performed in a quartz cuvette, which included the prepared 1D oxide/carbon/chalcogenide photoanode, a Pt mesh cathode, and a leak free Ag/AgCl reference electrode. A 0.1 M solution of Na$_2$S was used as the electrolyte.
Figure 4.1: (A) SEM image of the nanorods grown using the seed mediated approach, (B) SEM image of the nanorods after surface treatment using the titanium butoxide precursor, (C) XRD over a $2\theta$ range of 20°C to 80°C of (A) indicating rutile TiO$_2$, and (D) absorbance spectra before and after surface treatment.
4.3 Results

4.3.1 Surface and Optical Characterization

Microscopy, surface, and optical analyses of oxide layer

The formation of the oxide layer following the seed mediated approach and the effects of the subsequent surface treatment were examined using microscopy and XRD analysis. The exposure of the seeded substrate to an acidified solution of titanium(IV) precursor under hydrothermal treatment leads to the evolution and growth of the 1D structures as indicated in Figure 4.6A. The directional growth and epitaxial arrangement of several physically similar nanorods with a distinctly smooth side walls, an inter-rod spacing, and a square cross-section, are evident from the SEM image. The physical dimensions of the rods are noted to be $50\pm5$ nm laterally and $\sim 4$ microns in length. Once these nanorods are subjected to the titanium precursor treatment, the formation of surface deposits with evidence of an increase in surface roughness, especially along the side walls, is noted as indicated in figure 4.1B. However, there is no distinguishable change in the overall physical dimensions of the nanorod suggesting the treatment leads to a very thin layer of coverage. It is also evident that the surface passivation step does not significantly affect the spacing between the rods.

XRD analysis of the 1 D nanorods was performed to determine the crystallinity and phase before and after surface treatment. The presence of distinct peaks suggests that both seed-grown and surface-passivated nanorods become polycrystalline after thermal treatment. The sample peaks were indexed to the $<101>$, $<002>$, and $<112>$ planes, using the standard JCPDS database, as shown in Figure 4.1C, and that indicates that the 1D nanorods belong to the rutile TiO$_2$ phase (Joint Committee on Powder Diffraction Standards (JCPDS) File No. 88-1175). The samples formed after the surface passivation step did not show any significant change in the XRD
Figure 4.2: The XRD of sample prepared by depositing the surface treatment solution on an ITO slide performed over a 2θ range of 20°C to 80°C of anatase TiO₂.
patterns. This could be attributed to the deposition of a very thin layer of precursor (consistent with the SEM observations). Therefore, to identify this phase a thicker layer was formed from the same precursor solution using multiple deposition steps. The XRD analysis of these deposits indicated the formation of a polycrystalline film identified as TiO\(_2\) of the anatase phase, as shown in Figure 4.2 (JCPDS File No. 84-1826). The corresponding absorbance spectra of the rutile rod versus the anatase-coated rutile rod (labeled henceforth as r-TiO\(_2\) and a-r-TiO\(_2\), respectively) are shown in Figure 4.1D. The absorbance of the two oxide nanorods are almost the same, with an overlapping onset at ∼413 nm. This observation indicates that the surface passivation layer does not distinguishably alter the optical properties of the TiO\(_2\) nanorod.

**Characterization of the carbon allotrope deposits on the TiO\(_2\) nanorods**

The various carbon allotropes were deposited over the TiO\(_2\) nanorods using the approach discussed in section 4.2.4 and imaged using microscopy. The HRTEM image and the corresponding EDS analysis of the 1D oxide-various conductive carbon-chalcogenide nanocomposite is shown in Figure 4.3. The HRTEM images indicate the general assembly of the a-r-TiO\(_2\)/C/CdS nano-composite while the EDS analysis shows that the participating elements are detected once the assembly of the nanocomposite is completed. The SEM analysis was also performed on all of the samples. An important aspect to note early on is the unique physical forms these carbon materials have and are likely to evolve into when deposited on the nanorods. Their distribution and density can be influenced by the stearic hindrances posed by their natural physical dimensions. Since circumventing or controlling them is not an option when we are studying their relative effects, it is expected that these hindrances will play a definitive role in influencing the photoelectrochemical performance of the
Figure 4.3: The figure shows the HRTEM images (A, B, and C) and the EDS results (D,E, and F) indicating the detection of the participating elements in the a-r-TiO$_2$/C/CdS nanocomposite. Detailed analysis of the GQD is shown in the main manuscript. The various carbon allotropes represented here are: RGO [A and D], CNT [B and E] and C$_{60}$ [C and E].
heterostructure and the mass transport of the electrolyte. Considering this aspect, one approach to perform a comparative evaluation of their contributions that was followed, is to individually optimize the loading of each of the carbon forms on the 1D TiO$_2$ nanorods prior to the deposition of the chalcogenide.

