CHAPTER 6

POLYANILINE AND ITS NANOCOMPOSITES

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CHAPTER 6

POLYANILINE AND ITS NANOCOMPOSITES

6.1. INTRODUCTION:

The combination of the semiconductors nanoparticles with polymers, plastic, glass and other semiconductors has proved to be an important initial step for the fabrication of many photonic as well as optoelectronic devices. Various inorganic-polymer nanocomposites composed of different combinations of two or more components have attracted progressive attention in today’s world due to their interesting physical properties and potential applications. These particles possess the advantageous properties of both metals and polymers, as well as exhibit many new characteristics different from the single-phase materials. The embedding or encapsulation of nanoparticles in polymer, may lead to termination of the growth of the nanoparticles by controlling of their nucleation by the polymer. Moreover, it facilitates in casting of the film and attainment of the desired particle size distribution. The materials with delocalized conjugated structures have been widely experimented in this regard due to their rapid photoinduced charge separation and relatively slow charge recombination.

Hence, Polyaniline (PANI) being a conducting polymer with an extended \( \pi \)-conjugated electron system, proved to be a promising candidate due to its high absorption coefficients in visible-light range and high mobility of charge carriers. Furthermore, PANI in its undoped or partially doped states act as electron donors upon photoexcitation, is a good hole conductor, and can carry current with several milliamperes. Thus, the combination of PANI with inorganic materials specially semiconductor (SC) nanomaterials is gaining importance because PANI has good processibility, ease of preparation, environmental stability, photoelectric property, cost effectiveness and potential in the field of catalysis, biosensors, batteries, electronics, opto-electronics and electronic technology and enable control of particle size and lead to uniform distribution of nanoparticles (NPs).

Polyaniline is an intensively studied polymer since last two decades. During 1830’s, polyaniline was commonly known as “aniline black”, a term used for any product.
obtained as a result of oxidation of aniline\(^\text{15}\). This conducting polymer was well-known for its ease of synthesis, environmental stability, and unique acid/base doping/dedoping and oxidation/reduction chemistry\(^\text{16,17}\). The conducting properties of polyaniline were rediscovered in the early 1980s, since then it has been extensively studied for many potential applications including lightweight battery electrodes, electromagnetic shielding devices, anticorrosion coatings, and sensors\(^\text{18}\).

PANI can be synthesized by either chemical or electrochemical oxidation of aniline under acidic conditions. Chemical method is quite efficient for the synthesis of PANI nanocomposites in comparison to electrochemical polymerization\(^\text{15,16,19}\). Chemical method is more effective for mass production of PANI and electrochemical method is more effective for PANI thin films\(^\text{17}\). Polymerization of aniline by chemical oxidation method has been extensively used for synthesizing polyaniline in bulk quantities due to its ease and low manufacturing cost\(^\text{16,20}\). A chemical synthesis method of polyaniline requires aniline, an oxidant and a strong mineral acid dopant\(^\text{18}\). The advantages of chemical method lie in the fact that during this method PANI can have various morphological and electrochemical properties depending upon polymerization reaction conditions such as reaction time, stirring speed, reaction temperature, type of solvent, type of oxidant, dopant acid, surfactant and concentration of the reactants\(^\text{20-22}\).

Polymerization of aniline is an exothermic process, hence is generally carried out at low temperatures with one reactant slowly added into the other under vigorous stirring\(^\text{16}\). The mineral acid dopant used can be inorganic acids (hydrochloric, sulfuric, perchloric, fluoroboric acids), organic acids (p-toluenesulfonic, benzenesulfonic, p-styrenesulfonic acids), or polymeric acids (polyamic, polyacrylic, polyvinylsulfonic acid)\(^\text{11,23}\). The various oxidants often reported are sodium or ammonium peroxydisulfate (VI), ammonium peroxydisulfate/ammonium cerium (IV) nitrate mixture, chromate (VI) potassium, ammonium persulfate and hydrogen peroxide\(^\text{22,24}\). The organic solvents used includes benzene, hexane, toluene, methylene chloride, diethyl ether, carbon tetrachloride, chloroform, carbon disulfide, or o-dichlorobenzene\(^\text{18}\). Polyaniline can exist in three isolable oxidation states as “salts” or “bases”, leucoemeraldine (LEB-white/clear or LES-colorless), emeraldine (EB-green or ES-blue), and pernigraniline (PB-blue or PS-violent), among which emeraldine salt (ES) is partially oxidized form of polyaniline and is the only electrically conductive form\(^\text{14,25}\). The various forms of polyaniline are shown in Figure 6.1.
The polyaniline has electronic, magnetic, and optical properties similar to metals, in addition to the flexibility and processibility of conventional polymers\textsuperscript{20}. PANI has potential applications in various technologies like electromagnetic shielding\textsuperscript{26}, conductive coatings\textsuperscript{27}, corrosion protection\textsuperscript{28}, artificial muscles\textsuperscript{29}, bio-sensing\textsuperscript{30}, molecular electronics\textsuperscript{31}, light-emitting diodes\textsuperscript{32}, field-effect transistors\textsuperscript{33}, photovoltaic cells\textsuperscript{34}, sensors\textsuperscript{35,36}, secondary battery electrodes\textsuperscript{37}, supercapacitors\textsuperscript{38,39}, catalyst substrate\textsuperscript{40}, photocatalyst\textsuperscript{22,41} and conducting molecular wires\textsuperscript{20}.

Considering these good properties, potential applications of PANI and ability to support positive as well as negative charge carriers due to the presence of conjugated \(\pi\)-electrons along the backbone\textsuperscript{42}, it can be used in synthesis of heterostructure nanocomposites (NCs). Polyaniline-semiconductor nanocomposites are known to possess quite different chemical, physical, optical and electrical properties from those characteristic of the parent polyaniline due to the interaction of delocalized carriers between semiconductor quantum dots and PANI\textsuperscript{13,21,26}. These nanocomposite materials plays a promising role in the fabrication of electronic devices that combine superior electronic, magnetic and optical properties\textsuperscript{26,31,43}. The large surface to volume ratio in nanocomposites enables an efficient separation of photoinduced charges, which is important for photo voltaic and photocatalytic applications\textsuperscript{34,41,44}. As the size and extent of aggregation of the particles play a significant role in the optical and catalytic properties, stabilization of the particles in suitable matrix is essential\textsuperscript{1,42}.

**Figure 6.1:** Different isolable oxidation states of polyaniline.
There have been several reports describing the synthesis of photoactive nanocomposites of polyaniline (PANI) with semiconductors such as PANI/TiO$_2$, PANI/BiVO$_4$, PANI/SiO$_2$, PANI/SnO$_2$, PANI/CdS, PANI/V$_2$O$_5$ and PANI/Fe$_3$O$_4$/SiO$_2$/TiO$_2$.

Naked CdS nanoparticles are not stable in aqueous solutions under irradiation in a photocatalytic reaction due to electrochemical corrosion, but it has been reported that the supported CdS has a performance and stability superior to that of the unsupported one, because the active ingredient is dispersed on the supports, and the supports provide heterojunctions for electrons and holes that restrict the charge recombination and $S^{2-}$ oxidation. PANI is a p-type while CdS nanoparticles are n-type semiconductor, therefore it is expected that useful photoconducting and photocatalyting nanocomposites can be created by combination of PANI and CdS nanoparticles. Other II–VI group semiconductor nanomaterials such as PbS, ZnS, ZnSe and CdSe have also been studied extensively due to their strongly size-dependent optical properties. Nanoscale metal particles of silver, gold and titania provide a very exciting research field due to their interesting properties and potential use in vast technological applications. Nanoparticles containing titanium (TiO$_2$) are appealing because of their excellent physical and chemical properties as well as their extensive use in many areas, such as coatings, solar cells, and photocatalysts. TiO$_2$ and ZnS due to their wide band gaps are an efficient photocatalysts but the major drawback is that they can only be excited under UV light which is only 4–6% of total solar radiation. It was reported that the band gap of PANI–TiO$_2$ composites is smaller than that of pure TiO$_2$ nanoparticles and thus allows PANI–TiO$_2$ to absorb more photons, and thus, will enhance the photocatalytic efficiency of TiO$_2$ under sunlight. PANI/TiO$_2$ nanocomposites show improved properties because PANI and TiO$_2$ can act as an electron donor and acceptor, respectively.

