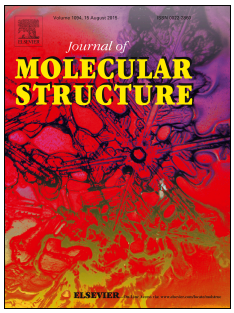

Synthesis, characterization of porphyrin and CdS modified spherical shaped SiO_2 for Reactive Red 120 degradation under direct sunlight

Balu Krishnakumar, S. Ravikumar, V. Pandiyan, V. Nithya, S. Sylvestre, P. Sivakumar, C. Surya, N. Agnel Arul John, Abilio J.F.N. Sobral

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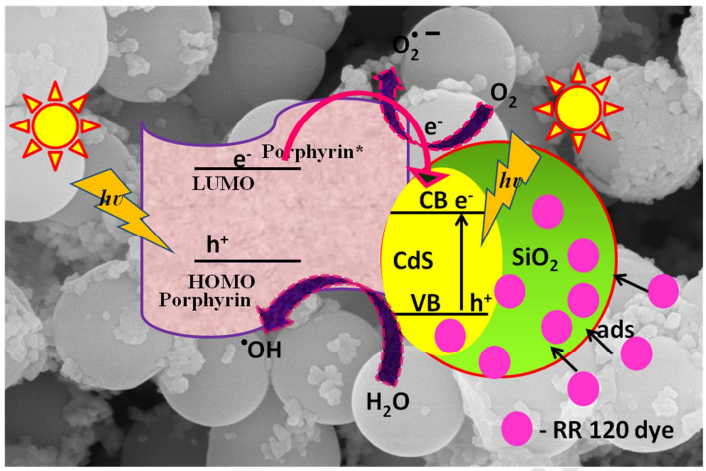
Graphical Abstract



Synthesis, characterization of porphyrin and CdS modified spherical shaped SiO_2 for Reactive Red 120 degradation under direct sunlight

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ABSTRACT

Initially, sphere shaped SiO_2 was explored by adopting simple sol-gel method without any template. Later, the sphere like SiO_2 was modified with cadmium sulfide (CdS) semiconductor and porphyrins. The formation of composites (CdS/SiO_2-porphyrins) brought out by diverse characterization techniques that include XRD, Raman, FT-IR, FE-SEM, EDS, DRS and PL measurements. The photocatalytic activity of CdS/SiO_2 was slightly influenced by porphyrins such as meso-tetra-phenyl-porphyrin (TPP) and 5,10,15,20-meso-tetra-(*para*-amino)-phenyl-porphyrin (TPAPP). The mechanism which has been proposed for Reactive Red 120 (RR 120) degradation by CdS/SiO_2- porphyrins under sunlight.

Key words: SiO_2 ; CdS; TPP; TPAPP; Sunlight; RR 120.

1. Introduction

Semiconductor nanoparticles of different materials and shapes are investigated according to their viz., size dependent electronic and photocatalytic properties. One may understand that the electronic, magnetic and optical characteristic one-dimensional nanostructures such as nanowires, nanotubes and nanofibers are prerequisite as they have varying different physico-chemical properties compared to the bulk material. CdS is an important II–VI semiconductor material with a wide band gap (Energy 2.53 eV), marvellous features in luminescence and photochemistry. Mixing SiO_2 with CdS nanoparticles is an apt candidate method to prevent decomposes, and improving luminescence performance and further functionalization [1-13]. The dual functional microencapsulated phase change materials modified CdS/SiO_2 dual-layered shell effectively utilized for degradation of methylene blue (MB) under natural sunlight illumination [14]. The n-eicosane@SiO_2/CdS microcapsules revealed an excellent solar photocatalytic activity to MB dye degradation under the natural sunlight, and approximately 90 percent degradation was observed at 240 min. Moreover, the same nanocomposite exhibited good performance in solar thermal energy storage, thermoregulation and phase-change reliability. A sequence of magnetic Fe_3O_4/SiO_2/CdS nanocomposites has been synthesized by adopting a facile and convenient method by Eskandari and Kazemi [15]. Initially, Fe_3O_4/SiO_2 was prepared followed by surface modifications with 3-(mercaptopropyl) trimethoxysilane (MPTMS). The surface modified Fe_3O_4/SiO_2 was coated with CdS and effectively utilized for Photocatalytic reduction of nitrobenzene. In another study, Byungwoo Park's group examined Surface-plasmon-enhanced photoluminescence of CdS nanoparticles with Au/SiO_2 nanocomposites [5].

Porphyrins have an acute absorption in the 400–450 nm regions (Soret band) and weak absorption in the 500–700 nm regions (Q bands). More importantly, and when the Soret and Q bands are red-shifted, that improves the overlap between the absorption and solar energy

distribution on the earth [16-21]. Porphyrin compounds play a pivotal role in the domains viz., photosynthesis, transport and storage of oxygen, and electron transfer. From the point of view, we have prepared two porphyrins with the reported procedures [22], and used to modify SiO_2 along with CdS. The structure of prepared porphyrins such as meso-tetra-phenyl-porphyrin (TPP) and 5,10,15,20-meso-tetra-(para-amino)-phenyl-porphyrin (TPAPP) are given in Fig. 1. People working for water purification and environment are concerned for our water resources constituting both groundwater and polluted wastewater. Now a day, with increasing revolution in science and technology there is a high demand in industries for newer chemicals to be used to control water pollution.

Regarding photocatalytic degradation of toxic dyes, it has brought a new revolution to reduce water pollution [23-26]. Recently, Lotfi *et al.,* [27] reported PAMAM/SiO_2 (polyamidoamine/ silica) nanohybrid as new and appropriate adsorbent for pharmaceuticals. It can be attributed that the contaminant removal was occurred in homogenous surface cites of the PAMAM/SiO_2. Mahy *et al.,* [28] reported hydrodechlorination and absolute degradation of chlorinated compounds with the concerted action of Pd/SiO_2 and Fe/SiO_2 catalysts. The catalytic activity of the dual catalysts has been examined by taking hydrodechlorination of 2,4,6-trichlorophenol (TCP) in water. The complete degradation of TCP was followed by two different mechanisms viz., hydrodechlorination with Pd/SiO_2 catalyst and photo-Fenton phenol degradation with Fe/SiO_2 catalyst. Since SiO_2 is an insulator, it is not directly used as a photocatalyst for degradation experiments until mixed with semiconducting materials. In the process of continuous exploration on environmental remediation [20, 21], the present work is focused on the modification of SiO_2 with CdS semiconductor and two different porphyrins. The prepared composites effectively utilized for Reactive Red 120 (RR 120) degradation under direct sunlight.

