CHAPTER 6

CdSe/g-C$_3$N$_4$ Nanocomposites for Efficient UV Light photocatalytic Hydrogen Evolution

This chapter describes result on CdSe quantum dots (QDs)-graphitic carbon nitride (g-C$_3$N$_4$) nanocomposite for photocatalyst system. The synergistic effect of g-C$_3$N$_4$ and CdSe QDs percentage is studied for the separation of photogenerated charge carriers, and photocatalytic H$_2$ evolution under UV irradiation. 10% CdSe QDs showed maximum photocatalytic activity of 1900 µmol/g in the UV light. The composites were characterized by X-ray diffraction (XRD), Ultraviolet-visible diffuse reflection spectroscopy (UV-Vis-DRS), Fourier Transform Infrared spectroscopy (FTIR), High resolution transmission electron microscopy (HRTEM), and Photoluminescence spectroscopy (PL).
6.1 Introduction

Sustainable progress of human civilization requires pollution free source of energy. Clean and green energy has been motivated due to scarcity in the petroleum supplies and increasing concerns over issues such as climate change and energy security. Although hydrogen economy and related green chemistry solutions have been proposed for many years, generation of energy from renewable sources in a safe and reversible manner still remains a big challenge [1-3]. Semiconducting photocatalysts have attracted extensive attention in recent years owing to their great potential in environmental purification and hydrogen energy production [4-6]. Hydrogen is widely considered to be the future clean energy carrier in many applications, such as environmentally friendly vehicles, domestic heating, and stationary power generation [7]. To date, various semiconductors have been explored for this hydrogen generation; most of them are metal-based inorganic solids such as oxides [8-9], metal (oxy)sulfides [10] and metal (oxy) nitrides [11].

Photocatalytic water splitting holds particular interest since it utilizes the inexpensive natural resource water. Also it has the simplicity of using a powder in solution and sunlight to produce H\textsubscript{2} and O\textsubscript{2} from water and can provide a clean, renewable energy source, without producing greenhouse gases or having many adverse effects on the atmosphere. Semiconductors have a band structure in which the conduction band is separated from the valence band by a band gap with a suitable width. When the energy of incident light is equal to or greater than that of a band gap, electrons and holes are generated in the conduction and valence bands, respectively. The photogenerated electrons and holes cause redox reactions similarly to electrolysis. Water molecules are reduced by the electrons to form H\textsubscript{2} and are oxidized by the holes to form O\textsubscript{2} for overall water splitting. Essential point in the semiconductor photocatalyst material is the width of the band gap and levels of the conduction and valence band. The bottom level of the conduction band has to be more negative than the redox potential of H\textsuperscript{+}/H\textsubscript{2} (0 V vs Normal Hydrogen Electrode (NHE)), while the top level of the valence band be more positive than the redox potential of O\textsubscript{2}/H\textsubscript{2}O (1.23 V). Therefore, the theoretical minimum band gap for water splitting is 1.23 eV that corresponds to light of about 1100 nm. The materials exploit for photocatalytic reaction must convince several functional requirements with respect to band gap energy and electrochemical properties: (i) suitable solar light absorption capacity also
conduction and valence band edges straddling the reduction oxidation potentials of water (ii) rapid charge transfer (iii) minimization of energy losses related to charge transport and recombination of photoexcited charges (iv) chemical stability to corrosion and photocorrosion in aqueous environments (v) kinetically suitable electron transfer properties from photocatalyst surface to water interface. (vi) overall, the best photocatalyst has a high quantum yield and gives a high rate of gas evolution [12]. TiO₂ is the most widely used photocatalyst due to its non-toxicity, good stability and excellent photocatalytic activity [13-14].

Recently, Wang et al. [15] reported that a metal-free polymeric photocatalyst, organic semiconductor graphitic carbon nitride (g-C₃N₄), showed a good photocatalytic performance for hydrogen production via water splitting under suitable light irradiation. The metal-free g-C₃N₄ photocatalysts possess very high thermal and chemical stability as well as appealing electronic properties, which make them valuable materials for photocatalysis-driven applications. The g-C₃N₄ is composed of carbon and nitrogen only, and the optical band gap was determined to be 2.7 eV. In addition, g-C₃N₄ is stable under light irradiation in solution with pH = 0 – 14 due to the strong covalent bonds between carbon and nitride atoms. There are several phases of g-C₃N₄ that naturally exists, including α, β, cubic, pseudocubic, and graphitic structures [16-17]. Among these various allotropes, the g- C₃N₄ is considered the most stable one under ambient conditions. Though the performance of g-C₃N₄ in photocatalytic reactions is rather limited by the low quantum efficiency, owing to the high recombination rate of photogenerated electron-hole pairs for this pristine g-C₃N₄. To overcome this difficulty, many efforts have been carried out to improve the photocatalytic performance of g-C₃N₄, such as nonmetal doping [18-20], noble metal deposition [21-22], preparation of nano-porous g-C₃N₄ [23-27], graphene [28-29], activated protonation [30],organic days [31] and nanocomposites with MWCNT [32].