In our previous work (Chapters 3-5), though successful enhancement in the photocatalytic activity of CdS could be done by combining it with TiO$_2$ and ZnS, forming CdS-TiO$_2$ and CdS-ZnS sandwich type nanocomposites, but they showed poor stability after few repetitive cycles, which might be due to the photocorrosion of CdS. Thus, in an attempt to prevent Cd$^{2+}$ ion leaching, in the present work, CdS and its nanocomposite systems (CdS-ZnS and CdS-TiO$_2$) were supported onto stable support of polyaniline.
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CdS, CdS-ZnS and CdS-TiO₂ nanomaterials were added to PANI in order to study the effect of PANI over the stability, structural, physical, thermal, optical and photocatalytic properties of these nanomaterials. Overall, this work would provide new insights into the fabrication of conducting polymer/semiconductor nanocomposites with desired nanostructure as high performance photocatalysts and would facilitate their applications in environmental purification and solar energy conversion.

6.2. MATERIALS AND METHODS:

6.2.1. Synthesis:

PANI was synthesized by chemical method by oxidizing aniline in H₂SO₄ (Sulphuric Acid) with the help of APS (Ammonium Persulphate). Polymerization of aniline into polyaniline was found to take place quickly as observed by color change of the reaction mixture from pale to bluish green and finally to dark green in few minutes after the addition of APS. Thus in order to slow down the polymerization processes to obtain nanosized particles, the reactions were preceded at low temperatures. PANI and its various nanocomposites were synthesized as follows:

a) Polyaniline (PANI):

A solution of aniline (0.2M) was prepared in 100mL chloroform (2.462M). Another solution of APS (0.05M) was prepared in 100mL H₂SO₄ (1M). The second solution was added slowly into first and kept at 4-5°C overnight for polymerization.

b) CdS-PANI Nanocomposite (PC):

Synthesis of PC took place by in-situ polymerization of PANI in CdS nanoparticles by single pot chemical precipitation method. 100mL aqueous solution of Cd(NO₃)₂ (0.085M) was prepared and 50mL methanol (24.44M) was added to it with vigorous stirring. To this 100mL aniline (0.2M) solution prepared in chloroform (2.462M) was added with vigorous stirring, which was continued for additional 1 hour. The reaction was then carried out in H₂S atmosphere for 1 minute with vigorous stirring, which was continued for 2 hours. A solution of APS (0.05M) was prepared in 100mL H₂SO₄ (1M) in a separate vessel. This solution was added slowly into previous one and kept at 4-5°C overnight for polymerization. The solution turned out to be dark green in color.
c) CdS-ZnS-PANI Nanocomposite (CZP):

50mL methanol (24.44M) was added into 100mL aqueous ZnCl$_2$ (0.15M) drop wise with continuous stirring. The reaction was then carried out in H$_2$S atmosphere for 1 minute with vigorous stirring, continued for additional 2 hours. The solution turned from transparent to milky white. In another reaction vessel 100mL aqueous Cd(NO$_3$)$_2$ (0.085M) was taken and 50mL methanol (24.44M) was added drop wise with continuous stirring. The reaction was then carried out in H$_2$S atmosphere for 1 minute with vigorous stirring, which was continued for 2 hours. The solution turned from transparent to light yellow. The two solutions were added together with vigorous stirring which was continued for 2 hours. The resulting solution was yellow in color. To this reaction mixture 100mL aniline (0.2M) solution prepared in chloroform (2.462M) was added with vigorous stirring, which was continued for additional 1hour. A solution of APS (0.05M) was prepared in 100mL H$_2$SO$_4$ (1M) in a separate vessel. This solution was added slowly into previous one and kept at 4-5°C overnight for polymerization. The solution turned out to be dark green in color.

d) CdS-TiO$_2$-PANI Nanocomposite (CTP):

In a reaction vessel 100mL aqueous Cd(NO$_3$)$_2$ (0.085M) was taken and 50mL methanol (24.44M) was added drop wise with continuous stirring. The reaction was then carried out in H$_2$S atmosphere for 1 minute with vigorous stirring, which was continued for 2 hours. The solution turned transparent to yellow. To this solution 3.53mL TTIP (Titanium Tetra Isopropoxide) (0.1M) was added drop-wise (20 drops per minute). Stirring was continued to additional 2 hours. The solution turned light yellow in color. To this reaction mixture 100mL aniline (0.2M) solution prepared in chloroform (2.462M) was added with vigorous stirring, which was continued for additional 1hour. A solution of APS (0.05M) was prepared in 100mL H$_2$SO$_4$ (1M) in a separate vessel. This solution was added slowly into previous one and kept at 4-5°C overnight for polymerization. The solution turned out to be dark green in color.

All the precipitates were washed with water and acetone several times before drying in air.
6.2.2. Characterization:

The elemental analyses were carried out by Fourier Transform Infrared (FTIR) Spectroscopy, Energy Dispersive X-ray Spectroscopy (EDS). The structural and morphological properties were studied by X-Ray Diffraction (XRD) Spectroscopy, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). Thermal properties were determined by Thermal Gravimetric Analysis (TGA). The Optical properties were determined by employing UV-Vis Spectroscopy.

6.2.3. Photocatalytic Experiment:

The photocatalytic experiments were carried out using PANI and its nanocomposites (PC, CZP and CTP) as photocatalysts for the decolorization of a dye derivative Acid Blue-29 (AB-29) in the presence of visible light. A conventional immersion well photoreactor consisting of an inner and outer jacket was used. It was made of Pyrex glass equipped with a magnetic bar, a water circulating jacket and an opening for molecular oxygen. Irradiation was carried out using a halogen linear lamp (500W, 9500 Lumens). Initially in the photocatalytic experiment 180mL of the dye solution of desired concentration (0.06mM) containing the optimized dosage of the catalyst (1gL$^{-1}$) was magnetically stirred in the dark, in the presence of atmospheric oxygen for at least 20 minutes to attain adsorption–desorption equilibrium between dye and catalyst surface. Then, the first portion (5mL) of sample (0 minute) was taken out and irradiation was started. Other portions of samples (5mL each) were collected at regular intervals during the irradiation and analyzed after centrifugation. A continuous supply of molecular oxygen was maintained throughout each experiment and the constant reaction temperature (20±0.3°C) was maintained using a refrigerated circulating liquid bath. The decolorization of AB-29 was monitored by the change in absorption using UV-vis spectroscopic analysis technique (Shimadzu UV-Vis 1601). The concentration of dye was calculated by standard calibration curve obtained from the absorbance of the dye at different known concentrations. For the purpose of practical implementation, it is essential to evaluate the stability and reuse of the catalyst. The photocatalytic performances of the nanomaterials were studied for five consecutive cycles using the same portion of catalyst nanomaterials and a fresh solution of dye sample every time under similar conditions.
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6.3. RESULTS AND DISCUSSION:

6.3.1. ELEMENTAL ANALYSES:

The elemental analyses were carried out by Fourier Transform Infrared Spectroscopy (FTIR) Spectroscopy and Energy Dispersive X-ray Spectroscopy (EDS).