Since SWNT and fullerenes were commercially obtained and used as is, their individual properties were not independently characterized. The characterization of the in-house synthesized RGO has been systematically performed using FTIR and Raman and reported elsewhere. [137] The procedure followed for graphene quantum dot or GQD synthesis was obtained from published literature and the Figure 4.4 discusses the confirmation of the synthesized product as GQD. Briefly, the UV vis absorbance of the in-house synthesized product shown in figure 4.4(A) is consistent with the results reported elsewhere, [142, 143, 144] indicating GQD formation. Further, GQD shows luminescent properties as indicated in the photograph shown in figure 4.4(B). To confirm the luminescent properties, a photoluminescence analysis was performed ($\lambda_{ex} = 340$ nm) and shown in figure 4.4(C). This observation is also consistent with the published literature [142] on GQD synthesis confirming that the material produced in this work is GQD.
Figure 4.5: The XRD pattern of the powder form of the SILAR deposits performed over a $2\theta$ range from 20°C to 80°C indicating the formation of CdS nanocrystals.

Optical analyses of chalcogenide formation on carbon-free a-r-TiO$_2$

The SILAR approach was used to prepare the chalcogenide deposits. The reasons for the choice of this process are (i) it is simple and scalable, (ii) it leads to stoichiometric chalcogenide deposits, and (iii) it forms nanocrystals of similar sizes in the presence of some of the carbon forms, as evident from our earlier studies.[145, 146, 147] The SILAR approach leads to the formation of varying density chalcogenide deposits by the process of ionic interaction with every subsequent cycle.[147] Therefore optimizing the number of chalcogenide deposition cycles is required for maximizing the chalcogenide coating on the 1D TiO$_2$. Using UV-vis analysis, the absorbance spectra of the carbon-free a-r-TiO$_2$ with the SILAR deposited samples was tracked and the results
Figure 4.6: Absorbance spectra of the anatase-coated rutile TiO$_2$ and CdS nanocrystals formed by varying the number of SILAR deposition cycles. The number of cycles performed were (a) 5, (b) 10, (c) 15, and (d) 20.

reported in figure 4.6. With an increase in the number of SILAR cycles, the optical absorbance increases in the visible region and stabilizes at an O.D. of 0.62. The XRD analysis of the deposits formed from the SILAR process is shown in figure 5 and indicates the presence of <002>, <110>, and <201> peaks, characteristic to CdS nanocrystal formation (JCPDS file # 77-2303).

The absorbance pattern of the SILAR deposits in figure 4 demonstrates an onset at a wavelength of 564nm and is also consistent with CdS deposition. At the completion of 15 SILAR cycles the absorbance appears to stay constant indicating a maximum in CdS loading has reached. Any further increase in the number of the SILAR cycles actually led to a decrease in the CdS loading on the carbon-free a-r-TiO$_2$ (as indicated
in the figure 4.6 with 20 SILAR cycles). This observation can be attributed to the lack of adsorption of the ions to form the deposits. A similar trend in the general chalcogenide absorbance profile on both 0D and 1D oxides has been documented elsewhere. [138, 145]

**Optimization of the carbon allotrope deposits and CdS on the 1D a-r-TiO<sub>2</sub>**

To optimize the carbon allotrope content, various coatings of the carbon were deposited first on the a-r-TiO<sub>2</sub>. The CdS then was prepared on the a-r-TiO<sub>2</sub>/C composite. At this point, the number of SILAR cycles was kept at a constant of 15 cycles, based on the results from section 3.1.3. The absorbance spectra of the a-r-TiO<sub>2</sub>/C/CdS samples thus prepared with only a variation in the carbon coating is presented in Figure 4.7. The baseline C-free samples [a-TiO<sub>2</sub>/CdS] shows a smaller absorbance compared to samples with the carbon attributable to greater CdS deposition in the presence of carbon. For RGO, fullerene, and CNT, two coatings with concentration of 1 mg mL resulted in an optimal absorbance (note RGO optimization has been reported elsewhere [137]). Whereas, for GQDs, the optimal absorbance was obtained at 10 coatings with a GQD solution having a concentration of 0.6 mg/mL. Any further increase in the number of carbon coating decreased the absorbance. This is attributed to a decrease in the CdS deposition.

