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Research Article

MORPHOLOGICAL AND PHOTOCATALYTIC STUDIES OF SoL-GeL DERIVED CdS NANOSTRUCTURES

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ABSTRACT

The systematic influences of structure and sizes of nanoparticles have greatly advantage in numerous application fields, conversely structure of nanoparticle has been much more difficult to achieve. Hence investigation of novel method for synthesis of differently shaped nanoparticles is inspiring research area. In present study Cadmium Sulfide (CdS) nanoparticles synthesized using various reducing agents such as Polyethylene Glycol (PEG), Polyvinyl Propylene (PVP), Sodium Dodecyl Sulphate (SDS) and Co-Block Polymer. The synthesized nanoparticles were characterized using X-ray Diffraction, FTIR, UV-Visible spectroscopy, Scanning Electron Microscope. The photocatalytic activities of as synthesized CdS nanoparticles were estimated by photo degradation of methylene blue (MB) dye under visible light irradiation.

INTRODUCTION

Semiconductor photocatalysts have fascinated and extensive attention for a long time from the arenas of catalysis, electrochemistry and photochemistry that can be accredited to their significant effects on unraveling environmental problems [1]. Nanostructured materials have attracted due to abundant deal of attention in unique characteristics owed to quantum size effects and surface effects. Current developments and quantum size effects in nanotechnology, implies the novel devices of the future will be based on properties of nanomaterials. Nanomaterials have drawn interests and attentions due to their special characteristics that differ from the bulk solids and molecules. Since novel properties of nanomaterials depend on their size, structure and shape, as well as a new direction of synthesis protocols [2]. Nanoparticles can display novel optical, electronic, magnetic, chemical, and structural properties that might find many important technological applications [3]. The electrical and optical properties are directly associated with the quantum confinement of charge carriers leading to the blue shift of the band gap with the shrinkage of their size [4]. Nanocrystals (NCs) are being used greatly in many applications. One of the unique properties of the semiconductor NCs is their band gap increase with decreasing particle size due to carrier confinement effects. Luminescence from within the band gap is also affected by the grain size and nanoparticle composition [5].

Nanostructured II–VI semiconductors have been studied very intensively in recent time due to their industrial implementation in nanoelectronic devices. The CdS nanoparticle are one of the most studied materials among the II–VI compounds [6] and also proved to be an excellent photoactive and charge transport material in optoelectronic devices and its direct band-gap of 2.4 eV is appropriate to be an acceptor in organic photovoltaic devices [7]. Semiconducting CdS nanomaterial has received much attention due to its direct band gap resulting in emission in the visible wavelength and widely investigated for applications in semiconductor laser. The photocatalytic properties of CdS semiconducting nanomaterial depend on not only the particle size but also the morphology. Hence, a number of methods have been developed to synthesize the CdS nanomaterials with different morphologies and structures such as nanocrystals, quasi-nanospheres, nanorods, nanowhiskers, nanowires, nanobelts and nanotubes [8] have attracted much interest due to their size dependent properties and great potential in several applications such as nonlinear optics, photo electrochemical cells, heterogeneous photocatalysis, optical

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switching, and single electron transistors. Surfactants like block copolymers and dendrimers have been used for the preparation of semiconductor nanoparticles [9].

The application of advanced oxidation processes (AOPs) has been proposed as an efficient approach for the degradation of various organic pollutants such as organic dyes in the aqueous phase. One of the most widely used AOPs for treating colored wastewater is photocatalytic processes [10]. Semiconductor photocatalysis is the basis for a variety of current and future applications in many different fields, such as surface technology, pollution management, and medicine. The fundamental principle is the ability of a photocatalyst to absorb photons creating reactive electron−hole pairs which are capable of oxidizing most organic and inorganic compounds. When a photon with sufficient energy is absorbed, an electron is excited from the valence band to the conduction band of the semiconductor. Simultaneously, a positively charged hole is created in the valence band. Recombination of these two species will result in the re-emission of a photon or in the emission of heat. However, once these two reactive species reach the surface of the semiconductor, they can undergo a variety of reactions with surface-adsorbed molecules [11].