2. Experimental

2.1. Materials and measurements

Cadmium acetate dihydrate, thioacetamide, tetraethyl orthosilicate (TEOS), ammonia solution, 2-propanol, benzaldehyde, 4-nitrobenzaldehyde, pyrrole, tinchloride, propionic acid, RR 120 (CAS No: 61951-82-4, molecular weight- 1496.98 g/mol, molecular formulae- $C_{44}H_{24}Cl_2N_{14}Na_6O_{20}S_6$) and other chemicals used in this study were obtained from Aldrich and used as received. The dye structure and its UV-Vis spectrum are given in Fig. 2. Double distilled water has been used to prepare experimental solutions. FT-IR spectra have been recorded with the help of a Thermo Nicolet 380 FT-IR spectrophotometer, wavelength range from 4000 to 400 cm^{-1}. It contains DLaTGS detector, resolution: 0.5 cm^{-1}, S/N ratio: 2000:1 ppm for a minute scan and wavelength accuracy: 0.01 cm^{-1}. Powder X-ray diffraction (PXRD) patterns of solids have been recorded with the help of a PANalytical X'Pert PRO powder X-ray Diffractometer with 15KVA UPS support. Raman spectra were explored with a micro Raman Spectrometer, imaging spectrograph STR 500 mm Focal Length Laser Raman spectrometer with flat field : 27 mm(W) × 14 mm(H) and resolution : 1 / 0.6 cm^{-1}/pixel. In addition a field emission scanning electron microscope (FE-SEM) observation has been carried out on a BRUKER FE-SEM instrument along with energy dispersive X-ray spectrum (EDS). DRS-UV–Vis absorption spectra of solid samples were obtained from a UV-Vis-NIR spectrophotometer with thermofisher Evaluation 220 from 190 to 1100 nm range. Photoluminescence (PL) spectra have been registered by employing a Varian Cary Eclipse Photoluminescence spectrophotometer with oxford low temperature LN2 77K set up. The absorption spectra have been recorded by using an Perkin-Elmer UV spectrometer lambda 35.

2.2. Preparation of SiO_2

The sol-gel method was adopted for the synthesis of SiO_2. About 4 mL of water and 3 mL of ammonia solution has been added drop wise to the solution containing 10 mL of TEOS

in 90 mL of 2-propanol under vigorous stirring. The formed colloidal white precipitate was stirred continuously over night at room temperature. The gel attained was filtered, washed with DI (distilled water) and ethanol followed by a process of drying in an air over at 90 ^{o}C for 6 h . Further, the sample was calcinated at 450 ^{o}C in a muffle furnace for 6 h.

2.3. Synthesis of CdS/ SiO_2

About 1 g of prepared SiO_2 was dispersed in 25 mL ethanol solution. To this, 10 mL solution (1:1 ethanol/water) containing 3 mmol (0.7995 g) of cadmium acetate dihydrate was added under stirring, the stirring continued for another 10 min. At this time, 10 mL solution (1:1 ethanol/water) containing 3 mmol (0.2253 g) of thioacetamide was added under stirring, the stirring was keep on overnight. The obtained product was filtered, cleaned with DI (distilled water) and ethanol followed by a dry in an air over at 90 ^{o}C for 6h . In addition, the sample was calcinated at 450 ^{o}C in a muffle furnace for 6 h. This material contains 30.2 wt% CdS with respect to SiO_2.

2.4. Surface modification of CdS/SiO_2

About 500 mg of CdS/SiO_2 composite was dispersed in 20 mL of ethanol under stirring followed by the addition of 500 mg of Glycidoxypropyltrimethoxy silane (GPTMS), is a an exemplary coupling agent and it is able to chemically bond in both metal oxides and amino terminated organic molecules [21]. Then, it was stirred for 6 h at 50 ^{O}C, the GPTMS modified CdS/SiO_2 composite was filtered, washed several times with ethanol, to absolutely eradicate the unreacted GPTMS, and made dry in an air oven at 80 ^{O}C for 4 h.

2.5. Activation of CdS/SiO_2 by TPP and TPAPP

About 250 mg of surface modified CdS/SiO_2 nanoparticles were dispersed 20 mL of dichloromethane (DCM) in two different conical flasks. Stock solution of TPP & TPAPP was prepared separately by dissolving 4 mg of each in 10 mL of DCM, and then 0.1 mL of these stock solutions was added to the CdS/SiO_2 DCM dispersion separately. This was stirred for 6 h

at room temperature. The composites (CdS/SiO_2-TPP & CdS/SiO_2-TPAPP) were obtained by evaporation of the solvent and drying the solid at 65 ^{O}C for 4 h in an air oven. This catalyst contains 0.016 wt% of TPP & TPAPP with respect to CdS/SiO_2.

2.5. Photodegradation experiments

Photocatalytic activiy of the as-obtained composites was assessed by the deterioration of RR 120 azo dye in direct sunlight. Solar photocatalytic degradation experiments were performed under similar conditions on sunny days between 11.30 a.m. and 2.30 p.m. It was found that the solar intensity remained almost constant during the experiments [29]. In each examination, the reaction suspension consisting of 10 mg of the composites in 10 ppm of RR 120 solution (100 mL), has been magnetically stirred in the darkness for 30 min to ascertain the adsorption/desorption equilibrium between the composite particles and RR 120 dye. Then the suspension was brought out to the direct sunlight irradiation, and aliquots (3 mL) were taken at given time intervals and centrifuged to eradicate composite particles. The supernatants were analyzed by registering the absorbance variations of an absorption band (533 nm) in the UV-Visible spectrum of RR 120.

3. Results and Discussion

3.1. Characterization of the prepared composites

The prepared composites CdS/SiO_2, CdS/SiO_2-TPP & CdS/SiO_2-TPAPP were characterized by X-ray diffractometry (XRD), Raman, Fourier transform infrared spectroscopy (FT-IR), filed emission scanning electron microscopy (FE-SEM) along with energy dispersive spectra (EDS), diffuse reflectance spectroscopy (DRS) and photoluminescence spectra (PL). Fig. 3 shows the XRD patterns of CdS/SiO_2, CdS/SiO_2-TPP and CdS/SiO_2-TPAPP. The XRD patterns of all composites contains only CdS phase (Fig. 3), no peak of SiO_2 was detected, suggesting that SiO_2 was amorphous. Although in our previous work [21], the XRD pattern of SiO_2/ZnO contains both SiO_2 and ZnO peaks, the broad peak of amorphous SiO_2 between

degrees 19 and 30 may be merged with CdS peaks appeared at the same region in SiO_2/CdS composites (Fig. 3). The peaks appeared at 26.28, 43.57 and 51.83 degrees corresponds to (111), (220) and (311) diffraction peaks of CdS [4]. The crystallinity including homogeneity and surface conditions of semiconducting materials could be studied using Raman spectroscopy. Crystalline materials give sharp peaks whereas very broad peaks can be observed for amorphous or polycrystalline material. Raman spectra of the prepared materials are exhibited in Fig. 4. The intense sharp peak observed at around 300 cm^{-1} and less intense peak at 600 cm^{-1} is ascribed to the CdS fundamental longitudinal optical mode phonon (1LO) and its overtone (2LO), respectively [30]. There was no peak observed for SiO_2 in SiO_2/CdS composites, although SiO_2 gave most noticeable bands at 436, 716, 1265, 1392, 1665, 1704 and 1760 cm^{-1} [31], this can be caused by amorphous nature of SiO_2 and also very less intense bands only observed for pure SiO_2 [31]. As shown in Figs. 4b and 4c, the Raman spectra provide additional piece of evidence for the strong interaction between the porphyrins (TPP and TPAPP) and the surface of SiO_2/CdS composite, as indicated by the distinctive differences between the Raman spectra of the free SiO_2/CdS and porphyrins modified composites (CdS/SiO_2-TPP and CdS/SiO_2-TPAPP). The in-plane band that appears in both porphyrins modified composites between the regions 850-950 cm^{-1} and the band at 472 cm^{-1} in CdS/SiO_2-TPAPP (Fig. 4c) allotted to in-plane bending of the porphyrin core [32].