There are a few noteworthy takeaways from the general profile of the absorbance spectra of the nanocomposite. First, the onset absorbance indicates that the CdS nanocrystals are successfully deposited on the 1D TiO<sub>2</sub>/C. The presence of any form of carbon allotrope does not impede the deposition of the CdS on the a-r-TiO<sub>2</sub>. In fact, in some cases, it may be providing additional sites for the CdS deposition and distribution. Second, upon close examination of Figures 4.6 and 4.7, it may be noted that, in the presence of any forms of carbon, there is an increase in visible absorbance.
Figure 4.7: Figure shows the absorbance spectra of the a-r-TiO$_2$ with (A) C60, (B) GQD, and (C) CNT deposits followed by CdS deposition using the SILAR approach. The SILAR cycles were kept constant at 15 for the different carbon allotropes. The ordinate scale is the same for panels (A), (B), and (C).

For example, the absorbance at 450 nm is 0.62 and 0.75 with a-r-TiO$_2$/CdS and a-r-TiO$_2$/C/CdS, respectively. This aspect is likely to be beneficial since an enhancement in absorbance is the first step toward a better solar-to-electric conversion, as well as boosting photocatalytic activity.

Microscopy and surface analyses of the overlying carbon allotropes

SEM images after the deposition of the different carbon allotropes on the a-r-TiO$_2$ nanorods are shown in Figure 4.8. The image in figure 4.8A shows that the RGO is mostly present over the nanorod surface as a screen. The image in the inset is shown at a lower RGO loading to indicate that the nanorods are underlying with respect to the RGO position; as if the RGO is suspended by these rods (a detailed characterization of this assembly is reported elsewhere).[138] Figure 4.8B indicates the presence of long and slender dispersed tubes, characteristic of the CNT, interspersed between the nanorods. Figure 4.8C shows the small fragments of the nanosheet deposited on the surface of 1D nanorods suggesting the formation of the GQD. Figure 4.8D shows
Figure 4.8: SEM images of the a-r-TiO$_2$ nanorods containing the various carbon allotropes: (A) RGO, (B) CNT, (C) GQD, and (D) C$_{60}$.
Figure 4.9: Figure shows the SEM images of SILAR-treated CdS formed over a-r-TiO$_2$ containing the various carbon allotropes: (A) RGO, (B) CNT, (C) GQD, and (D) C$_{60}$. The image after fullerene deposits; the images do not indicate any distinguishable differences from a fullerene-free sample. This could be attributed to the very small dimensions of fullerene in compare to other carbon forms.

**Microscopy analysis of the chalcogenide deposits on a-r-TiO$_2$/C**

The CdS deposits formed using the optimized SILAR cycles on the carbon-deposited a-r-TiO$_2$ was again examined using microscopy. These images are shown for each of the carbon allotropes in Figure 4.9. The aspects common to all the samples are i) a general decrease in the TiO$_2$ inter-rod spacing and ii) absence of any distinguishable clustering of the CdS nanocrystals. The latter conclusion is based on the fact that
the onset of absorbance with C-free and C-based films are the same, i.e. 550 nm as
evident from figures 4.6 and 4.7. Upon closer examination of the SEM images, the
nature of the CdS deposit formed appears to be markedly influenced by the underlying
TiO$_2$/C. For example, the CdS seems to assemble as a continuum of a cluster on the
GQD and RGO compared to the fullerene and the CNT.
4.3.2 Photoelectrochemical Characterization

