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Research Paper

Enhance photocatalysis performance and mechanism of CdS and Ag synergistic co-catalyst supported on mesoporous g-C_3N_4 nanosheets under visible-light irradiation

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ABSTRACT

In the present work the photocatalytic activity of CdS(x)/Ag/g-C_3N_4 (x = 10, 20, 40, 60 wt% of the CdS) hybrid heterostructured photocatalyst was investigated. Prior the depositions of CdS over the surface of g-C_3N_4, an optimal concentration of Ag nanoparticles as electron conducting bridge were deposited between the interfaces of CdS and g-C_3N_4 nanosheets. Being as a plasmon metal, the Ag nanoparticles were deposited to increase the absorption of visible light via surface plasmon resonance effect. The deposition of Ag between the interfaces of CdS nanospeheres and g-C_3N_4 can greatly facilitate the migration of electron and reduce the electron-hole recombination during the photocatalytic degradation of organic pollutants. The hybrid heterostructure shows significant photocatalytic activity and photostability compare with pure g-C_3N_4, CdS and CdS/g-C_3N_4 samples. It is concluded that the hybrid heterostructure provide significant photocatalytic degradation activity through an efficient and facilitated electron transfer mechanism.

1. Introduction

Semiconductor photocatalyst attracted propound intention with the growing energy crises and environmental problems, and providing us a green rout for hydrogen evolution from water splitting, CO_2 reduction to hydrocarbon, environmental pollutants degradations and energy storage materials etc [1–3]. Titanium Oxide is one of the most capable photocatalyst due to its low cost, non toxic and high photocatalytic efficiency. However, its photocatalytic efficiency is only limited to the UV light that limits its photocatalytic activity. Graphitic carbon nitride shows considerable intention in photocatalysis because of its potentials for organic pollutants degradation [4–6], water splitting for hydrogen evaluation [7–10] and O_2 reduction for solar fuel cell [11,12]. Recently Wang et al. [13] reported metal free polymeric graphitic carbon nitride photocatalyst with enhanced visible light photocatalytic activity and chemical and thermal stability. However the high recombination rate of electron-hole and low surface area of pure g-C_3N_4 limit its photocatalytic application for visible light absorption.

To overcome the recombination rate of photo generated electrons and hole many efforts have been proposed such as deposition of non-metal, changing textural design and morphology, coupling semiconductor heterojuction system etc. Among these silver nanoparticles by its surface Plasmon resonance effect can effectively reduce the recombination of photoexcited electron/hole [14]. Additionally, coupling of semiconductor and graphitic carbon nitride exhibit promising charge transfer between the coupled semiconductor and photoexcited electron/hole separation due to its heterojuction-transfer mechanism or Z-scheme mechanism [15–18]. Therefore constructing semiconductor heterojuction system with well matched band gap energy with g-C_3N_4 is important. The previous study reveals that the band gap energy level of CdS and graphitic carbon nitride g-C_3N_4 is very well matched [19,20].

CdS a well known n-type semiconductor with narrow band gap energy of ($E_g \approx 2.40$ eV, conduction band level -0.9 eV vs. NHE, pH = 7) is a promising material in visible light driven photocatalysis for hydrogen evolution and photodegradation of various organic pollutants [21]. Two major drawbacks should be tackled to become CdS a promising material both for the visible light photodegradation and significant hydrogen production from water splitting. First the fast charge recombination of the photoexcited charges restricted the photocatalytic efficiency of CdS [22], secondly the most reported CdS undergoes photocorrosion under strong illumination. Its Sulphur can be

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self oxidized by the photoexcited hole prior the water oxidation [23,24]. Unluckily, the fast recombination of the photogenerated charge carrier, self oxidation of the CdS caused by the excited hole shortens the photocatalytic efficiency and stability of the CdS.

Enormous modification has been carried out to overcome the recombination of the photoexcited charge carriers and photo-corrosion of the CdS. For instant, various semiconductors was coupled with CdS such as Ta_2O_5, ZnO, TiO_2 [25–27] noble metal [28,29], to create electric field interface by band edge offset, which can efficiently increase the separation of photoexcited charge carriers. It has been reported that the g-C_3N_4 nanosheets exhibit excellent performance in biosensing and photocatalysis because of its large surface area as well as fast charge transfer [30–32]. Being as a π-conjugated material, coupling g-C_3N_4 with other semiconductor can progressively enhance its visible light photocatalytic response [33–35]. However, when examining the band-edge position of CdS and g-C_3N_4, it was found that the photoexcited holes in CdS can easily transfer to the valance band of g-C_3N_4 because of the lower band maximum of CdS versus the HOMO level of g-C_3N_4 [36–38]. So it can be concluded that the heterojuction of the CdS and g-C_3N_4 is the possible solution to overcome the drawbacks of the CdS low efficiency and deprived photostability.

Here in this article we report ternary heterostructure composite catalyst of CdS/Ag/g-C_3N_4 for the photodegradtion of Methylene blue (MB) and 4-Aminobenzoicacid (4-ABA) under visible light irradiation. The morphology, chemical composition, photocatalytic and photoelectrical properties were completely characterized using different analytical characterization technique and the possible photocatalytic mechanisms were also discussed.

2. Experimental section

2.1. Materials and reagents

The entire chemical used during the experiment was pure analytical grade that includes cadmium acetate dihydrate ($Cd(CH_3COO)_2{\cdot}H_2O$), thioacetamide (C_2H_5NS), melamine, ammonium bicarbonate (NH_4HCO_3), ethanol, distilled water, methylene blue and 4-Aminobenzoicacid. No further purification of chemicals needed during the whole experimental procedure.