In the present work, the morphology-controlled CdS photocatalysts of solid nanospheres, hollow nanospheres, and nanorods were synthesized by sol-gel protocol without changing other experimental parameters. Their activities for photocatalytic degradation of Mythelene Blue were then evaluated. The formation mechanism and effect of different morphologies on the activity were also investigated.

Experimental Work

5.0 mL portion of $CdCl_2$ stock solution was add to 10.0 mL of correspond solvent, followed by addition of 5.0 mL of Na_2S stock solution in corresponding solvent under the stirring. CdS concentration of the 0.5 mM in the resulting stable CdS colloidal solutions were stored at 20 ^{0}C in the dark and were characterized normally after 24 h of aging.

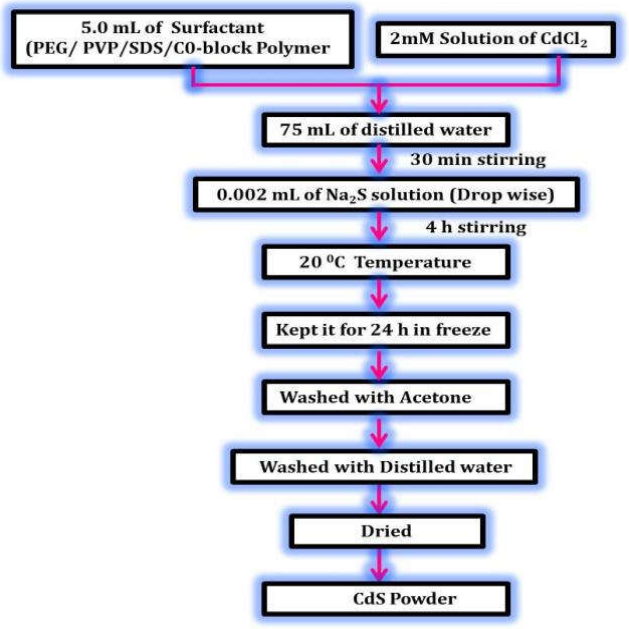

Fig 1 Schematic representation of CdS nanoparticles synthesis

For preparing pure CdS, 2 mL solution of $CdCl_2$ was added to 5.0 mL of surfactant (PEG, PVP, SDS, Co-block polymer). Added 75 mL of distilled water and stir it for 30 minutes. Then added 0.002 mL of Na_2S solution drop wise, stirred it for 4 h and kept in the freezer for 24 h, then washed it with acetone followed by distilled water. Dried it until the moisture content is evaporated by leaving the CdS powder. The synthesis procedure for CdS nanoparticles is schematically represented in Fig.1.

Characterization Studies

X-ray Diffraction Pattern (XRD)

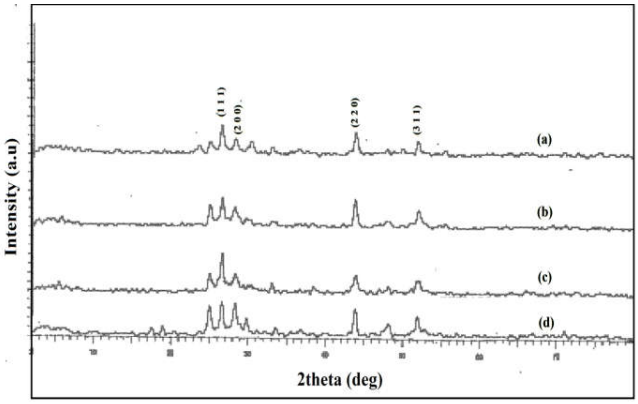

Fig 2 XRD patterns of CdS Nanoparticles with Different Surfactants (a) Sodium dodecyl sulfate (SDS) (b) Polyvinyl propylene (PVP) (c) Polyethylene glycol (PEG) and (d) Co-block polymer