Activity of the TiO$_2$ nanorods

The performances of the r-TiO$_2$ and the a-r-TiO$_2$ were evaluated by using them as an electrode (photoanode) in a photoelectrochemical or PEC cell with Pt as a counter electrode and Ag/AgCl as the reference electrode. The chronoamperometry results of the 1D nanorods are shown in figure 4.10. The rods display an immediate step change in the photocurrent magnitude indicating they are instantaneously photoactive. The direction of the current is consistent with TiO$_2$ of the n-type. [148, 149] The photocurrent after the anatase layer formation shows an increase in current from 0.22 mA cm$^{-2}$ to 0.45 mA cm$^{-2}$. A 100% increase indicates that the presence of an overlaying anatase layer is beneficial to photoactivity of the 1D r-TiO$_2$. The anatase phase of TiO$_2$ has an indirect bandgap, whereas rutile phase has a direct bandgap. [150] As a result, anatase phase has a higher photoactivity than the rutile phase of TiO$_2$. Further, upon observing the optical spectra one can rule out the increase in surface area of nanorods. Finally, the multiple-on-off illumination cycles demonstrate a reproducible photocurrent indicating that the seed mediated growth followed by the deposition approach leads to a stable composite 1D oxide film.

Linear sweep voltammetry (LSV) of carbon-free TiO$_2$ with CdS deposits

The CdS-deposited TiO$_2$ nanorods (rutile and anatase + rutile) were tested using LSV. As indicated in the linear sweep voltammetry (LSV) curve of Figure 4.11, a doubling in the current at zero potential and a slight negative shift in the apparent flat band potential is noted simultaneously with the addition of the anatase coating on the r-TiO$_2$, consistent with the inferences drawn from Figure 4.10. However, a much larger negative shift in the apparent flat band potential is noted when CdS is deposited on the a-r-TiO$_2$. This shift is attributable to the more negative conduction
Figure 4.11: Current density/voltage (J/V) plot of (a) rutile TiO$_2$ nanorod, (b) anatase TiO$_2$-coated rutile TiO$_2$ nanorod, and (c) anatase TiO$_2$-coated rutile TiO$_2$ nanorod with CdS deposits. [PEC conditions: CE, Pt; RE, Ag/AgCl; electrolyte, 0.1 N Na$_2$S.]
Figure 4.12: The XXY plot shows the correlation between the effect of the SILAR cycles on the absorbance of the a-r-TiO$_2$/C/CdS (left) and the corresponding photocurrent generated using these heterostructures (right).

Band edge of CdS.\cite{97, 146, 151} Furthermore, an increase in the number of SILAR cycles correspondingly increases the photocurrent. Beyond an optimal loading of 15 cycles, the absorbance is reduced, as indicated in the XXY plot of Figure 4.12 in the Supporting Information, and so does the photocurrent, indicating that CdS is not deposited beyond the 15 cycles limit. It is also to be noted, that the anatase coating showed higher current at all SILAR cycles compared to the anatase-free rutile TiO$_2$. Nevertheless, the photocurrent using the a-r-TiO$_2$ with the CdS shows a maximum of $\sim$1.2 mA$^{-2}$ at 0 V with respect to Ag/AgCl.
Photocurrent response with various carbon allotropes

The photocurrent was then examined with samples containing the various forms of carbon allotropes and the overlying CdS. The comparative results of the chronoamperometry studies are shown in Figure 4.13 A. All samples show instantaneous and reproducible photocurrent upon illumination and in the same direction as the underlying TiO$_2$ (confirming that the assembly also demonstrates n-type characteristics). The optimized photocurrent values are respectively noted to be 2.8, 2.2, 1.9, and 1.6 mA cm$^{-2}$, indicating the following: $J_{\text{GRD}} > J_{\text{RGO}} > J_{\text{CNT}} > J_{\text{fullerene}}$. GQD RGO CNT fullerenes. Thus, compared to the carbon-free TiO$_2$/CdS, the presence of any of the four carbon allotropes uniformly indicate an increase in the photocurrent beyond the 1.2 mA cm$^{-2}$ noted for the C-free samples.
Linear sweep voltammetry with various carbon allotropes