6.3.1.1. Fourier Transform Infrared (FTIR) Spectroscopy:

Figure 6.2 shows the FTIR spectrum of polyaniline (PANI) and its composite nanomaterials (PC, CZP and CTP).

The main characteristic peaks of PANI can be assigned as follows: the band at 3460cm\(^{-1}\) and 3230cm\(^{-1}\) can be attributed to the free (non hydrogen bonded) N–H stretching vibration and hydrogen bonded N–H bond between amine and imine sites\(^{17,59,60}\), the absorption peak at 1572cm\(^{-1}\) was the C=C bond stretching vibration peak in quinone ring, the absorption peak at 1497cm\(^{-1}\) was the C=C bond stretching vibration peak in benzene ring\(^{17,61}\), the absorption peak at 1301cm\(^{-1}\) was the C-N bond stretching vibration peak in quinone ring, the absorption peak at 1245cm\(^{-1}\) was the C-N bond stretching vibration peak in benzene ring\(^{4,59,60,62}\), peaks observed in the region 1000-1200cm\(^{-1}\), were due to the aromatic in-plane C-H bending modes\(^{61,63}\). The strong band at 1173cm\(^{-1}\) was considered to be a measure of the degree of electron delocalization and thus it is a characteristic peak of PANI conductivity\(^{60}\). The out-of-plane deformations of C-H in the 1,4-disubstituted benzene ring were located at 870cm\(^{-1}\)\(^{4,62,64}\). The FTIR spectrum obtained for synthesized PANI was consistent with the previous results\(^{4,22,59,62,63,65}\).

The FTIR spectrum for PC showed the characteristic peak for CdS at 405 cm\(^{-1}\)\(^{50,66,67}\). The incorporation of CdS nanoparticles caused the shift of some peaks of PANI. The absorption peak corresponded to polyaniline at 3506cm\(^{-1}\) showed a blue shift with respect to pure PANI peak at 3460cm\(^{-1}\) while the other absorption peaks of pure PANI at 1561cm\(^{-1}\), 1489cm\(^{-1}\), 1298cm\(^{-1}\), 1245cm\(^{-1}\), 1126cm\(^{-1}\) and 813cm\(^{-1}\) showed a red shift, and they were moved to 1548cm\(^{-1}\), 1451cm\(^{-1}\), 1290cm\(^{-1}\), 1243cm\(^{-1}\), 1119cm\(^{-1}\) and 784cm\(^{-1}\). The presence of peak at 1119cm\(^{-1}\) indicated the formation of polyaniline in the nanocomposite\(^{60,61,63}\). In PC, CdS and PANI formed a coordination bond and the electrons transferred from PANI to CdS, which lead to weakened bond strengths and the conjugated system of PANI and thus weakened vibration of PANI. This also
led to increased density of electrons in CdS and hence increased amount of photoelectrons, thus improved photocatalytic activity of nanocomposites\textsuperscript{59}.

Similar to the results of PC, CZP showed a red shift in the peaks corresponding to pure PANI at 1555cm\(^{-1}\), 1475cm\(^{-1}\), 1287cm\(^{-1}\), 1227cm\(^{-1}\), 1108cm\(^{-1}\) and 807cm\(^{-1}\), indicating the weakened bond strengths and the conjugated system of PANI and increased density of electrons in CdS, thus improved photocatalytic activity of CZP. The presence of peaks at 405cm\(^{-1}\) and 612cm\(^{-1}\) confirmed the presence of CdS\textsuperscript{50,67} and ZnS\textsuperscript{68,69} in CZP respectively. The broad peaks around 400–800cm\(^{-1}\) of CTP were due to the Ti–O and O–Ti–O bond in the TiO\(_2\)\textsuperscript{60,65}. This broad peak overlapped the peak of PANI at 813cm\(^{-1}\) and the characteristic peak of CdS at 405cm\(^{-1}\). The peak at 1629cm\(^{-1}\) in CTP nanocomposite was due to the typical bending mode of water molecules adsorbed on TiO\(_2\) surface\textsuperscript{65}. The presence of peak at 1139cm\(^{-1}\) endorsed the formation of PANI in CTP\textsuperscript{43,60}. The incorporation of TiO\(_2\) particles caused the shift of some peaks of PANI. For example, the peaks at 3426cm\(^{-1}\), 3079cm\(^{-1}\), 1560cm\(^{-1}\), 1486cm\(^{-1}\), 1290cm\(^{-1}\) and 1238cm\(^{-1}\), were shifted to lower wave-numbers (red shift), implying that the bond strengths and the conjugated system of PANI were weakened after coupling with TiO\(_2\)\textsuperscript{4,65}. Thus, this led to increased density of electrons in TiO\(_2\) and hence improved photocatalytic activity of CTP.

Figure 6.2: FTIR spectra of PANI and its nanocomposites (PC, CZP and CTP).
It was observed that in comparison to PANI, the IR spectra of PANI-nanocomposites (PC, CZP and CTP) showed a red shift (lower wave-number) and hence improved photocatalytic response. The comparison and significance of various peaks obtained by IR spectra of PANI and PANI-nanocomposite (PC, CZP and CTP) are given in Table 6.1.

Table 6.1: Peaks obtained by FTIR spectra of PANI and its nanocomposites (PC, CZP and CTP) and their significance.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>FTIR Peaks (cm⁻¹)</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PANI</td>
<td>PC</td>
</tr>
<tr>
<td>A</td>
<td>3460</td>
<td>3506</td>
</tr>
<tr>
<td>B</td>
<td>3150</td>
<td>3150</td>
</tr>
<tr>
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<td>1126</td>
<td>1119</td>
</tr>
<tr>
<td>H</td>
<td>813</td>
<td>784</td>
</tr>
</tbody>
</table>

6.3.1.2. Energy Dispersive X-ray Spectroscopy (EDS):

Figure 6.3 shows the EDS spectra of PC, CZP and CTP nanocomposites. The EDS spectra clearly showed the presence of CdS in PC, CdS and ZnS in CZP and CdS and TiO₂ in CTP. Thus, confirming the inclusion of desired semiconductors in PANI.

![Figure 6.3: The EDS spectra of (a) PC, (b) CZP and (c) CTP.](image)
6.3.2. STRUCTURAL ANALYSES:

The structural analyses were done by X-Ray Diffraction (XRD) Spectroscopy, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

6.3.2.1. Microscopic Studies:

Microscopic studies were done using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

*Scanning Electron Microscopy (SEM):*

Figure 6.4 shows SEM images of PANI, PC, CZP and CTP nanocomposites which revealed that the catalysts have mixture of agglomerated and non-agglomerated fluffy particles similar to the result reported before\(^5\).

![SEM images of PANI, PC, CZP and CTP](image)

**Figure 6.4:** The SEM images of PANI, and its composite nanomaterials (PC, CZP and CTP).

*Transmission Electron Microscopy:*

Figure 6.5 (a) and (b) shows the TEM images of synthesized polyaniline nanostructures (PANI). A large quantity of interconnected branched polyaniline nanofibers could be seen. The diameters of most fibers were less than 50nm.
Figure 6.5 (c) shows TEM images of PC. It can be seen that uniform spherical CdS nanoparticles were found well dispersed on the PANI nano-fibers. The incorporation of CdS in PANI was confirmed previously by FTIR and EDS. Because of participation of PANI in the composites, it was found that PANI prevented the agglomeration of CdS particles to a certain extent. As it was already mentioned for PC, this enabled electron transfer easy from PANI to CdS, and excited photoelectrons readily in CdS, hence, improved the photocatalytic activity of nanocomposite (PC) for dye degradation. A representative diagram of PC is given in Figure 6.5 (d).

Figure 6.5: TEM images of (a) PANI at 25,000 times magnification, (b) PANI at 50,000 times magnification, (c) PC at 60,000 times magnification and (d) representative diagram of PC.