The structural properties, crystallite size and phase identity of the CdS nanoparticles were resolute by X-ray diffractometer. Fig. 2 demonstrations the XRD patterns of cadmium sulfide nanoparticles synthesized using different surfactants by Sol-Gel protocol in which the planes are indexed (111), (200), (220) and (311) at 26.52^o, 30.83^o, 43.99^o and 52.17^o respectively. The XRD pattern of all the CdS samples are well matched with the standard JCPDS data card no. #100454 which reveals pure cubic phase of CdS structure. The face centered lattice parameters of synthesized CdS nanoparticles are obtained as a=b=c= 5.818A^o.

FTIR

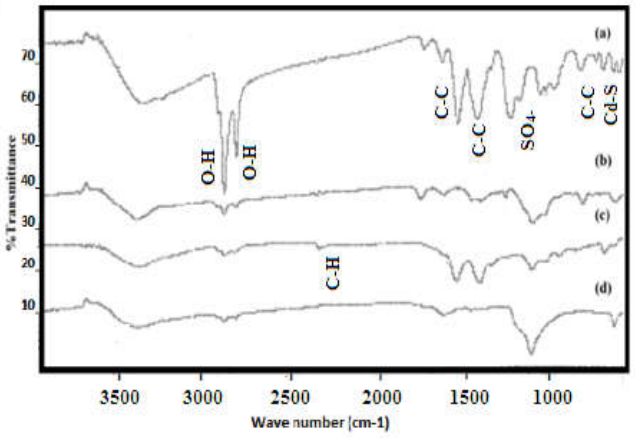

Fig 3 FTIR spectra of CdS nanoparticles synthesized by (a) Sodium dodecyl sulfate (SDS) (b) Polyvinylpropylene (PVP) (c) Polyethylene glycol (PEG) and (d) Co-block polymer

Figure 3 shows the FTIR spectra of CdS nanoparticles synthesized by sodium dodecyl sulfate, polyvinyl proplene, polyethylene glycol & co-block polymer. The transmittance peaks in all the spectra corresponds to Cd-S strectching bonds. The peaks between 3387 cm^{-1} to 3450 cm^{-1} is assigned to O-H stretching of water molecule which is due to the presence of moisture in the synthesized sample. The peaks at 2851.19 cm^{-1} and 2921.15 cm^{-1} corresponds to C-H bonds which are araised in the CdS nanoparticles synthesized by sodium dodecyl sulfate. The peaks between 1542.07 cm^{-1} and 1762.20 cm^{-1} correspond to C-C stretching vibration which is observed in all the four CdS samples. The peaks from 1226.32 cm^{-1} to 1458.48 cm^{-1} are due to the stretching vibrations of sulfate groups in the sample. The peaks from 1019.59 cm^{-1} to 1105.02 cm^{-1} correspond to SO^{4-} which is observed in all the spectra. Peaks between 811.17 cm^{-1} and 607.56 cm^{-1} correspond to Cd-S stretching vibrations which is also observed in all the four samples.

FESEM

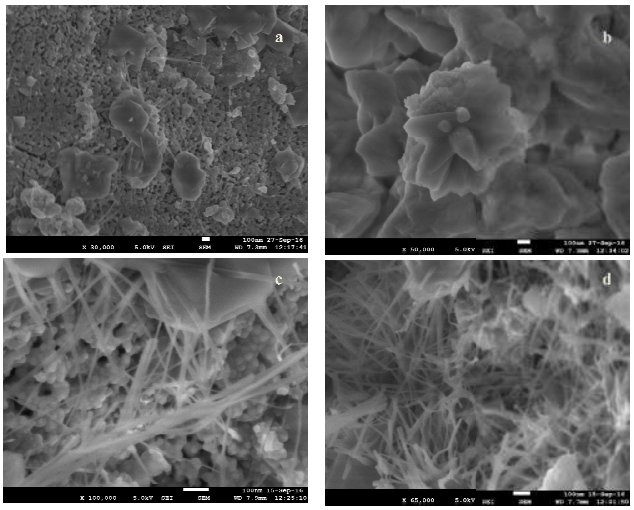

Fig 4 SEM images of as synthesized CdS nanoparticles (a) Sodium dodecyl sulfate (SDS) (b) Co-block polymer (c) Polyethylene glycol (PEG) and (d) Polyvinyl propylene (PVP)