The corresponding LSV response of the electrodes with each of the carbon additives is shown in Figure 4.13 B. The j/V responses follow the same trend with various carbon allotropes as the photocurrent responses. At 2.7 mA$^{-2}$, the GQD shows the highest current with the TiO$_2$/CdS. A corresponding shift in the apparent flat band potential by a magnitude of 0.9 V is also noted. The photocurrent of a-r-TiO$_2$/GQD/CdS, a-r-TiO$_2$/RGO/CdS, a-r-TiO$_2$/CNT/CdS and a-r-TiO$_2$/fullerene/CdS annealed in nitrogen is increased by 240 %, 180 %, 125 %, and 83 % respectively compared to the 1.2 mA cm$^{-2}$ noted with a-r-TiO$_2$/CdS in figure 10. The fact that the presence of the carbon allotropes increases the photocurrent and simultaneously leads to a shifts of the apparent flatband, indicates that the carbon allotropes at the interface of the TiO$_2$ and the CdS facilitates improved charge separation as well as charge transportation. Thus the increase in the current noted in sections 3.2.3 and 3.2.4 is attributed to the i) greater distribution of the CdS (concluded from absorbance studies of figures 4.6 and 4.7 ) and ii) ability of the carbon to promote charge transport. The carbon allotropes used here serves the purpose of electron shuttling, as indicated in earlier works using metal nanoparticles. [152] Besides, metal nanoparticles can assist with other functions besides charge transport such as light absorbance [153] and electron flow regulation [154] and should be considered if such multifunctionality is desired. Alternatively, the carbon allotropes could be a cost- effective option to metal nanoparticles should electron transport be the only criteria.
4.4 Discussions

4.4.1 Effects of N\textsubscript{2} and NH\textsubscript{3} Annealing

All the samples tested so far had been annealed under reductive conditions using N\textsubscript{2}. However it is known that all the forms of carbon used here respond differently under different reductive conditions. For example, we had recently reported, that the surface functionalities such as OH, -COOH present in RGO can be removed or reduced when annealed under reductive conditions that are reactive. [137] To evaluate if changing the reductive medium can have an effect on photoelectrochemical responses, we have studied the effects of samples annealed in the presence of ammonia (NH\textsubscript{3}). The results of this analysis are shown in figures 4.14A and 4.14B. The addition of RGO leads to a current of 2.2 mA cm\textsuperscript{-2} upon N\textsubscript{2} annealing. Whereas, annealing in an NH\textsubscript{3} atmosphere under similar conditions, results in a photocurrent of 3.4 mA cm\textsuperscript{-2} as shown in figure 4.14A. This is a 180 % higher photocurrent increase. The increase
in photocurrent due to annealing in the presence of NH$_3$ may be attributed to the incorporation of nitrogen among the carbon atoms. [155, 156, 157] Such an effect can lead to the localized electronic states leading to more effective charge transport. The figure 4.14B shows the corresponding LSV of the a-r-TiO$_2$/C/CdS. The trends in the LSV results correspond to the trends noted in figure 12A:

\[ J_{\text{GRD}} > J_{\text{RGO}} > J_{\text{CNT}} > J_{\text{fullerene}} \]

The photocurrent of the a-r-TiO$_2$/GQD/CdS sample annealed under NH$_3$ shows a $\sim$ 8-fold increase in the photocurrent compared to a-r-TiO$_2$. These results indicate that a-r-TiO$_2$/GQD/CdS sample annealed under NH$_3$ significantly enhances the photoelectric response compared to samples annealed in N$_2$. The results of the corresponding open circuit voltage or Voc for each of the samples are shown in Supporting Table 4.1. The increase in the Voc of a-r-TiO$_2$/GQD/CdS alludes to a more efficient charge separation of photoelectrons in a-r-TiO$_2$/GQD/CdS with NH$_3$ treatment.

### 4.4.2 Electrochemical Impedance Analysis

To further evaluate the effects of NH$_3$ treatment, one has to fully understand the electronic properties of the composite assembly. The standard (P)EC characterization techniques are generally focused on providing information only on the overall characteristics. Alternately, the electrochemical impedance spectroscopy measurements provide complementary information on the extent of charge transport in the composite photoelectrodes. To this end, the Nyquist plot and Bode plot of the sample with and without graphene quantum dot are presented in Figure 4.15. The charge transfer resistance is proportional to the diameter of the arc of the Nyquist plot at constant bias voltage. [74, 158] The complex impedance plane or Nyquist plot suggests that the charge transfer resistance is lowest for the NH$_3$ annealed sample having GQD, in comparison to the sample without GQD and sample with GQD annealed in the
Table 4.1: The open circuit voltage, $V_{oc}$, obtained using the nanocomposite containing the different carbon allotropes at the interface of the a-r-TiO$_2$ nanorod and the SILAR deposited CdS nanocrystals