FT-IR spectroscopy is used to examine the chemical bonds and to identify the organic species present in the compounds or materials. The presence of chemical bonds in prepared composites is studied by FT-IR spectrometer in the range of 400 cm^{-1}– 4000 cm^{-1} at room temperature. Fig. 5 shows the FT-IR spectra of (a) CdS/SiO_2, (b) CdS/SiO_2-TPP and (c) CdS/SiO_2-TPAPP. The bands appeared between 800 and 1110 cm^{-1} corresponds to Si–O–Si bonds [21]. A peak observed between 430 and 490 cm^{-1} is ascribed to the presence of Cd–S bond, peaks observed this region is assigned to Metal–Sulfur bond [33]. A peak observed

between 1600 to 1660 cm^{-1} is ascribed to H-O stretching vibration that might have been from adsorbed water during preparation or from the atmosphere. The GPTMS altered samples (Fig. 5b and c) exhibit the peaks in the range 2850–2990 cm^{-1} corresponding to the stretching vibrations of CH_2 in the GPTMS. The new bands appeared between 1200 to 1300 cm^{-1} in CdS/SiO_2-TPP and CdS/SiO_2-TPAPP corresponds to C-N (aromatic primary amine) vibrations of porphyrins. Although, there was no peak was observed between 900 and 970 cm^{-1} relates to the epoxy group of GPTMS in CdS/SiO_2-TPP [21]. The amino group peaks of TPP and TPAPP in CdS/SiO_2-TPP and CdS/SiO_2-TPAPP modified samples were observed in the range between 3300 and 3500 cm^{-1} (Figs. 5b and 5c).

The morphology of the prepared composites was analysed by FE-SEM. The FE-SEM images of CdS/SiO_2 (a&b) CdS/SiO_2-TPP (b&c) and CdS/SiO_2-TPAPP (d&f) with different magnifications are shown in Fig.6. We could not observe any morphological change in porphyrins modified composites after modification of CdS/SiO_2 with TPP & TPAPP. In all the images, the spherical shaped particles with smooth surfaces are clearly seen for SiO_2, and CdS particles are embedded on the surface of SiO_2. The diameter of SiO_2 sphere is in the range between 500 and 600 nm. The EDS of prepared composites were analyzed and do not have much difference in their composition. EDS of CdS/SiO_2 composite is given in Fig. 7. The elements Si, O, Cd and S gave their corresponding peaks in the spectrum. Furthermore, as expected the atomic percent of Cd and S is found to almost 1:1.

UV–Vis–DRS spectroscopy is a vital technique to observe the optical properties of materials. The diffuse reflectance spectra of the as-prepared composites are recorded using UV–Vis–DRS spectrophotometer at the temperature of room. The diffuse reflectance spectra (DRS) of CdS/SiO_2, CdS/SiO_2-TPP and CdS/SiO_2-TPAPP are depicted in Fig. 8. It is observed that there has been a rise in the absorbance at entire visible region (400-800 nm) in porphyrins modified composites when compared to CdS/SiO_2. This is caused by the presence of porphyrins

(TPP & TPAPP) in the porphyrins modified CdS/SiO_2 composites. The visible light absorbance of CdS/SiO_2-TPAPP is slightly higher than of CdS/SiO_2-TPP. DRS study strongly confirms the existence of TPP and TPAPP in the porphyrins modified composites. To calculate the band gap energies of the composites, Kubelka-Munk function was used. The band gap energies of the prepared composites were attained from the plot of the modified Kubelka-Munk function $(F(R)E)^{1/2}$ versus the energy of the absorbed light E and shown in Fig. 9. The band gap energies of bare CdS/SiO_2, CdS/SiO_2-TPP and CdS/SiO_2-TPAPP are found to be 2.29, 2.30 and 3.31 eV, respectively.

The photoluminescence emission spectra of CdS/SiO_2, CdS/SiO_2-TPP and CdS/SiO_2-TPAPP were estimated at room temperature and shown in Fig. 10. The of CdS/SiO_2 composites gave ten peaks at 361, 374, 412, 456, 495, 504, 524, 535, 582 and 593 nm. Modification of CdS/SiO_2 with porphyrins (TPP & TPAPP) does not shift the emission of CdS/SiO_2, but the intensity of PL emission is slightly higher when compared to pristine CdS/SiO_2 composite, although, the PL emission intensity decreased in some of the metal porphyrins modified semiconductors [34, 35]. In porphyrins modified samples, the emission wavelength does not vary with dopants ie., porphyrins as may be seen from Fig. 10. This implies that the energy level of defect states/sulfur vacancies (in CdS) related to the valance band nearly keeps unchanged. It is also clear from Fig. 10 that luminescence intensity is slightly enhanced on doping with porphyrins. This may be due results in enhanced surface defects result in soar up in the PL intensity of porphyrins modified composites. This indicates that porphyrins seem to be acting as sensitizing agent, and thus enhances the radiative recombination processes. Hence, the fluorescence efficiencies of porphyrins modified samples are prominent than that of the pristine CdS/SiO_2 [36].

3.2. Photocatalytic degradation of RR 120 dye

The research in the area of water purification technology and environmental remediation are concerned for our water resources constituting both groundwater and polluted wastewaters. Nowadays, with increasing revolution in science and technology there is a high demand in industries for newer chemicals to be used to control water pollution. In the point of view, the prepared composites are effectively utilized for an azo dye RR 120 degradation under direct solar light. It was already reported that RR 120 dye with stands to self-photolysis under direct solar light [37]. RR 120 underwent 60.7 and 67% of degradation occurred with CdS/SiO_2-TPP and CdS/SiO_2-TPAPP, respectively at 30 min irradiation (Fig. 11). Under the same conditions, unmodified CdS/SiO_2 gave only 50% of degradation. Both porphyrins modified composites were noticed to be very efficient toward RR 120 degradation when compared with pristine CdS/SiO_2. The order of activity is CdS/SiO_2-TPAPP > CdS/SiO_2-TPP > CdS/SiO_2.