TEM images (Figure 6.6 (a) and (b)) of CZP showed the presence of two different sized spherical nanoparticles scattered in the polyaniline matrix. Two different sizes and spherical structures, thus confirmed the formation of CdS and ZnS Sandwich type (SW-type) quantum dots (QDs) scattered in the PANI matrix as also indicated by
EDS and FTIR. The CdS and ZnS could be seen in close proximity to each other in the polymer matrix hence suggesting a strong interaction between two, which was also indicated by FTIR. A representative diagram of CZP is given in Figure 6.6 (e).

Similarly, TEM images of CTP shown in Figure 6.6 (d) and (e) revealed the presence of compactly packed two different sized QDs of CdS and TiO$_2$ on the surface of PANI matrix. A representative diagram of CTP is given in Figure 6.6 (f). As also suggested by EDS and FTIR, two different sized spherical nanostructures in close proximity each other, confirmed the formation of CdS and TiO$_2$ SW-type NCs in PANI matrix with strong interaction between them. Figure 6.6 (f) gives a representative diagram of CTP.

![Figure 6.6](image)

**Figure 6.6:** TEM images of (a) & (b) CZP at 60,000 and 100,000 times magnification respectively, (d) & (e) CTP at 12,000 and 24,000 times magnification respectively and (c) & (f) representative diagrams of CZP and CTP respectively.

**6.3.2.2. Diffraction Studies:**

The diffraction studies of the synthesized nanomaterials were carried out by X-Ray Diffraction (XRD) Spectroscopy.

**X-Ray Diffraction (XRD) Spectroscopy:**

**Figure 6.7** Shows the XRD pattern of PANI and PC. The figure shows, the XRD pattern of PANI with characteristic broad peak of amorphous PANI centered at
29°=25°. The XRD pattern of PC with peaks similar to cubic CdS centered at 29°=25.955° (111), 29.428° (200), 43.372° (220), 51.395° (311) suggested the formation of cubic CdS QDs embedded in PANI. The XRD peaks obtained for PC were slightly broad, which might be due to the addition of PANI. The estimated crystal size of CdS was calculated by Scherrer formula using 29°=25.955°, which came out to be 6.4nm.

The XRD pattern of CZP is shown in Figure 6.8. The figure reveals the XRD pattern centered at 29°=24.471°, 26.018°, 27.740°, 36.093°, 43.458°, 47.645° and 51.507° corresponding to hexagonal ZnS (29°=24° (100), 26° (002), 27° (101), 36° (102), 43° (110), 47° (103) and 51° (112)) and cubic CdS with characteristic peaks at 29°=26° (111), 29° (200), 43° (220), and 51° (311) suggesting the presence of hexagonal ZnS and cubic CdS QDs embedded over PANI matrix. Considerable broadening due to PANI was also seen in the XRD spectra. The estimated crystal size of CZP was not possible due to overlap of the peaks corresponding to CdS, ZnS and PANI.

The XRD spectrum of CTP is shown in Figure 6.9. A broad peak was found at 29°=25°, which could be a combined result of anatase TiO2, cubic CdS and PANI. Other peaks found at 37.8° (103), 48.07° (200), 54.18° (105), 62.42° (204) and 75.2° (215) were related to anatase TiO2, while peaks at 29.239° (200), 43.372° (220)
and 51.395° (311) were due to cubic CdS\textsuperscript{47,59,71}. The estimated crystallite size for CTP based on the X-ray diffraction peak was also not possible due to the presence of mixed peaks of anatase TiO\textsubscript{2}, cubic CdS and PANI.

![XRD pattern of CZP](image1.png)

**Figure 6.8:** XRD pattern of CZP in comparison to cubic CdS, hexagonal ZnS and PANI.

![XRD pattern of CTP](image2.png)

**Figure 6.9:** XRD pattern of CTP in comparison to cubic CdS, Degussa P-25 TiO\textsubscript{2} and PANI.
6.3.3. THERMAL ANALYSIS:

Thermal analysis was done by Thermal Gravimetric Analysis (TGA).

Thermal Gravimetric Analysis (TGA):

Figure 6.10 shows the TGA thermograph of pure PANI and its nanocomposites (PC, CZP and CTP). In the TGA thermograph of PANI, it was observed that the loss of weight occurred at two temperature periods, ranging from 30 to 100°C and around 300°C. The first mass loss of the sample started at 20°C and abruptly finished at 100°C. This effect is frequently observed in different polymers, and is mainly contributed by the evaporation of absorbed moisture, elimination of impurities, residual water and unreacted monomers. The polymer degradation began just above 210°C (the most often cited temperature is closer to 300°C)\textsuperscript{22,47}. The degradation was rather slow and the observed mass loss was less important, as it does not exceed 46% at 800°C. This analysis confirmed above average heat resistance of the synthesized polyaniline.

![TGA pattern](image)

Figure 6.10: TGA pattern of PANI, and its composite nanomaterials (PC, CZP and CTP).

The thermal stability for the nanocomposite PC was improved significantly as higher decomposition temperature (370°C) was observed for the samples as compared to pure PANI (280-300°C) in the TGA profile\textsuperscript{22,47}, and also a steady thermal stability from 600°C to 1000°C was observed. It might be related to the combination of CdS
nanoparticles in the polymer matrix, which yielded stronger binding force due to the interaction between CdS nanoparticles and the lone pair electrons of N atom in the polymer backbone.\(^{67}\)

In CZP the main weight loss due to the oxidative degradation of the polymer backbone was observed at much higher temperature (400°C) (this however, starts between 280–300°C) and continued upto 980°C for the composites indicating, increased stability of the composite due to inorganic semiconductors nanoparticles.\(^{47}\) The first mass loss of the sample due to moisture, impurities and unreacted monomers was not observed suggesting absence of moisture, impurity and unreacted monomers. The enhanced thermal stability exhibited by the CZP nanocomposites compared to pure PANI might be due to the existence of a strong interaction between CdS-ZnS.

The first mass loss of the sample due to moisture, impurities and unreacted monomers was observed at 20-80°C. The enhanced thermal stability exhibited by the CTP nanocomposites compared to pure PANI might be due to the existence of a strong interaction between PANI and CdS-TiO\(_2\).\(^{64}\)

### 6.3.4. OPTICAL ANALYSIS:

**UV-Vis Spectroscopy:**

The optical properties were determined by the UV-Vis Spectrometer using the sample in N-methylpyrrolidinone (NMP) solution. NMP is a rare example of a non-protonating polyaniline solvent.\(^{22}\)

The absorption spectra of PANI (Figure 6.11) showed two absorption peaks at 320nm and 630nm which coincide with the emeraldine base form of polyaniline. The peak at 320nm was attributed to the \(\pi-\pi^*\) transition in the benzenoid ring and the peak at 630nm was associated with a benzenoid to quinoid excitonic transition.\(^{50,77,78}\) The presence of characteristic peaks of \(\pi-\pi^*\) transitions without any traces of transition involving polarons (at \(\lambda=420-450\)nm and 760-800nm), confirmed that the synthesized PANI was emeraldine base form of polyaniline.\(^{22}\)
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Figure 6.11: UV-visible spectra of PANI in the range 200 to 800nm.

The absorption spectrum of PC is shown in Figure 6.12. The absorption spectrum of PC showed two strong peaks at 320nm and 630nm with one shoulder at 420nm. The peaks at 320nm and 630nm were attributed to the $\pi-\pi^*$ transition in the benzenoid ring and benzenoid to quinoid excitonic transition of polyaniline respectively suggesting emeraldine base type polyaniline. The shoulder at 420nm was attributed to CdS QDs it showed considerable blue shift from its bulk (510nm)\textsuperscript{79}. Thus, indicating a strong interaction between CdS and PANI.