Semiconductor QDs such as PbS [33], CdTe [34], CdS [35] and CuInS₂ [36] have been used as photocatalysts to improve their photocatalytic activity in the solar spectrum. CdS/CdSe co-sensitized photoelectrode for efficient hydrogen generation [37-38]. CdSe QDs are the most extensively investigated class of II–VI semiconductor nanocrystals, owing to their valuable optical properties and the availability of reliable synthesis procedures [39]. CdSe is an n-type semiconductor with direct band gap (1.74 eV) and an exciton Bohr radius of ~ 6 nm and exciton
binding energy 16 meV [40-43]. CdSe QDs used for H₂ evolution reported by Andrew Frame et al. [44] and also their nanocomposites CdSe-MoS₂ reported by Andrew Frame et al. explored for hydrogen evolution [45]. CdSe QDs used as photocatalysts to improve their photocatalytic activity in the solar spectrum [46]. Recently shown CdS coupled with g- C₃N₄ for efficient photocatalytic hydrogen generation by Lei Ge et al. [47].

6.2 Materials and Methods

Cyanamide (Aldrich 99% purity), Selenium powder (99%), trioctylphosphine (90%), oleic acid and 1-octadecene were procured from Sigma Aldrich. Thioglycolic acid (TGA), CdO (extra pure) procured from Merck. All the chemicals were used directly without further purification.

6.2.1 Synthesis of g-C₃N₄

The g-C₃N₄ sheets were synthesized by using cyanamide as precursor [15]. Cyanamide was heated in a programmable furnace at 550 °C in air for 4 hrs with a ramp rate of 2.3 °C min⁻¹.

6.2.2 Synthesis of CdSe QDs

CdSe QDs are synthesized by hot injection or organometallic method. In the typical synthesis, first (trioctylphosphine selenide) TOPSe was synthesized with mixture of 4mM selenium(Se) powder and 5 ml trioctylphosphine (TOP) dissolved in 5 ml of 1-octadecene by stirring in argon atmosphere. In another case, a mixture of 0.51 mg of Cadmium oxide (CdO), 25 ml 1-octadecene and 5 ml of oleic acid was heated in three necks round bottle flask at 2400C in argon atmosphere for one hour. Then TOPSe solution was quickly injected in the above mixture at 240 °C and was kept it for 90 seconds. Then the heater was removed and solution was kept for cooling. The precipitation of the red colored CdSe QDs was done by adding absolute ethanol solution. CdSe particle was obtained by centrifuging the solution. Then CdSe QDs was washed by dissolving the solution in toluene and again precipitation with ethanol followed by the centrifugation. This washing process carried out five times and then CdSe QDs stored by dispersing in toluene.

Oleic acid capped CdSe QDs were ligand exchanged with TGA using protocol as described with some modification [48]. Briefly 5 ml oleic acid capped CdSe QDs in
toluene solution containing approximately 250 mg of CdSe QDs which is mixed with 5 ml of TGA, 5 ml ethanol and 5 ml of acetone. The mixture of solution was then continuously stirred for 12 hours. The solution was then centrifuged at 3500 rpm for 5 min and collected the TGA capped CdSe QDs. The TGA capped CdSe QDs were washed 5-6 times with ethanol and dry in vacuum. Further used for nanocomposite preparation.

6.2.3 Synthesis of CdSe QDs- Polymeric g-C₃N₄ nanocomposite

The CdSe- g-C₃N₄ nanocomposite synthesized by using 0.1 g of g-C₃N₄ mixed 5, 10, 20, 35, 50 wt % of CdSe powders are added in absolute ethanol. The reaction further proceeds for 2 hrs at 80 °C under N₂ atmosphere. After completion of reaction, final product is centrifuged 3 to 4 times by ethanol and finally keep for vacuum drying. Here we used TGA capped CdSe QDs as above discussed for preparation of nanocomposites. During formation composite at 80 °C the TGA molecule of CdSe QDs gets removed, so electrostatic binding of between positively charged CdSe QDs and negatively charged g-C₃N₄ is possible.