<table>
<thead>
<tr>
<th>Sample</th>
<th>$V_{oc}$</th>
<th>$V_{oc}$</th>
<th>% Increase in, $V_{oc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a_r_TiO$_2$/</td>
<td>N$_2$</td>
<td>NH$_3$</td>
<td></td>
</tr>
<tr>
<td>Annealed</td>
<td>0.8</td>
<td>0.8</td>
<td>0</td>
</tr>
<tr>
<td>CdS</td>
<td>0.91</td>
<td>1.12</td>
<td>23</td>
</tr>
<tr>
<td>GQD/CdS</td>
<td>0.82</td>
<td>1.03</td>
<td>25</td>
</tr>
<tr>
<td>RGO/CdS</td>
<td>0.81</td>
<td>1.02</td>
<td>26</td>
</tr>
<tr>
<td>CNT/CdS</td>
<td>0.80</td>
<td>1.00</td>
<td>25</td>
</tr>
<tr>
<td>C$_{60}$/CdS</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.15: Figure shows the results of the electrochemical impedance measurements on a-r-TiO$_2$ nanorod with CdS nanocrystals containing GQD annealed under nitrogen and ammonia are shown. These include the (A) Nyquist plot, and (B) Bode plot representing the variation in the phase with respect to frequency for the samples annealed in the presence of nitrogen and ammonia.
presence of \( N_2 \). Further, from the Bode phase plot, quantitative information such as the average lifetime of the electron can be calculated using the following equation:

\[ \tau = \frac{1}{2\pi f_p} \]  

(4.1)

Where, \( f_p \) is the characteristic frequency of the samples, related to electrochemical reaction at sample and the electrolyte interface. The electron lifetime (in seconds) of sample with GQD (annealed in \( \text{NH}_3 \)), GQD (annealed in \( \text{N}_2 \)) and w/o GQD are estimated to be 260 ms, 50 ms and 32 ms respectively, which indicates that the electron transfer process is more effective in the presence of GQD annealed in \( \text{NH}_3 \). This result provides the basis for the observed increase in the photocurrent discussed in section 3. Furthermore, if the size of a semiconductor crystal is less than the Bohr radius of the bulk material, the electron distribution will be changed. As a result, the size dependent electronic properties such as bandgap and the energy relaxation dynamics can be observed. In graphene quantum dot, energy spacing in electronic states is much larger than the vibrational frequency required for emission of multiple vibrational spectra; this decreases the Franck-Condon factor in the coupling of the two states and as a result relaxation rate decreases. \[142, 143\] This could also contribute to improved charge transport properties in nanocomposites that contain GQD.

### 4.4.3 Surface Analysis of the 1D-TiO\(_2\)/GQD/CdS and Mechanism of Charge Transport

HR-TEM and FFT analysis of the TiO\(_2\)/GQD/CdS assembly was performed and shown in figure 14. The microscopy image shown in Figure 4.16 indicates a representative section of the sample with the participating species: CdS, GQD, and
Figure 4.16: Figure shows the TEM images of the (A) TiO$_2$/GQD/CdS (inset shows the EDX analysis at various spots), (B) GQD indicating an average particle size of 3 ± 1 nm (inset shows the fast Fourier transform (FFT) diffraction pattern), and (C) CdS indicating an average particle size of 7 ± 1 nm (inset shows FFT diffraction pattern).
Figure 4.17: The energy levels of CdS nanoparticles, titania, and GQD are qualitative and not drawn up to the exact scale.