SEM gives topographical, compositional, morphological information and in addition to this it can also detect surface fractures. Fig. 4(a) shows synthesized CdS nanoparticles with Sodium Dodicile Sulphate as surfactant and forms needle shaped nanoparticles, Fig. 4(b) shows synthesized CdS nanoparticles with co-block polymer as surfactant and forms flower with stamen like nanoparticles, Fig. 4(c) shows the synthesized CdS nanoparticles with polyethylene glycol as surfactant and forms nanotubes structures and Fig. 4(d) shows the synthesized CdS nanoparticles with polyvinyl pyrrolidone as surfactant and forms completely nanotubes structures.

EDAX

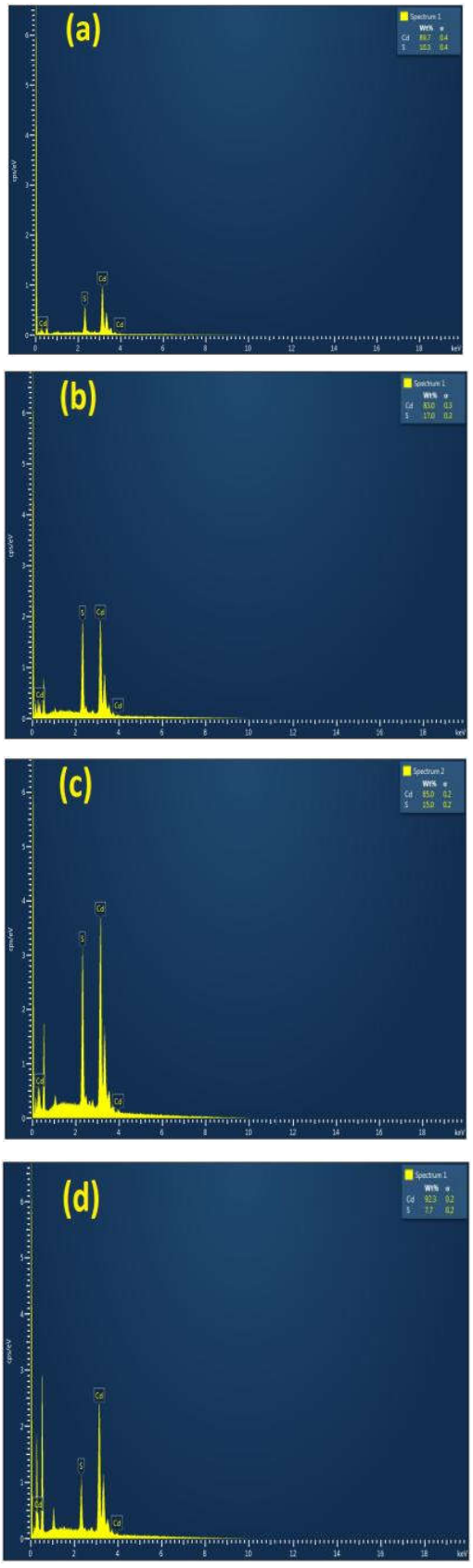

Fig 5 EDAX spectra of CdS nanoparticles synthesized by (a) PVP, (b) SDS, (c) PEG and (d) Co-block polymer

EDAX studies are carried out to test the purity of the sample by revealing the details of all the elements present in the synthesized CdS nanoparticles.