6.3 Basic Chracteriations and Hydrogen evolution measurement

The structure and morphology of the bulk and composite powders were characterized by X-ray powder diffraction (Philips X’Pert PRO) and High resolution TEM (FEI Tecnai 300). The optical properties were studied by diffuse reflectance spectroscopy (JASCO Instruments), UV-Visible spectroscopy (JASCO V-670 spectrophotometer), FTIR measurements were performed on a Perkin-Elmer Spectrum One spectrophotometer over the spectral range of 400– 4000 cm⁻¹ and PL measurements were performed on a Perkin-Elmer LS 55 spectrophotometer. Measurements of the hydrogen evolution as a result of water splitting were conducted in a closed quartz reaction cell of 80ml volume, having a provision for withdrawal of the gaseous samples at desired intervals. A sample weighing about 50 mg was placed in the reaction cell filled with 15 ml water, to which were added 0.35 M Na₂SO₃ and 0.24M Na₂S to serve as sacrificial agents. The cell was normally flushed with nitrogen prior to the commencement of the reaction. A UV light ( 400 W medium pressure, 225-400 nm, peak at 365nm) used for testing photocatalytic activity, all around with a flowing water channel of ~ 0.5 cm width to cut-off heat radiation. The reaction cell was positioned vertically at a distance of ~ 2 cm from the lamp. The reaction products
were analyzed on a gas chromatograph (Nucon-5765, India, 2.5 m molecular sieve-5A packed column using thermal conductivity detector at 360 K, Argon for carrier gas.

6.4 Result and Discussion

6.4.1 X-Ray Diffraction (XRD)

The X-ray diffraction patterns (XRD) of g-C₃N₄, CdSe QDs and CdSe QDs /g-C₃N₄ are shown in Fig.1 the two peaks are present for g-C₃N₄, the peak at ~13.14° corresponds to structural packing of tri-s-triazine units, which is indexed as (100) peak. The distance is calculated as $d=0.681$ nm. The peak at ~ 27.4° corresponds to interlayer stacking of aromatic segments with distance of 0.326 nm, which is indexed as (002) peak of the stacking of the conjugated aromatic system.

![X-ray diffraction patterns (XRD) of g-C₃N₄, CdSe QDs and CdSe QDs /g-C₃N₄ nanocomposites (5, 10, 20, 35, and 50 %) of CdSe.](image)

Figure 1: The X-ray diffraction patterns (XRD) of g-C₃N₄, CdSe QDs and CdSe QDs /g-C₃N₄ nanocomposites (5, 10, 20, 35, and 50 %) of CdSe.
The crystal planes measured for CdSe QDs, the theta values are ~ 25.51°, 42.10° and 49.56° corresponding to the crystal planes of (111), (220) and (311) and corresponding d-spacing are 0.351, 0.241 and 0.183 nm with cubic structure (JCPDS-190191) which is in good agreement with HRTEM images discussed in later section. The line broadening at the full width at half maximum (FWHM) allows approximate estimation of the mean size of the crystallites from the Scherrer formula. The estimated size of CdSe QDs ~3-4 nm calculated from Scherrer formula. The XRD peak positions and shapes of CdSe QDs/g-C$_3$N$_4$ nanocomposite samples reveal sheet-like structure decorated with crystalline CdSe QDs with different orientations, and the CdSe QDs are distributed randomly on the g-C$_3$N$_4$ sheets hardly change when compared with those of g-C$_3$N$_4$, indicating that the modification with CdSe QDs does not alter the structure of g-C$_3$N$_4$. The CdSe QDs attached via their crystal planes to the g-C$_3$N$_4$.

6.4.2 UV-Vis- Diffuse Reflectance Spectra (DRS)

The optical absorption of as-prepared g-C$_3$N$_4$ and CdSe QDs/g-C$_3$N$_4$ samples were measured using UV–vis diffuse reflectance spectra (DRS-Abs mode). As shown in Fig.2 the band gap absorption edge of g-C$_3$N$_4$ is around 455 nm [49]. The band gap energy of pristine g-C$_3$N$_4$ estimated with from the DRS–absorption spectra it is about 2.72 eV, which is in good agreement with the values reported in the literature [15]. Compared with g-C$_3$N$_4$, CdSe QDs/g-C$_3$N$_4$ shows more intensive absorption over the whole visible range of wavelengths shown in Fig 2.

The pure CdSe QDs have absorption in the visible range with a band edge at 550 nm CdSe QDs /g-C$_3$N$_4$ (10 %). CdSe QDs/g- C$_3$N$_4$ composite samples show a slight shift of the g-C$_3$N$_4$ band gap and a shoulder on the adsorption edge that reaches further out in the visible region. These observations are attributed to the interaction between g-C$_3$N$_4$and CdSe QDs in the composite samples. When the QDs size is reduced to dimensions less than the exciton Bohr radii of the electrons and holes, they are confined by a potential barrier in all directions. The quantum confinement of electrons and holes leads to size-dependent electronic energy levels, which is alike to discrete atomic-like electron and hole energy states. The size-dependence of electronic energy levels tender the flexibility to control the optical and electrical properties of
semiconductor QDs by changing the physical dimensions of the QDs, and hence, manipulating their effective bandgap energy \( (E_g) \) [50].

![Figure 2: Diffuse Reflectance Spectra (DRS) in Absorption mode (a) g-C\(_3\)N\(_4\), (b) 10 \%, (c) 20\%, (d) 35\%, (e) 50\% CdSe with g-C\(_3\)N\(_4\) nanocomposite and (f) Bare CdSe QDs (inset given Tauc plot)](image)

The spectral range covered increases with the increase of the CdSe QD weight ratios content. The total absorption of the composite samples increases the production of electron–hole pairs. Diffuse Reflectance Spectra (DRS) in absorption mode indicates a high dispersion of the CdSe QDs in the g-C\(_3\)N\(_4\) and their close contact, setting the stage for rapid charge transfer between the components of the composite.

6.4.3 Photoluminescence (PL)

![Figure 3](image)

Figure 3 (a) and (b) presents the photoluminescence spectra for pure g-C\(_3\)N\(_4\), 10 \% CdSe QDs/g-C\(_3\)N\(_4\) and CdSe QDs samples. The main emission peak is centered at about 460 nm for the pure g-C\(_3\)N\(_4\) sample, which can be attributed to recombination of electron–hole pairs in the g-C\(_3\)N\(_4\) [51]. Once CdSe QDs are added, the photoluminescence drops markedly. This demonstrates that the recombination of photogenerated electrons and holes is greatly inhibited by the addition of CdSe QDs, which indicates that the separation of photogenerated electrons and holes in the CdSe QDs/g-C\(_3\)N\(_4\) composites is more efficient than in pristine g-C\(_3\)N\(_4\).
The g-C₃N₄ is excited under light irradiation, and the excited state electrons are transported from the conduction band of g-C₃N₄ to CdSe QDs owing to the junction built between g-C₃N₄ and CdSe QDs, which prevents the direct recombination of electrons and holes. It is not obvious however whether increasing of the hydrogen evolution output can be solely attributed to this effect. The band alignment diagram of g-C₃N₄ and CdSe QDs [52] shown in below Fig. 4:

![Figure 4: The band structure comparison of g-C₃N₄ and CdSe QDs](image-url)
6.3.4 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra shown in Fig. 5 of TGA capped CdSe QDs shown peaks at 2904 cm\(^{-1}\) that corresponds to S-CdSe bond. Also peaks 1606 cm\(^{-1}\) and 1570 cm\(^{-1}\) corresponds to carboxylic (-COOH) salts of TGA. Absence of intense peak is around 1720 cm\(^{-1}\) that concludes complete removal of oleic acid from the surface of CdSe QDs [53-55].

![FTIR spectra of (a) CdSe, (b) g-C\(_3\)N\(_4\) and (c) 10\% CdSe nanocomposite.](image)

**Figure 5**: FTIR spectra of (a) CdSe, (b) g-C\(_3\)N\(_4\) and (c) 10\% CdSe nanocomposite.

In case of CdSe QDs /g- C\(_3\)N\(_4\) are nanocomposites the broad peak at 3000–3700 cm\(^{-1}\) in the spectra corresponds to the stretching mode of –OH, and the physically adsorbed H\(_2\)O also contributes to this broad peak. For the g-C\(_3\)N\(_4\), the peaks at 1250, 1325, 1546, and 1647 cm\(^{-1}\) [56-57] correspond to the typical stretching modes of CN heterocycles and also the characteristic breathing mode of triazine units at 806 cm\(^{-1}\) is observed. It confirms that TGA was completely removed from the surface of CdSe QDs and attachment between CdSe QDs and g-C\(_3\)N\(_4\) is pure electrostatic.
6.4.5 Transmission Electron Microscopy (TEM) and High Resolution (HRTEM)

TEM and HRTEM images measurements were performed to characterize the morphology and structure of CdSe QDs, g-C$_3$N$_4$ and CdSe QDs /g-C$_3$N$_4$. The g-C$_3$N$_4$ sheet about 200-300 nm size shown in Fig. 6. The HRTEM images of CdSe QDs shows well defined lattice fringes with $d$-spacings of $\sim$ 0.354, 0.243 and 0.185 nm corresponding to the (111), (220) and (311) planes of cubic structure. SAED pattern of CdSe QDs having diffuse reflecting ring which shows that much smaller size $\sim$ 3-4 nm of it shown in Fig. 7 below. In case of composites of CdSe QDs/g-C$_3$N$_4$, with 10% and 50% CdSe QDs shows homogenous distribution on g-C3N4 sheets shown in Fig. 8 and 9.

![TEM images of g-C$_3$N$_4$ taken at various magnification.](image)

*Figure 6: TEM images of g-C$_3$N$_4$ taken at various magnification.*
Figure 7: HRTEM images of CdSe QDs and corresponding SAED pattern.

Figure 8: TEM and HRETM images of CdSe (50 %) – graphitic-C$_3$N$_4$
Figure 8: TEM and HREM images of CdSe (50 %) – graphitic-C$_3$N$_4$

Figure 9: TEM and HREM images of CdSe (10 %) – graphitic-C$_3$N$_4$
6.4.6 Photocatalytic Hydrogen (H₂) evolution

Figure 10 shows photocatalytic H₂ evolution activity of bulk g-C₃N₄ and for nanocomposites with increasing wt % of CdSe QDs. The photocatalytic activity of CdSe/g-C₃N₄ composites of up to 50 % CdSe loading was higher as compared to the bulk g-C₃N₄. The highest activity is observed for the 10 % CdSe/g-C₃N₄ nanocomposite is about 1900 µmol/g. The increased photocatalytic hydrogen evolution activity of the nanocomposite compared to its pure components suggests that the separation of photogenerated electron–hole pairs to its components, so that their distance prevents efficient recombination and provides for longer lifetimes. For photocatalytic water splitting, the effects of quantum confinement have been established only qualitatively [52]. According to Gerischer theory [58], a widening of the semiconductor bandgap is expected to increase the electron transfer rate between a semiconductor and a redox couple in solution, because the thermodynamic potential of the photogenerated electron-hole pairs is increased.

![Photocatalytic H₂ evolution activity of g-C₃N₄ and its nanocomposites with CdSe QDs](image)

**Figure 10:** Photocatalytic H₂ evolution activity of g-C₃N₄ and its nanocomposites with CdSe QDs

The optimal loading at 10 wt % of CdSe shows maximum percentage of Hydrogen evolution. The photogenerated electrons in g-C₃N₄ are transferred to CdSe QDs due to the difference of Conduction band (CB) edge potentials. The valance band (VB) of
CdSe QDs may be lower than that of g-C₃N₄ due to the quantum size effect. The photogenerated holes on the VB of CdSe QDs can migrate to that of g-C₃N₄. Therefore, both the efficient electron–hole separation and the excited electrons from CdSe QDs lead to a significant enhancement of photocatalytic H₂ evolution in the CdSe QDs/g- C₃N₄ composite system. The CdSe QDs of ~3-4 nm size dispersed uniformly over the g- C₃N₄ sheets becomes evident in terms of the moles of H₂ produced per gram of CdSe QDs available in a particular nanocomposites.

6.5 Summary

In summary, a series of CdSe quantum dot -coupled graphitic carbon nitride (g-C₃N₄) photocatalysts with high UV light photocatalytic H₂ evolution activity were synthesized via a chemical method. After introduction of CdSe QDs, the g-C₃N₄ showed efficient separation of the photogenerated charge carriers and enhancement of the UV light photocatalytic H₂ evolution activity. The optimal CdSe QD content was found to be 10 wt %, and the corresponding H₂ evolution rate was 1900 μmol/g, which was higher than that of pure g-C₃N₄. The synergic effect was explained based on PL spectra and band alignment diagram. The novel CdSe QDs/g-C₃N₄ composite material can be a very promising candidate for the high-performance H₂ evolution via photocatalysts.
References:

47. X. Sun, J. Chen, J. Song, D. Zhao, W. Deng, and W Lei, Optics Express, 2010, 18, 1296.


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