TiO$_2$. Figure 14.16B and 4.16C show the location of the GQD [$\theta = 3 \pm 1$nm, 0.214 nm: $<100>$ plane of carbon] and the CdS [$\theta = 7 \pm 1$nm, 0.33 nm: $<002>$ plane of CdS] respectively and the crystallinity of the latter (insert of Figure 4.16C). The images demonstrate the existence of a synergistic coupling between the TiO$_2$, GQD, and CdS mainly because of the good mixing afforded by the similarity in the dimensions of the GQD and CdS. Consequently, the enhancement in the photoelectrochemical response is realized due to the boosting of photogenerated charge transport from the CdS to the TiO$_2$ by the GQD as indicated in scheme 4.17.
4.4.4 Decoupling the Contributors to Photocurrent Enhancement and Mechanistic of the Process

This work alludes to the intimate mixing of the GQD between the oxide and the chalcogenide and the excellent charge mobility of graphene as the dual basis for the observed efficient performance of the oxide-C-chalcogenide composite. Furthermore, it is noteworthy to mention that a property called photon downconversion, where GQD can absorb the shorter wavelength and then emit longer wavelength photons, has been recently reported. [95] The role of this phenomena in promoting enhanced photo- electrochemical response must be studied separately in a systematic manner.
From the results drawn in the preceding sections, the following key contributors to the systematic photocurrent enhancement can be inferred:

(i) the addition of an anatase TiO$_2$ layer on the underlying rutile TiO$_2$,
(ii) broadening of the light absorbance bandwidth with the addition of visible light harvester (CdS),
(iii) inclusion of a carbon layer in the form of GQD as the charge transport interface, and
(iv) a reductive thermal treatment to enhance charge transport.

Specifically, a 2-fold, 5-fold, 12-fold, and 19-fold increase has been noted with the addition of anatase, overlayer, CdS deposition, GQD addition, and varying annealing conditions, as summarized in Figure 12. It remains to be seen how the presented approach can be leveraged for light-driven applications such as photocatalysis and photovoltaics, using other oxides or chalcogenides.

### 4.5 Conclusions

The assembly of a heterostructure involving one-dimensional (1D) TiO$_2$ prepared using a seed-mediated approach and CdS, using the successive ionic layer adsorption and reaction (SILAR) approach, is presented. The addition of the carbon allotropes (carbon nanotubes (CNTs), fullerenes, graphene quantum dots (GQDs), and reduced graphene oxide (RGO)) as an interfacial layer between the TiO$_2$ and CdS is examined. Surface and optical studies indicate that carbon can be successfully integrated as a part of the heterostructure and it allows for a greater absorbance of the light upon deposition of the CdS using 15 SILAR cycles. The PEC properties of the TiO$_2$/CdS can be improved by (i) introducing a thin anatase layer on the surface of 1D TiO$_2$ of rutile form (which increase the photocurrent $\sim$2-fold) and the carbon interfacial layer. While all carbon allotropes shows an increase in the PEC response,
the presence of the GQDs at the TiO$_2$/CdS interface results in the highest improvement in the photoelectrochemical responses of the nanocomposite. Furthermore, thermal annealing in the presence of ammonia is shown to enhance the performance of all the carbon forms: A 19-fold increase in the photocurrent response is reported with the a-r-TiO$_2$/GQD/CdS nanocomposite, compared to the r-TiO$_2$ sample. Other combinations worthy of consideration in this configuration could be 1D ZnO, with alternative visible-light harvesters of the general formula XY (where X = Cd, Pb, or Zn and Y = S, Se, or Te). Note that such combinations do require the use of precursors amenable to assembly using the technique presented here.
Chapter 5

Summary and Future Work

5.1 Summary

Chalcogenide nanocrystal semiconductor nanoparticle sensitized TiO$_2$ photoanodes have been investigated in this research. The effects of carbon allotropes have also been studied in detail. Furthermore, the shape and the phase effects of TiO$_2$ nanostructure have been studied in detail. The key findings are summarized below.

5.1.1 Phase and Shape Transformation of TiO$_2$ Nano-structure

Titanium dioxide nanostructures prepared by a seed-mediated hydrothermal and electrochemical method are presented. TiO$_2$ nanotube was obtained by the electrochemical anodization method with controlled diameter and length while TiO$_2$ nanorod is fabricated using hydrothermal approach. The transformation of 1D nanorod to 3D branched architecture is achieved by using TiCl$_3$ treatment at 90$^\circ$ C. Surface, optical, chemical, and electrochemical response of titania nanostructures are thoroughly characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscope (SEM), energy dispersive X-ray (EDX), FTIR and
potentiostat. Surface characterization proves that a well defined nanostructure has been fabricated. Photocurrent and the absorbance spectrum demonstrate that the 3D branched architecture has much higher surface area and photoactivity compared to the 1D nanorod. The branching of TiO$_2$ nanorod improved the PEC response by offering more sites for sensitizer deposition.

