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CdS sensitized TiO_2 nano heterostructures as sunlight driven photocatalyst

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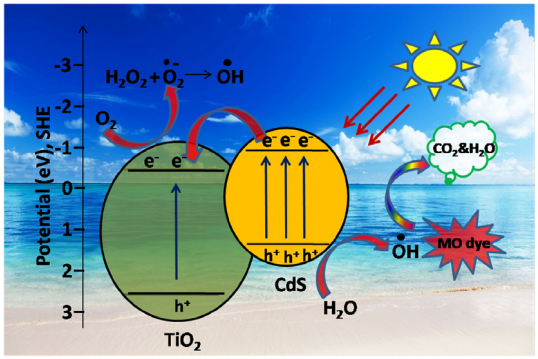
GRAPHICAL ABSTRACT



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ABSTRACT

Sunlight harvesting nano heterostructure materials with excellent photocatalytic activity has received considerable attention in recent years. Here we meticulously investigated the effect of CdS nano crystal loading on the light absorption capacity and the photocatalytic activity of TiO_2 nanomaterials by assembling TiO_2-CdS heterostructures. A distinct heterostructure was established in the presently reported hybrid system with 10 wt% CdS incorporation into TiO_2 and the photocatalytic study showed that TiO_2-CdS10 has 3.5 times higher catalytic activity than bare TiO_2. This superior photocatalytic performance is attributed to the excellent light absorption, high surface area and the slow rate of recombination of photogenerated charge carriers of TiO_2-CdS10 hetero structures. A mechanism was also proposed for the CdS sensitized sunlight driven photocatalytic degradation of methyl orange dye in presence of CdS–TiO_2 nano heterostructure.

1. Introduction

TiO_2 based heterogeneous catalysis becomes an efficient technique for the photocatalytic oxidative removal of dissolved organic and inorganic contaminants in water due to its cost effectiveness, and the distinctive photocatalytic activity [1–4]. It is the bandgap energy of TiO_2 (3.2 eV) that limits its application as solar harvesting photocatalyst [5,6]. Visible light response of TiO_2 has been modified by various approaches such as metal and nonmetal doping in an attempt to tailor the band gap [7,8], photosensitization by anchoring organic chromospheres [9] etc. In recent years heterojunction photocatalyst fabrication *via* hybridizing TiO_2 with suitable narrow band gap semiconductors such as CdS, Cu_2O, ZnO, *etc.* had received considerable attention among the scientific community due to its excellent light absorption ability, improved photocatalysis and also photo stability [10–12].

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CdS act as an excellent sunlight harvesting material owing to its narrow band gap (2.4 eV) and can be used as a sensitizer for wide band gap semiconductors [13]. Valance band and conduction band levels of CdS semiconductor lies above that of TiO_2 which facilitate effective charge separation by reducing the possibility for photo generated electron–hole pair recombination [14]. CdS sensitized TiO_2 catalysts have also been exploited as photocatalyst for hydrogen production from water [15,16] as photoelectrode in dye sensitized solar cells to improve the efficiency of the cells [17,18] and as highly efficient charge carriers in heterogeneous photocatalysis [19,20].

Photocatalytic activity of CdS sensitized catalysis by TiO_2 nanoparticles have been reported recently by Shuli Bai et al., and Li et al., for the degradation of Rhodamine B and NO gas oxidation respectively [21,22]. They found that the surface incorporation of CdS crystals had a marked effect on the photoactivity of TiO_2. The selective oxidation of alcohol to aldehyde in presence of CdS nanorods on the surface of TiO_2 was reported by Liu et al. [23]. Very recently tremendous work on visible light driven CdS decorated TiO_2 photocatalysts have been developed for the oxidative removal of organic dyes from aqueous textile effluents, which is one of the major components in water pollution [24,25]. Xu et al., [26] have developed a simple design for encapsulating CdS nano spheres into a thin TiO_2 shell in order to improve the charge transport properties and the selective redox reactions under visible light. In this work remarkable increase in photoactivity was obtained due to effective interfacial hybridization between CdS and TiO_2. As compared previous reports the present work embodies our attempt to fabricate CdS hybridized TiO_2 photocatalysts in which special attention was made to optimize the minimum concentration of CdS required to sensitize TiO_2 matrix. Hydrothermal method was adopted to fabricate the different compositions of TiO_2-CdS nano hybrid systems (0%, 1%, 5% and 10%), out of which 10% CdS incorporation was found to be the optimum concentration for the oxidative removal of organic pollutant. Toxic and mutagenic methyl orange dye [27] was selected as the reference system to study the photocatalytic properties of the CdS sensitized TiO_2 nano hybrid system. Hopefully the work would provide an insight for the further development of TiO_2 based nano hetero systems for energy and environmental applications.