Figure 6.12: UV-visible spectra of PC in comparison to bulk CdS and synthesized PANI.
The absorption spectrum of CZP is shown in Figure 6.13. The spectrum revealed the presence of only two peaks centered at 340 and 620nm with an increase in intensity of the spectrum in comparison to pure PANI. The increase in the absorption intensity of PANI with the inclusion of a semiconductor nano composites was reported by some authors\textsuperscript{42,64}.

![Figure 6.13: UV-visible spectra of CZP in comparison to bulk CdS & ZnS and synthesized PANI.](image)

The presence of the peaks at 340 and 620nm were attributed to emeraldine base type of polyaniline matrix. The peaks corresponding to CdS (512nm)\textsuperscript{79} and ZnS (336nm)\textsuperscript{31,80} were not observed instead the peak at 340nm showed broadening from 280 to 350nm with a tail in the visible region upto 400nm which was considered due to the strong interaction of CdS and ZnS nanoparticles with each other and PANI. In presence of the CdS-ZnS nanocomposite, the absorption spectrum of PANI registered a blue shift without showing any additional peaks and the enhancement in the absorption spectrum was observed throughout the spectral range. This was due to the strong interaction of CdS-ZnS nanocomposite with the spectra of PANI\textsuperscript{42,64}. Thus, an improved photo response was expected in comparison to pure PANI and CdS-ZnS sandwich nanocomposite.

Figure 6.14 shows the absorption spectrum of CTP. Two broad peaks centered at 330nm and 640nm, and a weak broad peak at 450nm was observed in the absorption spectrum of CTP. The absorption intensity of the CTP spectra was lowered in
comparison to that of pure PANI. The peaks centered at 330 and 640nm was attributed to emeraldine base polyaniline and the weak peak at 450nm was attributed to CdS QDs. Since the absorption of colloidal TiO$_2$ nanoparticles overlapped with that of PANI, the peak centered on 330nm became substantially broadened from 290 to 350nm with a tail in the visible region upto 400nm. The blue shift and the decrease in the intensity of the absorption spectra of CTP suggested strong interaction between QDs (CdS and TiO$_2$) and PANI$^{4,64}$. CTP can be activated by absorbing both UV and visible light ($\lambda= 190$-800nm) and hence can be considered a promising candidate for the photocatalytic applications.

![Figure 6.14: UV-visible spectra of CTP in comparison to synthesized PANI, bulk CdS and ZnS.](image)

**Figure 6.14:** UV-visible spectra of CTP in comparison to synthesized PANI, bulk CdS and ZnS.

### 6.3.5. PHOTOCATALYTIC ACTIVITY:

**Photocatalysis by PC:**

Figure 6.15 to 6.18 shows the photocatalytic response of PC. Our result indicated that although PANI could only exert slight effect on the activity of the photocatalyst, it was indeed beneficial for enhancement of the stability of the photocatalysts. It could be seen that PC showed enhanced activity for photocatalytic degradation in comparison to pure CdS and PANI. The reasons for this improved photocatalytic activity of PC can be given as; Firstly CdS and PANI formed a coordination bond that transferred photo excited electrons from PANI to CdS, resulting an increased density
of photoelectrons in CdS, on the other hand PANI itself is a hole scavenger and attracted all the holes form CdS to itself, hence improved the charge separation and increased the charge density at the surface of the catalysts, thus improved photocatalytic activity of PC. Secondly, the addition of CdS enabled the disordered structure of PANI to have a certain ordering and PANI prevented the agglomeration and size growth of CdS particles to a certain extent, which lead to improved photoexcitation of electrons in CdS and effortless migration of photogenerated charges to the surface of photocatalysts, hence efficient and rapid photodegradation of the adsorbed contaminations\textsuperscript{59,81}. Figure 6.15 gives the relative change in the concentration (C/C\textsubscript{0}) of AB-29 in the presence and absence of different photocatalysts (PC, PANI and pure CdS NP) as a function of time.

![Figure 6.15](image)

**Figure 6.15**: Change in concentration of AB-29 with time in the presence and absence of PC in comparison to PANI and CdS nanoparticles.

It could be seen from Figure 6.15, that 82.2%, 69.8% and 67.1% decolorization of AB-29 took place after 90 minutes of irradiation using PC, pure CdS NP and PANI respectively. On the other hand in the absence of photocatalyst no observable decrease in the dye concentration was seen. The decolorization curve (Figure 6.15) suggested pseudo first-order reaction as also depicted by plotting ln (C\textsubscript{0}/C) versus irradiation time as shown in Figure 6.16. The plot of ln (C\textsubscript{0}/C) versus t will yield a slope of k\textsubscript{app} (the apparent pseudo-first-order reaction rate constant (min\textsuperscript{-1})). The correlation constant (R\textsuperscript{2}) for the fitted lines was calculated to be about 0.99 for all the experiments.
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Figure 6.16: Change in concentration of AB-29 with time in the presence and absence of PC in comparison to PANI and CdS nanoparticles.

The rate constant obtained from Figure 6.16 was then used to calculate the decolorization rate (molL⁻¹min⁻¹) of AB-29 by various photocatalysts. The decolorization rate (molL⁻¹min⁻¹) calculated came out to be in the order $4.47 \times 10^{-4}$ (PANI) < $4.62 \times 10^{-4}$ (CdS) < $5.54 \times 10^{-4}$ (PC) respectively. Figure 6.17, shows the decolorization rate for the decomposition of AB-29 in the presence of different photocatalysts (PC, PANI and pure CdS NP).

Figure 6.17: The decolorization rate of AB-29 in the presence of synthesized PC in comparison to PANI and CdS nanoparticles.
For the purpose of practical implementation, it was essential to evaluate the stability and reuse of the catalyst. Figure 6.18 shows the repetitive photodegradation of AB-29 during five consecutive cycles with the same 1gL⁻¹ catalyst at 0.06mM dye concentration. After each cycle, the nanocomposite catalyst was washed with double distilled water and a fresh solution of AB-29 was added before each photocatalytic run. The relative decolorization using PC for the 5 cycling reuse were 82.3%, 81.8%, 81.6%, 81.1% and 80.8%, after 90 minutes of reaction time, respectively. The results showed that the catalytic activity of PC had only a slight decrease after first cycles as compared to pure CdS whose activity decreased remarkably. The reason for this slight shift might be the run off of the PC during washing and filtrating. However, the decolorization efficiency kept relatively stable in the following repeated experiments, which confirmed that CdS QDs were combined steadily within the PANI matrix. From this point of view, the recycle of PC photocatalyst confirmed the relative stability of the PC. Thus suggesting PC is a better photocatalyst as compared to pure CdS and PANI with enhanced activity and improved stability.

Figure 6.18: Stability and recycle of PC in comparison to pure CdS.

The mechanism behind the photocatalytic reaction of PC could be explained as, when CdS/PANI nanocomposites (PC) were irradiated under visible light, the electrons were excited from the VB of CdS to the CB of CdS (Equation 6.1) and the electrons of PANI were excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of PANI (Equation 6.2). On the basis
of the relative energy levels of PANI (π-orbital and π*-orbital) and CdS (conduction band, CB, and valence band, VB), which lead to synergic effect, the photogenerated holes in VB of CdS were directly transferred to the π-orbital of PANI (Equation 6.3). Simultaneously, the photogenerated electrons of π*-orbital of PANI were transferred to the CB of CdS (Equation 6.4), which resulted in charge separation and stabilization, thus hindering the recombination process. Figure 6.19 gives the schematic representation of the mechanism involving photoexcited electrons and holes of PC.

Figure 6.19: Representative diagram of mechanism of photocatalysis by PC.