TiO$_2$ exist in three main stable phases: rutile, anatase, and brookite. We have introduced a thin anatase layer on the surface of 1D TiO$_2$ of rutile form. Thin anatase layer coated 1D TiO$_2$ rutile and 1D TiO$_2$ rutile have absorbed nearly the same intensity of radiation. However, a two fold increase in the photocurrent has been observed indicating that anatase phase is more photoactive than the rutile phase.

5.1.2 One Pot Fabrication of the Chalcogenide Semiconductor

Heterostructure semiconductor is formed by coupling two semiconductors of different band gaps. On the basis of energy band gap and electron affinity of the semiconductor, there are three types of semiconductor heterojunctions, type I, type II, and type III. Schematic of the energy diagrams of the three types of semiconductor heterojunctions is presented in Figure ??.

There are various ways to couple the semiconductor to form the type II heterostructure semiconductor. These methods are either complex involving multiple steps or require complicated instruments. We have developed a one-pot, non-pressure
based, single precursor, and relatively low temperature, approach to assemble a type II heterostructure (TiO\textsubscript{2} nanotube /CdS). SEM, (HR) TEM, XRD, and EDX color mapping is used for thorough characterization of the nanocomposite. A photocurrent of 9.3 mA cm\textsuperscript{-2}, the highest value ever reported for this system is achieved because of the excellent electronic contact between two semiconductors.

These results will constitute the foundation for designing and developing other heterostructure involving several combinations such as A\textsubscript{a}O\textsubscript{b}/C\textsubscript{c}D\textsubscript{d} (A= Ti, Zn, or Fe / C = Cd or Pb / D= S, Se, or Te and a,b,c,d are constants). This method will have a large impact on the fabrication process of type II heterostructured materials used for hydrogen generation, solar cells, energy storage and sensors.

### 5.1.3 Charge Transformation Using Carbon Allotropes

Synthetic carbon allotropes have very high mobility of charge carriers. Thus, carbon allotropes can be integrated in the TiO\textsubscript{2}/CdS system to effectively promote charge transport. We have strategically integrated RGO in the branched TiO\textsubscript{2} CdS system.
Using RGO enhanced the photocurrent from 1.2 to 3.2 mA cm$^{-2}$. Furthermore, a reduction in the activity loss from 51\% to 6 \% over a 3 h continuous illumination of simulated solar radiation has been achieved by adding RGO.

After demonstrating the proof-of-concept using RGO in such a heterostructure, we have integrated different carbon allotropes in the 1D anatase coated TiO$_2$/CdS system. The charge transportation effect of the conducting carbon allotropes and the nitrogen doped conducting carbon allotropes has been studied in detail. All the carbon allotropes showed an increase in the photocurrent. The optimized photocurrent values after integrating GQD, RGO, carbon nanotube and fullerene are 2.8, 2.2, 1.9, and 1.6 mA cm$^{-2}$ respectively.

Additionally, the ammonia treatment has further increase the photocurrent of the heterostructured composite due to doping of the nitrogen atom in the carbon structure. This leads to the n-type electronic material. The optimized values of the photocurrent of GQD, RGO, carbon nanotube and fullerene integrated heterostructure after annealing in the ammonia atmosphere are 4.2, 3.4, 2.7 and 2.2 mA cm$^{-2}$ respectively. This result is inconsistent with the absorbance spectrum.

The graphene quantum dot has demonstrated the highest photocurrent compared to other carbon allotropes studied. Thus, systematic and thorough characterization has been done for this system.

5.2 Future Research

1) Since the branched TiO$_2$ structure shows high performance in the quantum dot sensitized photoanode, the material can be studied in the dye synthesized and per-
ovskites solar cell.

2) The one pot fabrication method is a very simple approach to sensitize the photoanode in TiO$_2$ nanotube with higher photoelectric response. This process can be studied in other combinations of nanocrystals and photoanode. This process can be the best solution processed method to fabricate quantum dots to wide band gap semiconductors.

3) In our study, we found that graphene quantum dots shows better charge transportation in chalcogenide nanocrystal sensitized photoanode. The effect of graphene quantum dot can be studied in electrode driven materials such as supercapacitors, solar fuel cells, and sensors.
Bibliography