A mechanism for the photocatalytic degradation of RR 120 with porphyrins modified composites under solar lights is proposed (Fig. 12). When the porphyrins modified composites are irradiated by solar light, the porphyrins (TPP & TPAPP) molecules can be induced along with CdS [20, 21]. In the composites, CdS and porphyrins acted as photoactive centre where SiO_2 acts as an adsorbent. Upon excitation of porphyrins, the electrons from the LUMO of porphyrins are transferred to the conduction band (CB) of CdS, and the electrons may result in reacting with adsorbed O_2 on the surface of CdS to produce super oxide radical anions ($O_2^{\bullet-}$). In the meantime, holes in the valence band (VB) of CdS react to water to produce hydroxyl radicals ($^{\bullet}OH$), both species are highly reactive toward RR 120 degradation. Moreover, the reactive holes (from HOMO) in TPP & TPAPP can oxidize RR 120 to its radical cation either directly or through a primarily formed $^{\bullet}OH$ produced by the oxidation of ubiquitous water. The same type of mechanism was proposed the degradation of dye by porphyrins modified semiconductors [21, 38, 39].

4. Conclusions

The synthesis and structural confirmation of porphyrins modified CdS/SiO_2 composites and their photoactivity was discussed. These prepared composites were evaluated in the deterioration of RR 120 dye in water under solar light irradiation. The method adopted for this synthesis is simple, eco-friendly and no individual tool is required. FT-IR spectra reveal that the band between 430 and 490 cm^{-1} is allotted to Cd–S (Metal–Sulfur) bond. Although the visible light absorbance of CdS/SiO_2-TPP and CdS/SiO_2-TPAPP is slightly greater than that of CdS/SiO_2, the band gap energy is slightly higher in porphyrin modified composites when compared with pristine CdS/SiO_2. FE-SEM analysis confirms the spherical shaped particles with smooth surfaces for SiO_2, and CdS particles are embedded on the surface of SiO_2. Photoluminescence intensity of CdS/SiO_2 is slightly enhanced on doping with porphyrins. This may be due results in enhanced surface defects leading to an increase in the PL intensity of porphyrins modified composites. This indicates that porphyrins seem to be acting as sensitizing agent. Both porphyrins modified composites noticed to be very efficient toward RR 120 degradation when compared with pristine CdS/SiO_2. The order of activity is CdS/SiO_2-TPAPP > CdS/SiO_2-TPP > CdS/SiO_2. A mechanism for the photocatalytic deterioration of RR 120 with porphyrins modified composites under solar lights is proposed.

Acknowledgments

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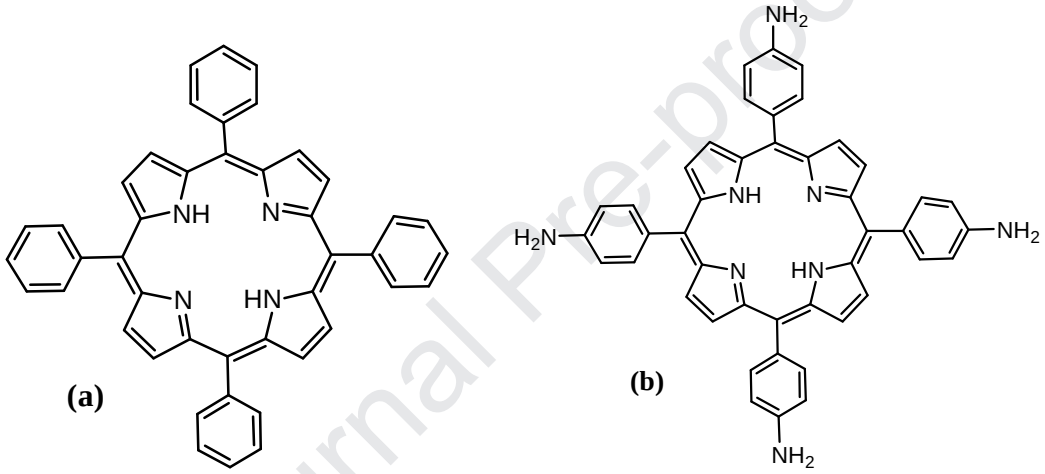