2. Experimental

2.1. Synthesis of CdS nanoparticles

All the chemicals used in these experiments were used as purchased without further purification. CdS nanoparticles were synthesized by hydrothermal method. In a typical procedure 0.1 M cadmium nitrate (Merck) was dissolved in 50 mL deionized water, then 0.3 M aqueous thiourea (Merck) solution was added to the above solution and the stirring continued for another 30 min. The homogeneous solution obtained was transferred to 100 mL Teflon lined stainless steel autoclave and kept at a temperature of 150 °C/12 h. The obtained precipitate was washed with water and dried at a temperature of 80 °C/12 h.

2.2. Synthesis of TiO_2-CdS heterostructure

TiO_2-CdS nano hetero systems with different weight percentage of CdS (0, 1, 5, and 10%) was prepared by hydrothermal method and the samples were labeled as TiO_2, TiO_2-CdS1, TiO_2-CdS5 and TiO_2-CdS10. Briefly, for the synthesis of the composite samples, calculated amount of synthesized CdS nano crystals were ultrasonically dispersed in 50 ml, 1:1 mixture of water and ethanol. The above dispersion was added carefully in to a 250 ml beaker containing 0.4 M titanium tertiary butoxide (Sigma Aldrich) in 50 mL isopropyl alcohol (Merck). The titania precursor undergo hydrolysis and condensation reaction in water–ethanol medium to form a sol. The obtained sol was vigorously stirred for 4 h and transferred to 100 mL stainless steel autoclave and kept at a temperature of 180 °C/12 h. The product was washed several times with ethanol acetone mixture, dried and calcined at 300 °C/2 h in a muffle furnace. Bare TiO_2 nanoparticles (TiO_2-CdS0) were also synthesized by a similar method without the addition of CdS.

X-ray diffraction studies of all the samples were carried out using Bruker X-ray diffractometer using CuK_α radiation. FTIR spectra was analyzed using Jasco-FT/IR-4100 spectrometer. UV–visible absorption and diffuse reflectance spectral studies were carried out on a Jasco-V-550-UV–vis spectrophotometer. HRTEM images were obtained from JEOL, JEM-ARM200F transmission electron microscope. Raman spectra of the samples were recorded on a Thermo scientific DXR 532 nm laser Raman microscope. X-ray photoelectron spectroscopy (XPS) analysis was carried out from Ultra axis Kratos Analytical, U. K, XPS instrument with an Al K_α X-ray source. BET surface area measurements (N_2 adsorption) of the samples were done by Micromeritics Tristar 2 USA surface area and porosity analyzer after degassing at 200 °C for 2 h. Photoluminescence of the different catalysts were measured using Perkin Elmer LS55 fluorescence spectrometer.

2.3. Photocatalytic study

Methyl orange (herein referred onwards as MO) degradation in presence of TiO_2-CdS heterostructure photocatalyst was investigated under natural sunlight with light intensity ~75,000 lux. Accurately 0.05 g in 500 mL (0.1 gL^{-1}) of the different catalysts was separately dispersed in 10^{-4} M MO solution for 20 min for better adsorption of the sensitizer on catalyst surface. After stirring in the dark, 5 mL of the analyte solution was taken out from the system, centrifuged to remove any catalyst present and initial concentration (C_o) was determined using UV–visible absorption spectrometer. The concentrations (C) of the analyte after the commencement of the photodegradation at different time intervals were measured by monitoring the decrease in intensity of the absorption maxima of the dye.

3. Results and discussion

3.1. Crystal structure and morphology

X-ray diffraction patterns of pure TiO_2 and CdS along with different composition of TiO_2-CdS is shown in Fig. 1. XRD peaks in Fig. 1(a) at 2θ values 25.4°, 38.1°, 48.1°, 54.6°, 62.9° is obtained from the diffracted beams from (101), (103), (200), (105) and (211) crystal planes of anatase TiO_2 (JCPDS No. 21-1272). Diffraction peaks in Fig. 1(e) at 26.5°, 43.9° and 52.0° could be indexed to (111), (220) and (311) phases of cubic crystalline CdS (JCPDS No. 10-0454). It was observed that the characteristic peaks of anatase TiO_2 and CdS (marked as *) are preserved at TiO_2-CdS10 (Fig. 1(d)) composite which indicates an effective hybridization between the two phases for this particular composition.

3.2. Transmission electron microscopy (TEM)

TEM was used to analyze the microstructure and the particle size of different catalysts. TEM images in Fig. 2(a) displays the homogeneous dispersion of CdS nano crystals in TiO_2 matrix with an average particle size of 10–15 nm. The crystallite size calculated from the XRD data by using Debye Scherrer method was found to be 8–10 nm. HRTEM image (Fig. 2(b)) of the TiO_2-CdS10 displays two types of lattice planes with interplanar distance 0.34 nm (101 plane of TiO_2) and 0.32 nm (111 plane of CdS) composite unequivocally confirm wonderful hybridization established between TiO_2 and CdS nanoparticles in TiO_2-CdS10 heterostructure photocatalyst.