2.2. Preparation of photocatalyst

2.2.1. Synthesis of g-C_3N_4 nanosheets

The co-thermolysis technique is used for the synthesis modified g-C_3N_4 nanosheets as described in the previously reported literature [39,40]. The melamine and ammonium carbonate powder were mixed and grind properly in 1:0.5 ratio. The mixed powder were put in a ceramic crucible and then transferred into muffle furnace. The furnace was heated to 520 °C for 4 h with heating rate of 3 °C/min. After completion of the reaction time the furnace was allowed to room temperature. The sample was removed and grind thoroughly and make it ready for further use. Ultrathin 2D g-C_3N_4 nanosheets were prepared by ultrasonication-assisted liquid exfoliating of bulk g-C_3N_4 [41–43]. Typically, 0.5 g of bulk g-C_3N_4 were dispersed in 20 ml ethanol and sonicated for 8 h. The exfoliated g-C_3N_4 nanosheets were removed by centrifugation and dried in oven at 60 °C for 12 h.

2.2.2. Synthesis of Ag/g-C_3N_4

The Ag/g-C_3N_4 nanocomposite was prepared by the photodeposition method. At first, 0.5 g of g-C_3N_4 were dispersed in 20 ml ethanol and ultrasonicated for 1 h. After that a specific amount of $AgNO_3$ solution (50 mm/L) were added to the above solution and vigorously stirred in dark for 30 min until the $AgNO_3$ completely dissolved. Subsequently the above solution was irradiated under 300W Xe lamp with an excitation wavelength of 420 nm for one hour with continues stirring to induce the Ag^+ species and Ag nanoparticles deposit over the surface of g-C_3N_4 nanosheets. After that the powder was collected, dried in oven for 12 h and make it ready for further reaction. Briefly the molar ratio of Ag to g-C_3N_4 was fixed at 0.05 based on optimal photocatalytic performance.

2.2.3. Synthesis of CdS/Ag/g-C_3N_4 nanocomposite

The CdS/Ag/g-C_3N_4 heterostructured composite were prepared by fissile hydrothermal method. At first 0.5 g of as prepared Ag/g-C_3N_4 was dissolved in 30 ml ethanol/water mixture (1:1 ratio) and sonicated for 30 min. Meanwhile, equimolar cadmium acetate dihydrate and thioacetamide were dissolved in 30 ml ethanol/water mixture (1:1 ratio) and sonicated for 30 min. The two solutions were then mixed and stirred for some time to attain the adsorption desorption equilibrium. After that the mixture solution was transferred into a 100 ml Teflon lined stainless steel autoclave, sealed and hydrothermally treated at 180 °C for 24 h. The obtained dark yellowish precipitates were washed with ethanol and distilled water for several times and then dried in vacuum oven for 24 h at 60 °C. For reference a sample of pure CdS and CdS/g-C_3N_4 were prepared by the above method without using the Ag/g-C_3N_4 and Ag between the interfaces of CdS nanospeheres and g-C_3N_4 nanosheets. The wt% ratios of CdS to Ag/g-C_3N_4 were 10 wt%, 20 wt%, 40 wt% and 60 wt% respectively and the samples were named as CdS1/Ag/CN, CdS2/Ag/CN, CdS4/Ag/CN, and CdS6/Ag/CN according to the wt% of the CdS to Ag/g-C_3N_4 and CN, Ag/CN, CdS for pure g-C_3N_4, Ag (0.05)/g-C_3N_4, CdS, respectively.

2.2.4. Characterization

The crystallinity and phase structure of the as prepared samples were analyzed by powder X-Ray diffractometer (XRD) Bruker D8 advance X-Ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å) operated at 40 kV and 40 mA. The morphology and crystal size were analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM JEOL-2100). The elemental analysis was investigated through the energy dispersive X-Ray spectroscopy along with the TEM analysis to find out the elemental percentage distribution of various species present in the prepared sample. To investigate the band-gap structure the samples were analyzed by UV/Vis diffused reflectance spectra (DRS) (Shimadzu UV-2500) from 200 nm to 800 nm at room temperature and $BaSO_4$ was used as the reflectance standard. The photoluminescence (PL) measurement (kex = 325 nm) were recorded on an FL3-TCSPC florescence spectrometer with excitation wavelength from 300 nm to 650 nm using a 1 nm slit. The photocurrents were collected at room temperature by electrochemical analyzer (CHI660A, CH instrument Co) in a slandered three electrodes system using the prepared sample as working electrodes. For the surface composition and binding energy of the photocatalyst the sample were analyzed by X-Ray photoelectron spectrometer PerkinElmer PHI5300 with an A1Kα radiation (1 = 8.4 Å) as an excitation source.

2.2.5. Photocatalytic measurement

The photocatalytic activities of the as prepared samples were investigated for the degradation of Methylene blue and 4-Aminobenzoicacid. A 300W Xe lamp was used as a visible light source during the photocatalytic evaluation with irradiation wavelength of 420 nm cut-off filter to remove light of < 420 nm. For the photocatalytic degradation of Methylene blue, 0.05 g of the catalyst was added into 50 ml of 20 mg/L Methylene blue and 4-ABA solution, respectively. To attain the adsorption-desorption equilibrium the solution was stirred for 30 min in dark at room temperature before the irradiation. After that, before the irradiation and at a given time interval 3 ml sample was taken from the reaction suspension, centrifuge at 9000 rpm for 2 min to remove the catalyst particles. The centrifuged samples were analyzed by UV/Vis spectroscopy at its excitation wavelength from 200 nm to 800 nm and the results were obtained. To make sure the reproducibility of the obtained results, duplicate runs were carried for averaging the results at each condition.