Fig. 1. Structure of porphyrins (a) TPP and (b) TPAPP

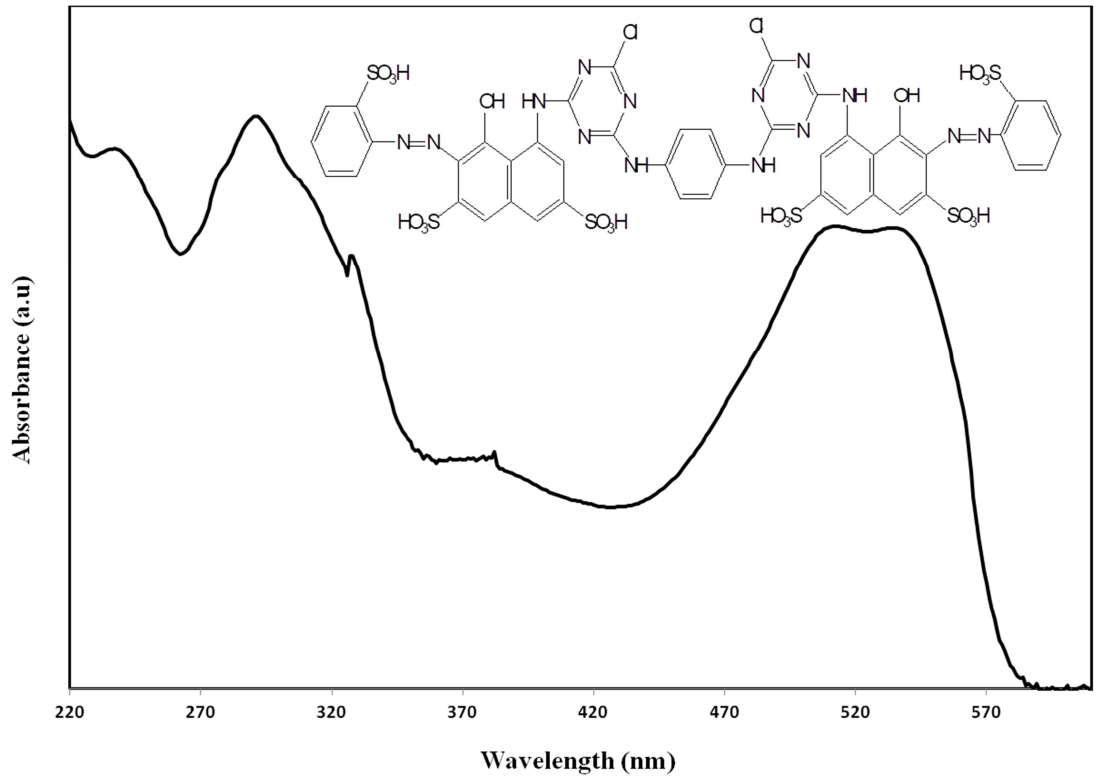


Fig. 2. Structure and UV-Vis spectrum of RR 120 dye

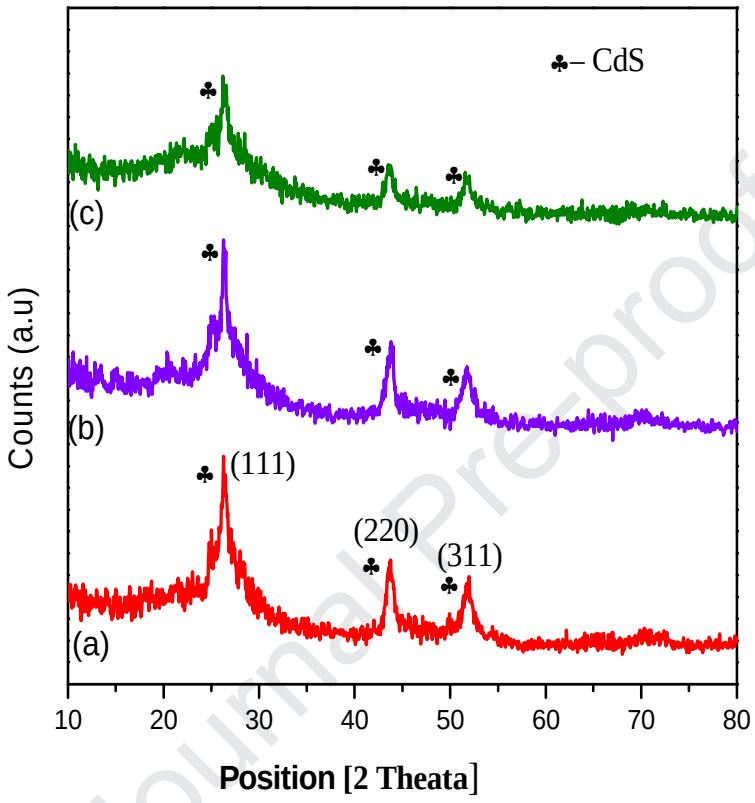


Fig.3 XRD patterns of (a) CdS/SiO_2, (b) CdS/SiO_2-TPP and (c) CdS/SiO_2-TPAPP

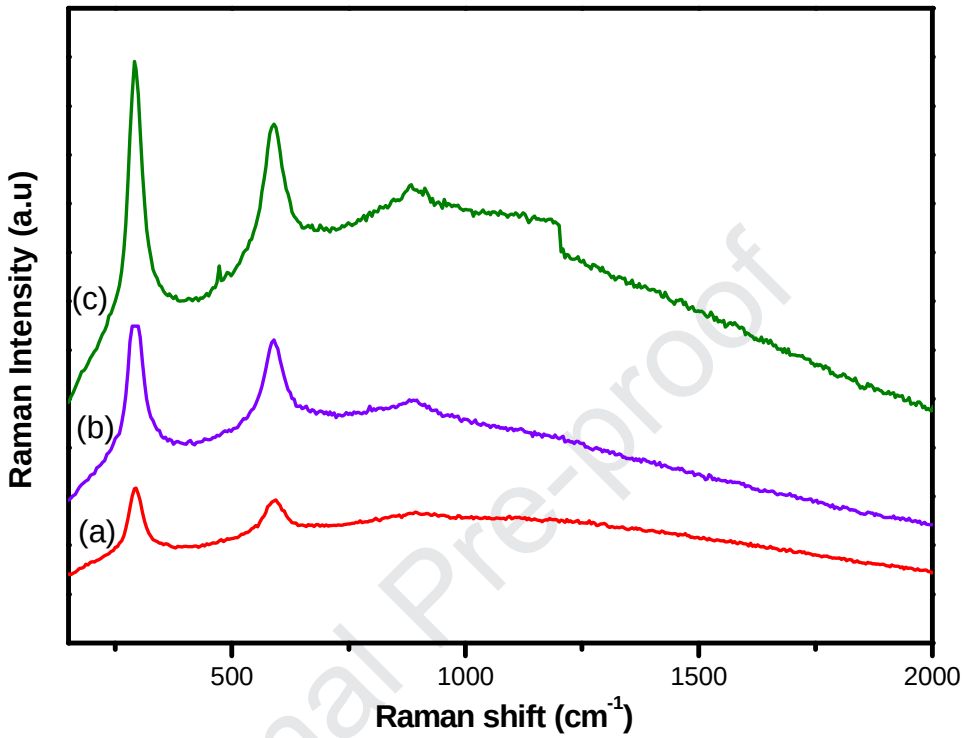


Fig.4 Raman spectra of (a) CdS/SiO_2, (b) CdS/SiO_2-TPP and (c) CdS/SiO_2-TPAPP

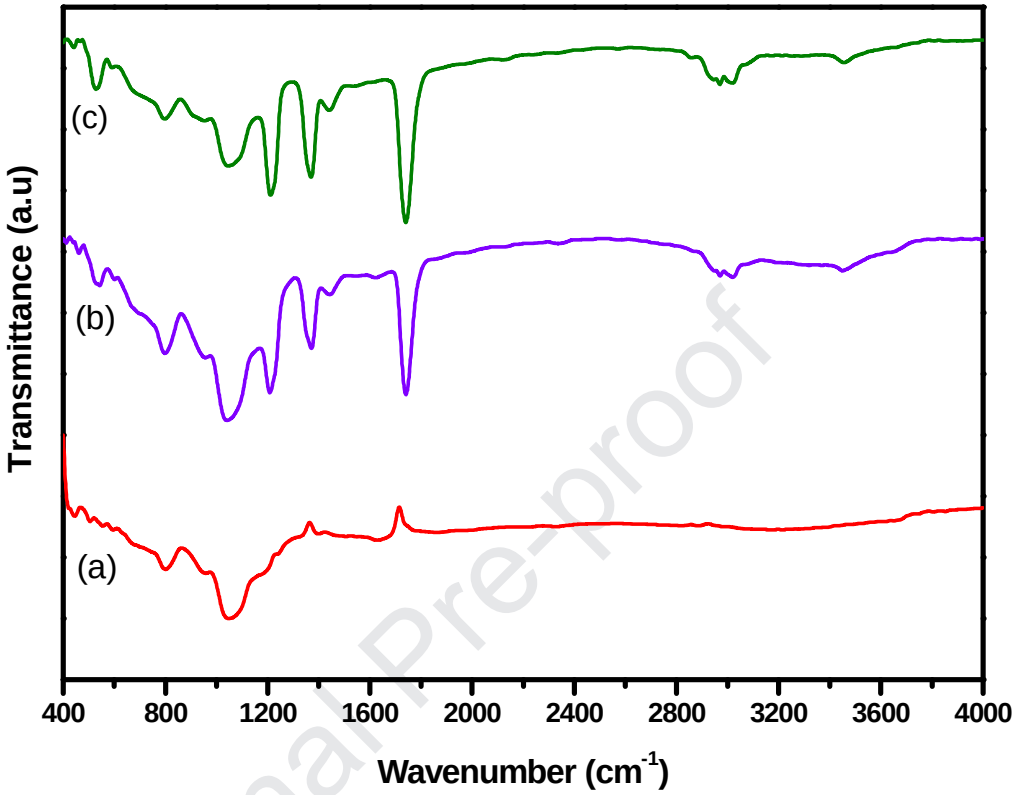


Fig.5 FT-IR spectra of (a) CdS/SiO_2, (b) CdS/SiO_2-TPP and (c) CdS/SiO_2-TPAPP

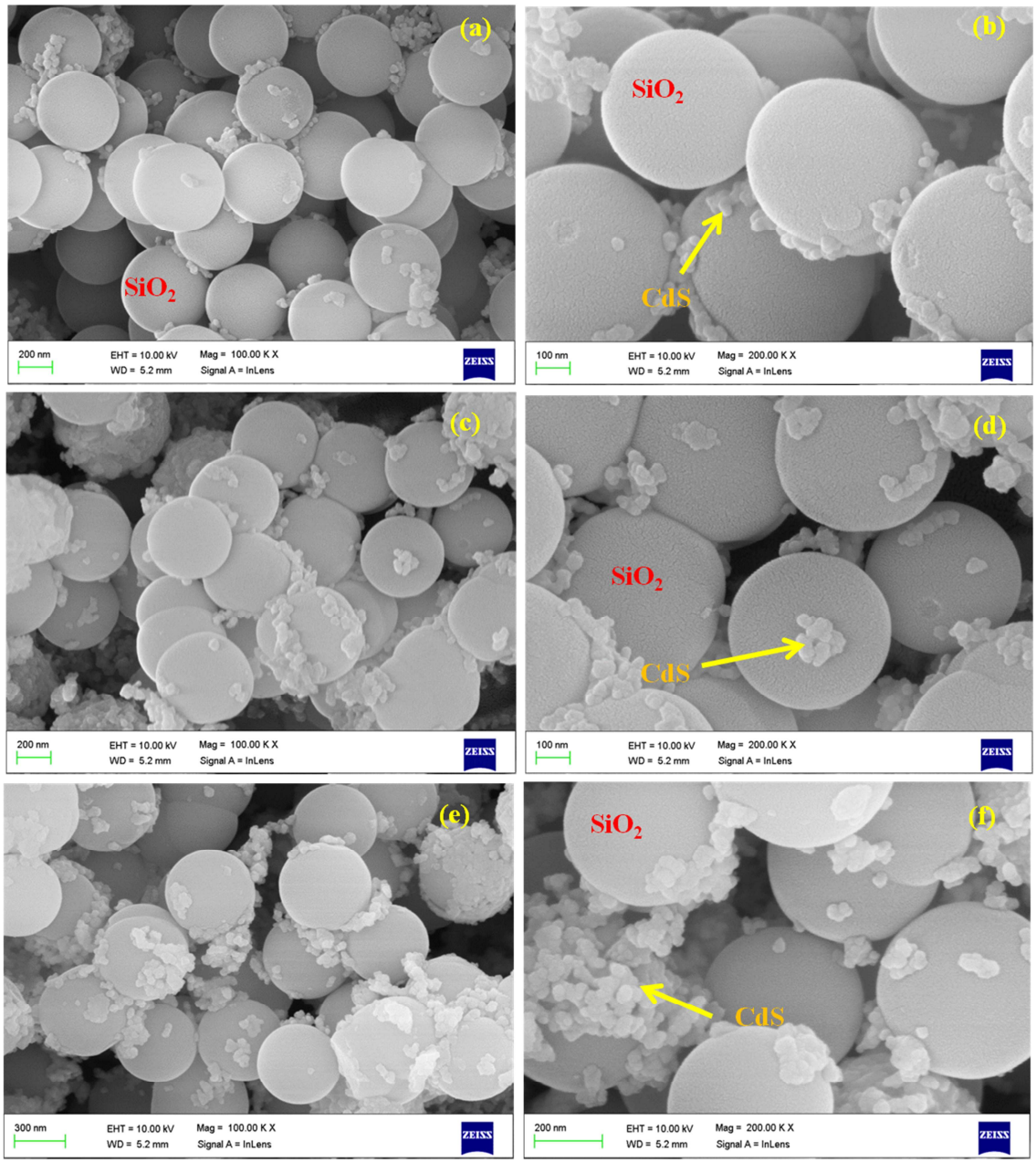
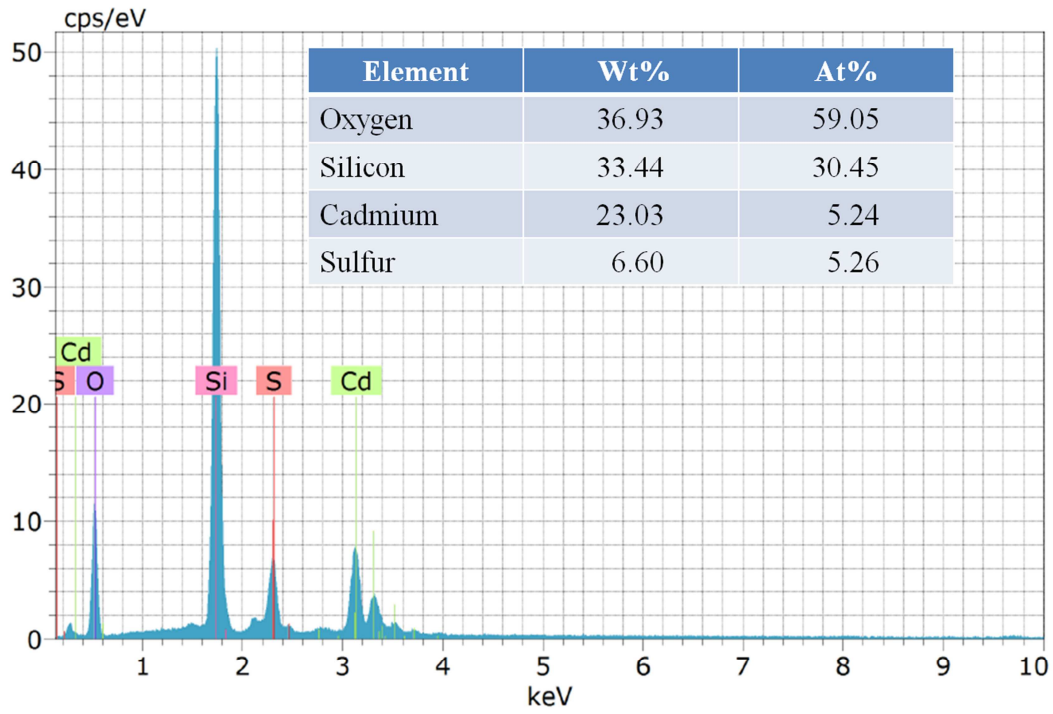


Fig. 6 FE-SEM images of CdS/SiO_2 (a&b), CdS/SiO_2-TPP (b&c) and CdS/SiO_2-TPAPP (e&f)



Element	Wt%	At%
Oxygen	36.93	59.05
Silicon	33.44	30.45
Cadmium	23.03	5.24
Sulfur	6.60	5.26

Fig. 7 EDS of CdS/SiO_2

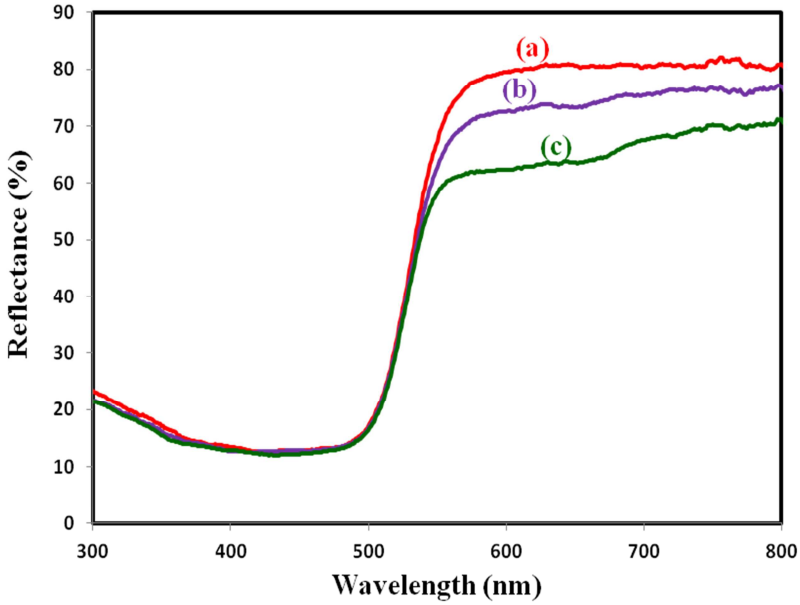


Fig. 8. DRS of (a) CdS/SiO_2, (b) CdS/SiO_2-TPP and (c) CdS/SiO_2-TPAPP

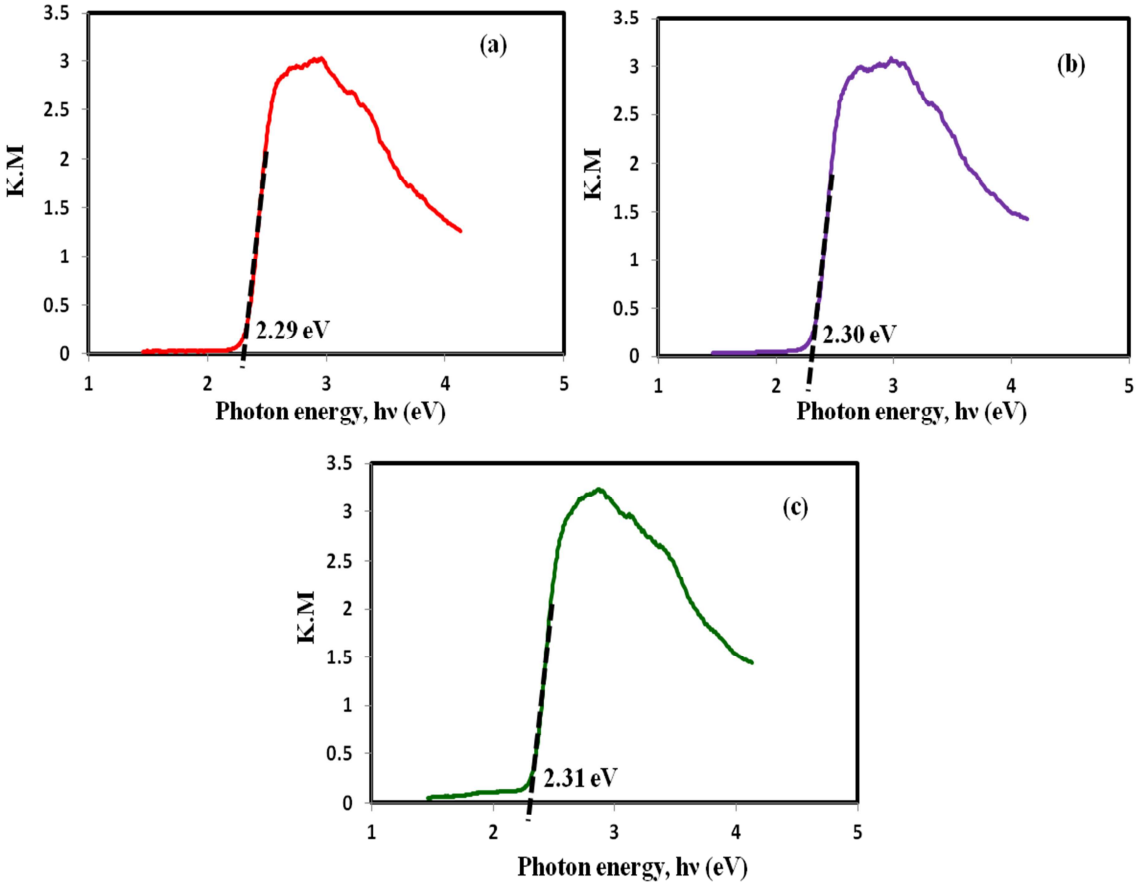


Fig. 9. KM plot of (a) CdS/SiO_2, (b) CdS/SiO_2-TPP and (c) CdS/SiO_2-TPAPP

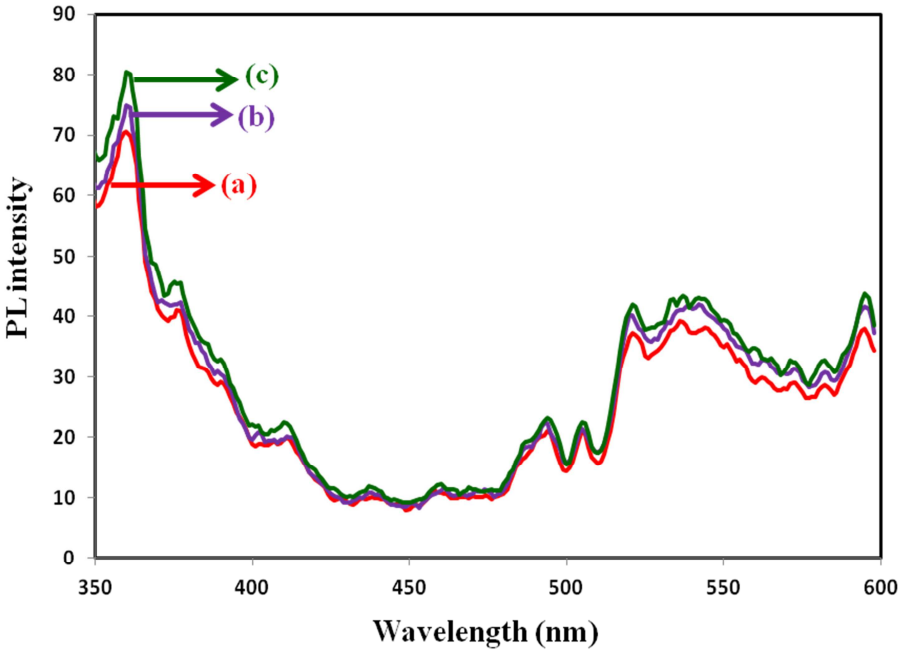


Fig. 10. PL spectra of (a) CdS/SiO_2, (b) CdS/SiO_2-TPP and (c) CdS/SiO_2-TPAPP

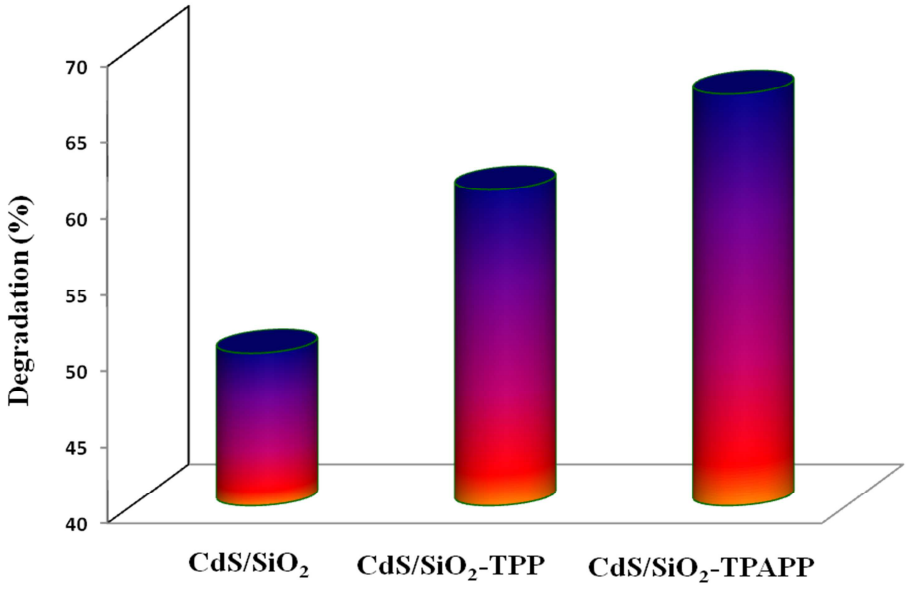


Fig. 11. Photodegradability of RR 120: [RR 120] = 10 ppm, catalyst suspension = 10 mg/100 mL, time of irradiation = 30 min

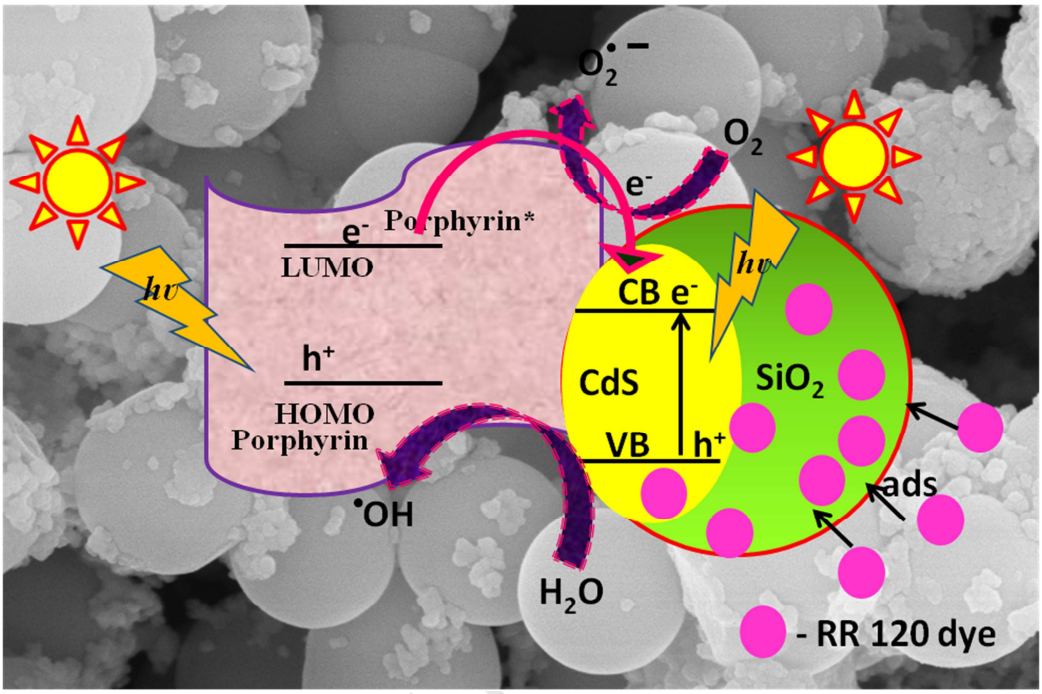


Fig. 12. Mechanism of degradation of RR 120 by Porphyrin modified CdS/SiO_2.

Research Highlights

- Sphere shaped SiO_2 was prepared by a simple sol-gel method without any template
- Photoluminescence intensity of CdS/SiO_2 is slightly enhanced on doping with porphyrins
- Both porphyrins modified composites were found to be very efficient toward RR 120 degradation when compared with pristine CdS/SiO_2

Impact Statement

Initially, sphere shaped SiO_2 was prepared by a simple sol-gel method without any template. Later, the sphere like SiO_2 was modified with cadmium sulfide (CdS) semiconductor and porphyrins. The formation of composites (CdS/SiO_2-porphyrins) was confirmed by different characterization techniques such as XRD, Raman, FT-IR, FE-SEM, EDS, DRS and PL measurements. The photocatalytic activity of CdS/SiO_2 was slightly influenced by porphyrins such as meso-tetra-phenyl-porphyrin (TPP) and 5,10,15,20-meso-tetra-(*para*-amino)-phenyl-porphyrin(TPAPP). Regarding photocatalytic degradation of toxic dyes, it has brought a new revolution to reduce water pollution. Since SiO_2 is an insulator, it is not directly used as a photocatalyst for degradation experiments until mixed with semiconducting materials. In the process of continuous exploration on environmental remediation, the present work is focused on the modification of SiO_2 with CdS semiconductor and two different porphyrins. The prepared composites effectively utilized for Reactive Red 120 (RR 120) degradation under direct sunlight. So, we feel that this work may be suitable for this journal.