The electrons were then scavenged by molecular oxygen O$_2$ to yield the superoxide radical anion O$_2^{-*}$ (Equation 6.5) and hydrogen peroxide H$_2$O$_2$ (Equation 6.6) in oxygen-equilibrated media. These newly formed intermediates interacted with each other to produce hydroxyl radical •OH (Equation 6.7). The photo-generated hole at PANI oxidized the hydroxyl groups (OH$^-$) (Equation 6.8) and water (H$_2$O) molecule (Equation 6.9) to produce hydroxyl radicals •OH. As it is well known that the •OH radical is a powerful oxidizing agent capable of degrading most pollutants thus the hydroxyl radical took part in the degradation of the dye AB-29 (Equation 6.10).\textsuperscript{14,81,82}
The reactions can be expressed as follows:

\[ \text{CdS/PANI} \rightarrow \text{CdS(e}^{-} + \text{h}^{+})/\text{PANI} \] \[ \text{[6.1]} \]

\[ \text{CdS/PANI} \rightarrow \text{CdS/PANI(e}^{-} + \text{h}^{+}) \] \[ \text{[6.2]} \]

\[ \text{CdS(e}^{-} + \text{h}^{+})/\text{PANI} \rightarrow \text{CdS(e}^{-})/\text{PANI(h}^{+}) \] \[ \text{[6.3]} \]

\[ \text{CdS/PANI(e}^{-} + \text{h}^{+}) \rightarrow \text{CdS(e}^{-})/\text{PANI(h}^{+}) \] \[ \text{[6.4]} \]

\[ \text{CdS(e}^{-})/\text{PANI(h}^{+}) + \text{O}_2 \rightarrow \text{CdS/PANI(h}^{+}) + \text{O}_2^{-} \] \[ \text{[6.5]} \]

\[ \text{CdS(e}^{-})/\text{PANI(h}^{+}) + \text{O}_2 + 2\text{H}^{+} \rightarrow \text{CdS/PANI(h}^{+}) + \text{H}_2\text{O}_2 \] \[ \text{[6.6]} \]

\[ \text{H}_2\text{O}_2 + \text{O}_2^{-} \rightarrow \cdot\text{OH} + \text{OH}^{-} + \text{O}_2 \] \[ \text{[6.7]} \]

\[ \text{CdS(e}^{-})/\text{PANI(h}^{+}) + \text{H}_2\text{O}_{\text{absorbed}} \leftrightarrow \text{CdS(e}^{-})/\text{PANI} + \text{H}^{+} + \cdot\text{OH} \] \[ \text{[6.8]} \]

\[ \text{CdS(e}^{-})/\text{PANI(h}^{+}) + \text{OH}_{\text{absorbed}} \leftrightarrow \text{CdS(e}^{-})/\text{PANI} + \cdot\text{OH} \] \[ \text{[6.9]} \]

\[ \cdot\text{OH} + \text{dye} \rightarrow \text{degradation products} \] \[ \text{[6.10]} \]

**Photocatalysis by CZP:**

Figure 6.20 to 6.23 shows the photocatalytic response of CZP in comparison to pure CdS, ZnS and PANI. CZP showed enhanced activity for photocatalytic degradation than that of pure CdS, ZnS, PANI and CdS-ZnS nanocomposite. Figure 6.20 showed the relative change in concentration (C/C₀) of organic dye AB-29 in the presence and absence of different photocatalysts (CZP, PANI pure CdS and ZnS QDs and CdS-ZnS NC) as a function of time. It can be clearly seen that CZP showed a remarkable improvement in the photoactivity as compared to that of pure CdS or pure PANI, but only slight enhancement in the photoactivity was observed in comparison to CdS-ZnS NC. Our result indicated that although PANI could only increase the photoactivity of CdS-ZnS NC (in CZP) to a lesser extent but was certainly favorable for enhancing the stability of the photocatalyst in comparison to pure CdS-ZnS NC (without PANI). This might be because PANI decreased the photocorrosion of CdS by attracting all holes towards itself. It could be seen from Figure 6.20, that 89.8%, 86.5%, 69.8%, 67.1%, and 14.2% decolorization of AB-29 took place after 90 minutes of irradiation using CZP, pure CdS-ZnS NC, CdS QD, PANI and ZnS QD respectively. On the other hand in the absence of photocatalyst no observable decrease in the dye concentration could be seen. The decolorization curve (Figure 6.20) suggested a pseudo first-order reaction which was also depicted by plotting...
\[
\ln(C_0/C) \text{ versus } \text{irradiation time as shown in Figure 6.21. The correlation constant (R}^2)\text{ for the fitted lines was calculated to be about 0.99 for all the experiments.}
\]

**Figure 6.20:** Change in concentration of AB-29 with time in the presence and absence of CZP in comparison to PANI, CdS & ZnS nanoparticles and CdS-ZnS nanocomposite.

**Figure 6.21:** Change in concentration of AB-29 with time in the presence and absence of CZP in comparison to PANI, CdS & ZnS nanoparticles and CdS-ZnS nanocomposite.
The decolorization rate (molL⁻¹ min⁻¹) of AB-29 by various photocatalysts was calculated by the rate constant obtained from Figure 6.21. The decolorization rate calculated came out to be in the order 0.89x10⁻⁴<4.47x10⁻⁴<4.62x10⁻⁴<5.63x10⁻⁴<5.84x10⁻⁴ molL⁻¹ min⁻¹ for ZnS, PANI, CdS, CdS-ZnS and CZP respectively. Figure 6.22, shows the decolorization rate for the decomposition of AB-29 in the presence of different photocatalysts (ZnS, PANI, CdS, CdS-ZnS and CZP).

**Figure 6.22:** The decolorization rate of AB-29 in the presence of synthesized CZP in comparison to PANI, CdS & ZnS nanoparticles and CdS-ZnS nanocomposite.

**Figure 6.23** shows the repetitive photodegradation of AB-29 during five consecutive cycles. The relative decolorization using CZP for the 5 cycling reuse were 89.8%, 88.9%, 88.0%, 87.9% and 87.1%, after 90 min of reaction time, respectively. The results showed that the photocatalytic activity of CZP had only a slight decrease after first cycles as compared to pure CdS-ZnS NC (without PANI) whose activity decreased remarkably (74.5%, 71.5%, 67.1%, 61.8% and 53.5%). The reason for this slight decrease might be the run off of the CZP during washing and filtering. However, the decolorization efficiency kept relatively stable in the following repeated experiences, which confirmed that CdS-ZnS NC was combined steadily within the PANI matrix. From this point of view, the recycle of CZP photocatalyst confirmed the relative stability of the CZP. Thus suggesting CZP is a better photocatalyst as compared to pure CdS-ZnS with enhanced activity and improved stability.
Figure 6.23: Stability and recycle of CdS-ZnS nanocomposite embedded in PANI (CZP), in comparison to free CdS-ZnS nanocomposite without PANI.

The reasons behind this improved photocatalytic activity and stability of PC can be given as; Firstly the generation of CdS$_{1-x}$Zn$_x$S solid solutions at interfaces of CdS and ZnS nanoparticles, embedding of CdS-ZnS over PANI surface and due to existence of CdS and ZnS moieties in close contact with each other and with PANI, as confirmed by FTIR, TEM, XRD and UV-vis. spectroscopy. Secondly the high surface-to-volume ratio and quantum size effect due to small particle size of CdS and presence of defect sites at CdS-ZnS interfaces played a vital role in the better photocatalytic activity of the CZP nanocomposite. Moreover, ZnS by itself displayed almost negligible photoactivity in visible region, but acted as an oxidation co-catalyst together with CdS. ZnS not only enhanced the photoactivity of CdS but also protected CdS from photocorrosion. Finally, PANI formed a layer of conductive network on the surface of CdS-ZnS, which promoted the generation of photogenerated electron (e$^-$) and holes (h$^+$), PANI possessed π electron conjugated system and acted as a hole scavenger attracting all the holes form CdS-ZnS to itself, which was helpful for the separation of photogenerated charge and prevented their recombination, thus PANI was favorable to enhance the charge separation and suppressed the photocorrosion of CdS.