Table 1 EDAX results of synthesized Cadmium Sulfide Nanoparticles

Sample	Cd %	S %	Total
CdS (PVP)	89.7	10.3	100%
CdS (SDS)	83	17	100%
CdS (PEG)	85	15	100%
CdS (Coblock polymer)	92.3	7.7	100%

Fig. 5 shows the EDAX spectra of CdS nanoparticles synthesized using different surfactants. The EDAX analysis shows that the CdS nanoparticles synthesized by PVP contain 89.7% of cadmium and 10.3% of sulphur in its composition. The EDAX analysis of CdS nanoparticles synthesized by SDS contains 83% of cadmium and 17% of sulphur in its composition. The EDAX analysis of CdS nanoparticles synthesized by PEG contains 85% of cadmium and 15% of sulphur in its composition and the EDAX analysis of CdS nanoparticles synthesized by co-block polymer contains 92.3% of cadmium and 7.7% of sulphur in its composition. The energy-dispersive spectroscopy of all the four CdS samples confirmed the presence of cadmium sulphide. The quantitative elemental analysis is tabulated in Table.1.

UV-Visible Spectrum

The UV-Visible spectrum of the CdS nanoparticles was recorded on a UV-Visible double-beam spectrophotometer. Fig. 6 depicts the optical spectra of nano CdS particles synthesized by PVP, SDS, PEG and Co-block polymer. The characteristic absorption peaks observed at 520 nm, 480 nm, 500 nm, and 520 nm for CdS nanoparticles synthesized by PEG, Co-block polymer, PVP and SDS, respectively. From UV results obtained, it is evident that the CdS nanoparticles were formed and this was confirmed by the surface Plasmon resonance exhibited.

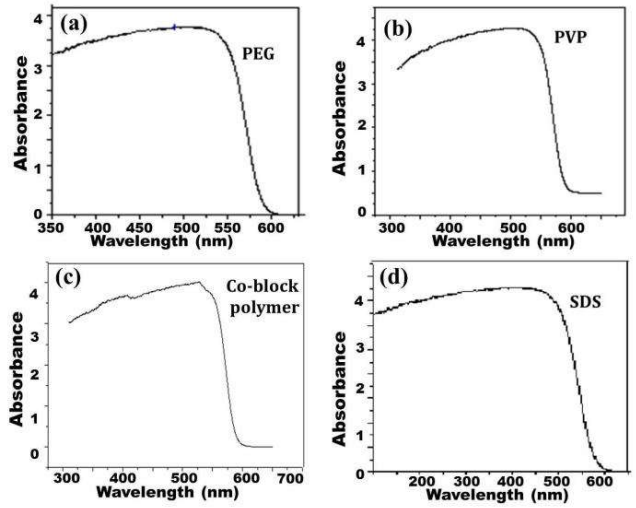

Fig. 6 UV-Visible Spectra of nano CdS particles synthesized by (a) PEG, (b) PVP, (c) Co-block polymer and (d) SDS.

Photo Luminescence

It shows the room-temperature photoluminescence spectra of the synthesized CdS nanoparticles obtained at existed wavelength 525 nm. The nanoparticles of different spectra has obtained at around 525 nm has been observed in the pure CdS nanoparticles. From the emission spectra, we find a hump at 525 nm and 528 nm, due to 'CdS' indicated with pink color. Blue line indicates the photo luminescence of SDS followed by Co-block polymer indicated with black followed by PEG which is red in color and PVP by using green color. Shift in the optical spectrum is due to the fact that the particles in nanosize regime exhibit quantum confinement effect. The peak at 525 nm is similar to all the nanoparticles and can be attributed to the surface related/ trap defects, due to the presence of cadmium vacancy.

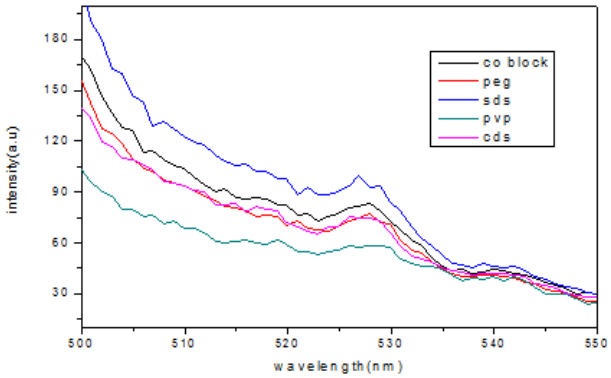

Fig 7 Photoluminescence spectra of CdS nanoparticles, PVP, SDS, PEG and Co-block polymer

Photocatalytic Activity of CdS nanoparticles

The photocatalytic activity of all CdS samples were evaluated by Photodegradation of methylene blue (MB) using HEBER Visible Annular Photo reactor, model HVAR1234 (Haber Scientific, India), under visible light irradiation using 450 W Tungsten lamp as a light source. The system was cooled by circulating water and maintained at room temperature. Photocatalytic activities of the synthesized nanomaterials were tested using Methylene Blue as a model pollutant. Methylene Blue is a major water pollutant and its degradation to safe levels is not an easy task due to its resistance to chemical and biological degradation. The photocatalytic activity study of synthesized nanomaterials was carried out under UV-VIS light irradiation and the results of photocatalytic performance are shown in the Fig.8

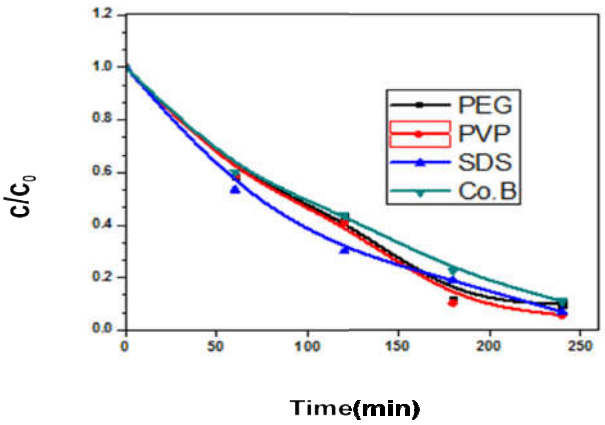

Fig 8 Degradation of Methylene Blue (a) PEG (b) PVP (c) SDS (d) Co-block Polymer

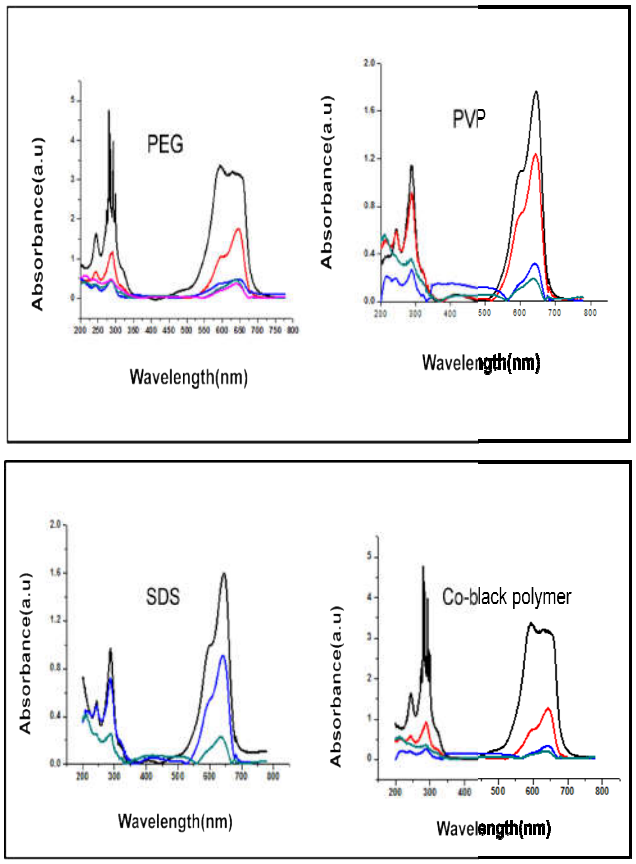

Fig 9 Photoctalytic degradation patterns of Methylene blue using CdS nanoparticles synthesized with PEG, PVP, SDS and Co-block Polymer

Fig. 9 shows the degradation patterns of methylene blue by CdS nanoparticles using PEG, PVP, SDS and Co-block polymer. The amount of Methylene Blue degradation was calculated using the following equation.

$D = (C\text{-}C_0/C_0) \times 100\%$

D is the percentage of degradation, C_o is the initial concentration of dye and C is the final concentration. The degradation is reported as C/C_0 where C is the concentration of dye at each irradiated time and C_0 is the concentration of dye when adsorption–desorption equilibrium was achieved. Catalyst was separated from the reaction mixture by centrifugation.

Mechanism of Photo degradation

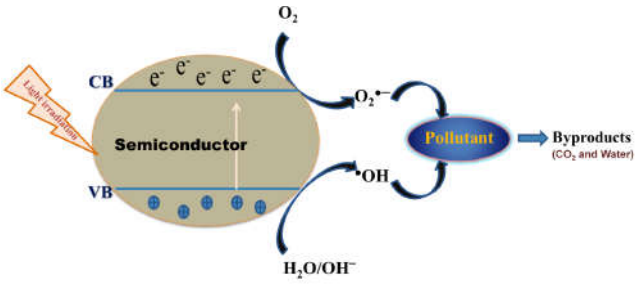

Fig 10 Photocatalytic degradation mechanism

When CdS is exposed to light, photocatalytic reaction is initiated. In fact, an electron which is in the filled valence band becomes excited and jumps to the empty conduction band upon the exposure to the light. Hence, the photon energy, *hv*, which equals or exceeds the band gap of the semiconductor photocatalyst leaves a hole in the valence band; i.e. electrons (e^-) and positive holes (h^+) are produced. The following chain reactions have been accepted to occur during the heterogeneous photocatalysis:

1. Photoexcitation: $CdS + hv \rightarrow e^- + h^+$
2. Oxygen ionosorption: $(O_2)\ ads + e^- \rightarrow O_2^{\bullet-}$
3. Ionization of water: $H_2O \rightarrow OH^- + H^+$
4. Protonation of superoxides: $O_2^{\bullet-} + H^+ \rightarrow HOO^{\bullet}$

The hydroperoxyl radical formed in (4) has also scavenging properties similar to O_2 thus it making the lifetime of photo hole two times longer:

5. $HOO^{\bullet} + e^- \rightarrow HO_2^-$
6. $HOO^- + H^+ \rightarrow H_2O_2$

Oxidation, reduction reactions occur at the surface of the photon excited semiconductor photocatalyst. The band gap of a semiconductor is either direct band gap or indirect band gap. Direct band gap semiconductors can absorb light energy efficiently. Since, the photon absorption process requires no assistance from lattice vibrations. Upon photon absorption, the electron is excited directly from the valence into the conduction band without changing their momentum. In indirect bandgap semiconductors such as Si or Ge, the photon absorption requires the absorption or emission of a photon.

CONCLUSIONS

In summary, CdS nanostructures with needle, flower with stamen and nanotube morphologies have been successfully synthesized by sol-gel process using different surfactants. The shape and size of CdS nanoparticles were modulated by surfactants. The as-prepared CdS nanostructures showed higher activity for methylene blue degradation under visible light irradiation and the photocatalytic activity was varied depending on their shape. Hence it is concluded that the morphology of the CdS nanoparticles is playing a vital role on its photocatalytic efficiency. These results highlight that the shape-controlled synthesis of material with favorable photocatalytic property is a promising strategy to develop highly efficient photocatalytic materials.

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