The mechanism behind the photocatalytic reaction of CZP could be explained as, when CdS-ZnS-PANI nanocomposites are irradiated under visible light, the
photoexcited electron-hole pairs are formed (Equation 6.11-6.13). On the basis of the relative energy levels of PANI (π-orbital and π*-orbital), ZnS (CB and VB), and CdS (CB and VB), which lead to the synergic effect, directed all the photogenerated electrons towards CB of CdS, and all the photogenerated holes away from VB of CdS towards π-orbital of PANI, resulted in charge separation and stabilization, thus hindered the recombination process (Equation 6.14-6.16). A schematic representation of the mechanism of CZP involving photoexcited electrons and holes is given in Figure 6.24.

![Figure 6.24: Representative diagram of mechanism of photocatalysis by CZP.](image)

The electrons were then scavenged by molecular oxygen O₂ to yield the superoxide radical anion O₂•− (Equation 6.17) and hydrogen peroxide H₂O₂ (Equation 6.18) in oxygen-equilibrated media. Then these intermediates interacted to produce hydroxyl radical •OH (Equation 6.19). The photo-generated hole at PANI oxidized the hydroxyl groups (OH⁻) (Equation 6.20) and water (H₂O) molecules (Equation 6.21) to produce hydroxyl radicals (•OH). The •OH radical being a powerful oxidizing agent degraded the dye AB-29 (Equation 6.22).

The reactions can be expressed as follows:

- \[ \text{CdS/ZnS/PANI} \rightarrow \text{CdS} (\text{e}^- + \text{h}^+) / \text{ZnS/PANI} \quad [6.11] \]
- \[ \text{CdS/ZnS/PANI} \rightarrow \text{CdS/ZnS/PANI} (\text{e}^- + \text{h}^+) \quad [6.12] \]
- \[ \text{CdS/ZnS/PANI} \rightarrow \text{CdS/ZnS} (\text{e}^- + \text{h}^+) / \text{PANI} \quad [6.13] \]
CdS\((e^- + h^+) / ZnS / PANI \rightarrow CdS(e^-) / ZnS / PANI(h^+)\) \[6.14\]

CdS / ZnS / PANI \((e^- + h^+) \rightarrow CdS(e^-) / ZnS / PANI(h^+)\) \[6.15\]

CdS / ZnS \((e^- + h^+) / PANI \rightarrow CdS(e^-) / ZnS / PANI(h^+)\) \[6.16\]

CdS\((e^-) / ZnS / PANI(h^+) + O_2 \rightarrow CdS / ZnS / PANI(h^+) + O_2^-\) \[6.17\]

CdS\((e^-) / ZnS / PANI(h^+) + O_2 + 2H^+ \rightarrow CdS / ZnS / PANI(h^+) + H_2O_2\) \[6.18\]

\(H_2O_2 + O_2^- \rightarrow \cdot OH + OH^- + O_2\) \[6.19\]

CdS\((e^-) / ZnS / PANI(h^+) + H_2O_{absorbed} \leftrightarrow CdS(e^-) / ZnS / PANI + H^+ + \cdot OH\) \[6.20\]

CdS\((e^-) / ZnS / PANI(h^+) + OH^-_{absorbed} \leftrightarrow CdS(e^-) / ZnS / PANI + \cdot OH\) \[6.21\]

\(\cdot OH + \text{dye} \rightarrow \text{degradation products}\) \[6.22\]

**Photocatalysis by CTP:**

**Figure 6.25 to 6.28** shows the effect of PANI on the photocatalytic performance of CdS-TiO\(_2\) NC under visible light irradiation. CTP showed enhanced activity for photocatalytic degradation than pure CdS, TiO\(_2\), PANI and CdS-TiO\(_2\) (without PANI). Our result indicated that PANI exerted only a slight effect on the activity of CTP whereas it enhanced the stability of CTP remarkably in comparison to CdS-TiO\(_2\) (CdS-TiO\(_2\) NC without PANI). Although the enhancement in the photoactivity was small, the stability of CTP was improved remarkably. The reasons for this improved photocatalytic activity of CTP could be because PANI inhibited the photocorrosion of CdS. By attaching TiO\(_2\) and PANI on the surface of CdS, it was possible to drive the photogenerated electrons and holes farther away from the CdS towards TiO\(_2\) and PANI respectively, thereby achieving more efficient charge separation in CTP\(^{43,49,84}\). On the other hand photoexcited electrons in \(\pi^*\)-orbital of PANI were also readily injected into the CB of TiO\(_2\) because their energy level matched well for the charge transfer\(^{43,49,65}\). As a result, a more active and stable photocatalyst was obtained. **Figure 6.25** shows the relative change in concentration \((C/C_0)\) of organic dye AB-29 in the presence and absence of different photocatalysts (CTP, PANI pure CdS and TiO\(_2\) QDs and CdS-TiO\(_2\)) as a function of time. It could be seen from **Figure 6.25**, that 86.4%, 83.2%, 69.8%, 67.1%, and 10.4%
decolorization of AB-29 took place after 90 minutes of irradiation using CTP, CdS-TiO$_2$, CdS QD, PANI and TiO$_2$ QD respectively. On the other hand in the absence of photocatalyst there was no observable decrease in the dye concentration. The photocatalytic results showed that CTP displayed a remarkable improvement in the photoactivity as compared to that of pure CdS, TiO$_2$ or pure PANI, but only a slight enhancement in the photoactivity was observed in comparison to CdS-TiO$_2$ NC. The decolorization curve (Figure 6.25) suggested pseudo first-order reaction as also depicted by plotting ln (C$_0$/C) versus irradiation time as shown in Figure 6.26. The correlation constant (R$^2$) for the fitted lines was calculated to be about 0.99 for all the experiments.

![Figure 6.25: Change in concentration of AB-29 with time in the presence and absence of CTP in comparison to PANI, CdS & TiO$_2$ nanoparticles and CdS-TiO$_2$ nanocomposite.](image)

The degradation rate (moL$^{-1}$ min$^{-1}$) of AB-29 by various photocatalysts was calculated by the rate constant obtained from Figure 6.26. The degradation rate calculated came out to be in the order 0.671x10$^{-4}$<4.47x10$^{-4}$<4.62x10$^{-4}$<5.37x10$^{-4}$<5.56x10$^{-4}$ moL$^{-1}$ min$^{-1}$ for TiO$_2$, PANI, CdS, CdS-TiO$_2$ and CTP respectively. Figure 6.27, shows the decolorization rate for the decomposition of AB-29 in the presence of different photocatalysts (pure TiO$_2$ QDs, PANI, CdS QDs, CdS-TiO$_2$ and CTP).
Figure 6.26: Change in concentration of AB-29 with time in the presence and absence of CTP in comparison to PANI, CdS & TiO₂ nanoparticles and CdS-TiO₂ nanocomposite.

Figure 6.27: The decolorization rate of AB-29 in the presence of synthesized CTP in comparison to PANI, CdS & TiO₂ nanoparticles and CdS-TiO₂ nanocomposite.

Figure 6.28 shows the repetitive photodegradation of AB-29 during five consecutive cycles. The relative decolorization using CTP for the 5 cycling reuse were 86.5%, 85.9%, 85.1%, 84.5% and 83.8%, after 90 minutes of reaction time, respectively. The results showed that the catalytic activity of CTP had only a slight decrease after first cycles as compared to pure CdS-TiO₂ NC whose activity decreased remarkably (83.3%, 79.5%, 75.2%, 72.4% and 70.1%). The reason for this decrease might be run
off of the CTP during washing and filtrating. However, the decolorization efficiency kept relatively stable in the following repeated experiments, which confirmed that CdS-TiO$_2$ NC was combined steadily within the PANI matrix. From this point of view, the recycle of CTP photocatalyst confirmed the relative stability of the CTP. This suggested that PANI prevented photocorrosion of CdS from CTP thus enhancing its stability. Therefore it can be concluded that CTP is a better photocatalyst as compared to pure CdS-TiO$_2$ with enhanced activity and improved stability.

![Figure 6.28: Stability and recycle of CdS-TiO$_2$ nanocomposite embedded in PANI (CTP) in comparison to free CdS-TiO$_2$ nanocomposite without PANI.](image)

The mechanism behind the photocatalytic reaction of CZP could be explained as, when CdS-TiO$_2$-PANI nanocomposites (CTP) were irradiated under visible light, the photo-excited electron-hole pairs were formed. On the basis of the relative energy level of PANI ($\pi$-orbital and $\pi^*$-orbital), TiO$_2$ (CB and VB), and CdS (CB and VB), which lead to synergic effect, and directed all the photogenerated electrons towards the CB of TiO$_2$ from the CB of CdS and $\pi^*$-orbital of PANI, and all the photogenerated holes away from VB of CdS and TiO$_2$ towards $\pi$-orbital of PANI, hence resulted in improved charge separation and stabilization, thus hindering the recombination process (Equation 6.23-6.28). A schematic representation of the mechanism involving photogenerated charges of CTP is given in Figure 6.29.

The electrons were then scavenged by molecular oxygen O$_2$ to yield the superoxide radical anion $O_2^{•−}$ (Equation 6.29) and hydrogen peroxide H$_2$O$_2$ (Equation 6.30) in
oxygen-equilibrated media. These new formed intermediates then interacted to produce hydroxyl radical •OH (Equation 6.31). The photo-generated hole at PANI oxidized the hydroxyl groups (OH\(^{-}\)) (Equation 6.32) and water (H\(_2\)O) molecule (Equation 6.33) to produce hydroxyl radicals (•OH). The •OH radical acted as a powerful oxidizing agent and degraded the dye AB-29 (Equation 6.34)

The reactions can be expressed as follows:

\[
\begin{align*}
\text{TiO}_2/\text{CdS}/\text{PANI} & \xrightarrow{hv} \text{TiO}_2/\text{CdS}(e^- + h^+)/\text{PANI} & [6.23] \\
\text{TiO}_2/\text{CdS}/\text{PANI} & \xrightarrow{hv} \text{TiO}_2/\text{CdS}/\text{PANI}(e^- + h^+) & [6.24] \\
\text{TiO}_2/\text{CdS}/\text{PANI} & \xrightarrow{hv} \text{TiO}_2(e^- + h^+)/\text{CdS}/\text{PANI} & [6.25] \\
\text{TiO}_2/\text{CdS}(e^- + h^+)/\text{PANI} & \rightarrow \text{TiO}_2(e^-)/\text{CdS}/\text{PANI}(h^+) & [6.26] \\
\text{TiO}_2/\text{CdS}/\text{PANI}(e^- + h^+) & \rightarrow \text{TiO}_2(e^-)/\text{CdS}/\text{PANI}(h^+) & [6.27] \\
\text{TiO}_2(e^- + h^+)/\text{CdS}/\text{PANI} & \rightarrow \text{TiO}_2(e^-)/\text{CdS}/\text{PANI}(h^+) & [6.28] \\
\text{TiO}_2(e^-)/\text{CdS}/\text{PANI}(h^+) + O_2 & \rightarrow \text{TiO}_2/\text{CdS}/\text{PANI}(h^+) + O_2^- & [6.29] \\
\text{TiO}_2(e^-)/\text{CdS}/\text{PANI}(h^+) + O_2 + 2H^+ & \rightarrow \text{TiO}_2/\text{CdS}/\text{PANI}(h^+) + H_2O_2 & [6.30] \\
H_2O + O_2^- & \rightarrow \cdot OH + OH^- + O_2 & [6.31] \\
\text{TiO}_2(e^-)/\text{CdS}/\text{PANI}(h^+) + H_2O_{\text{absorbed}} & \leftrightarrow \text{TiO}_2(e^-)/\text{CdS}/\text{PANI} + H^+ + \cdot OH & [6.32] \\
\text{TiO}_2(e^-)/\text{CdS}/\text{PANI}(h^+) + OH_{\text{absorbed}} & \leftrightarrow \text{TiO}_2(e^-)/\text{CdS}/\text{PANI} + \cdot OH & [6.33] \\
\cdot OH + \text{dye} & \rightarrow \text{degradation products} & [6.34]
\end{align*}
\]

**Figure 6.29:** Representative diagram of mechanism of photocatalysis by CTP.
6.4. Conclusion:
In the present work, semiconductor-polyaniline nanocomposites were synthesized by chemical precipitation methods under ambient conditions, in order to improve the physical, chemical, optical and catalytic properties of semiconductors. The semiconductor nanoparticles were found to be well embedded in the polyaniline matrix, and improved the thermal stability of PANI. On the other hand PANI improved the optical and photocatalytic properties of semiconductors.

PC is the CdS and PANI nanocomposite in which cubic CdS were found embedded on the emeraldine base type polyaniline nanofibers. The presence of CdS in PANI was confirmed by EDX and FTIR. The FTIR spectra revealed a shift in the frequency to lower value (red shift) which might be due to the transfer of electrons from PANI to CdS. Thus, suggesting a strong interaction between CdS and PANI which was the reason that PC showed improved photocatalytic response than CdS and PANI. A strong interaction between cubic CdS and emeraldine base type PANI was also supported by XRD and UV-vis. data. PC showed improved thermal stability and optical property. PC also showed improved photocatalytic stability than pure CdS, thus, suggesting that PANI reduced the photocorrosion of Cd$^{2+}$.

CZP is CdS-ZnS nanocomposite embedded in PANI film. EDX and FTIR confirmed the presence of CdS and ZnS in PANI while microscopic studies revealed that CdS and ZnS were in close proximity in the PANI matrix suggesting the formation of sandwich type CdS-ZnS NC in PANI. The XRD data revealed the presence of CdS-ZnS NC (with cubic CdS and hexagonal ZnS) embedded in emeraldine base type polyaniline matrix suggested by UV-vis spectrum. The FTIR spectra revealed a shift in the frequency to lower value (red shift) which might be due to the transfer of electrons from PANI to CdS-ZnS nanocomposite. Thus, suggesting a strong interaction between CdS-ZnS and PANI. CZP showed improved thermal stability and photocatalytic response and stability than CdS-ZnS.

CTP is CdS-TiO$_2$ nanocomposites embedded in PANI matrix. The XRD data revealed the presence of cubic CdS and anatase TiO$_2$. The UV-vis spectrum confirmed the presence of emeraldine base type PANI. Microscopic studies confirmed the presence of CdS-TiO$_2$ sandwich type nanoparticles embedded in PANI matrix. A strong interaction between CdS-TiO$_2$ and PANI was confirmed by FTIR, XRD, UV-
vis spectra and photocatalytic response. Improved stability of photocatalytic response was observed till 5 cycles in comparison to pure CdS-TiO$_2$ nanocomposite.

We can conclude that although PANI can only exert slight effect on the photoactivity of CdS and its nanocomposite photocatalysts (CdS-ZnS and CdS-TiO$_2$), it is indeed beneficial for improving the stability of these nanomaterial photocatalysts.
References:


