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Fabrication of CDs/CdS-TiO₂ ternary nano-composites for photocatalytic degradation of benzene and toluene under visible light irradiation

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Abstract: An efficient cadmium sulfide quantum-dots (CdS QDs) and carbon dots (CDs) modified TiO₂ photocatalyst (CdS/CDs-TiO₂) was successfully fabricated. The as-prepared ternary nano-composites simultaneously improved the photo-corrosion of CdS and amplified its photocatalytic activity. The introduction of CdS QDs and CDs could enhance more absorbance of light, prevent the undesirable electron/hole recombination, and promote charge separation, which was important for the continuous formation of •OH and \cdot O₂⁻ radicals. When the optimal mass ratio of CdS QDs to CDs was 3:1, above 90% degradation efficiencies were achieved for benzene within 1 h and toluene in 2 h, while that of pure TiO₂ (P25), CdS QDs-TiO₂, CDs-TiO₂ nano-composites was around 15%. Owing to the symmetric structure and conjugation of methyl with benzene ring, the degradation of toluene was more difficult than benzene to carry on. The new fabricated nano-composites showed good

prospective application of cleaning up refractory pollutants and the resource utilization.

Keywords: Benzene; Toluene; CdS/CDs-TiO₂ ternary nano-composites; Photocatalytic degradation

1. Introduction

The expanding organic environmental pollution has become the crucial issue which not only influences human being's health, but also impedes the development of society and economy. Volatile mono-aromatic compounds such as benzene and toluene are a class of environmental pollutants with potentially toxic, mutagenic or carcinogenic properties [1]. Benzene and toluene have higher water solubility than other hydrocarbons and a lower octanol-water partition coefficient, that leads to a slowly soil absorption and, consequently, a preferential water transport, contaminating groundwater reservoirs [2]. The World Health Organization (WHO) has established that the maximum permissible concentrations of benzene and toluene in potable water are 0.01 and 0.7 mg/L, respectively [3, 4]. Various techniques have been investigated aiming to control or remove aromatic hydrocarbons benzene and toluene from contaminated water such as adsorption [3], bioremediation [5], biodegradation [6], advanced oxidation [7] and photocatalytic oxidation [8, 9]. Highly efficient heterogeneous photocatalysts for the degradation of various kinds of organic contaminants have attached significant attention in the past two decades due to their extensive applicability and excellent performances [10, 11].

Among the photocatalysts, the photocatalytic properties of TiO₂ are attributed to

the production of photogenerated electrons in the conduction band (CB) and holes in the valence band (VB) which occur upon the radiation of ultraviolet (UV) light (10-400 nm). However, the photocatalytic efficiency of TiO₂ photocatalysts have been limited due to its wide band gap energy (3.0-3.2 eV) and high recombination rate, which accounts for merely 5% of the entire solar light, thereby limiting its photoresponse to ultraviolet light [11-17]. To improve the photocatalytic activity and the response in the visible region, two kinds of strategies were proposed: doping of TiO₂ with metals and non-metals [18-21] ions to widen the solar spectrum absorption window to visible radiation, or combination with narrow band gap nano-crystalline semiconductors and quantum dots [22-25] to inhibit efficiently the recombination between the photo-generated electrons and holes (e⁻-h⁺) [26-28].

Cadmium sulfide (CdS) has been extensively studied for applications in photocatalytic and photoelectrochemical water reduction due to its narrow band gap energy (2.4 eV) and relatively high visible absorption coefficient [29, 30]. When CdS was coupled with TiO₂, the two semiconductors were illuminated and simultaneously activated under incident light owing to the synergistic effect. On the other hand, the formation of heterojunctions wherein the contact interfaces could hamper electron-hole recombination dominating the charge separation [31]. Nevertheless, some drawbacks still associated with such semiconductor material, such as the rapid charge recombination and the well-known photocorrosion induced by the photo-induced holes, which obstructed its development and application [32, 33]. One of the most widely concerned photocatalysts was CdS-based photocatalysts which

combined CdS with other semiconductors or materials to effectively suppress photocorrosion of CdS.

Researches indicated that when compared to fluorescent semiconductor quantum dots like CdS, CdTe, PbS, and CuInS₂, carbon dots (CDs) had attracted increasing attention owing to its non-toxicity, unique electron reservoir, photoinduced electron transfer property, broad absorption spectrum, large absorption coefficient and good chemical stability. They have been applied to couple with various semiconductors to extend their light absorption to visible or even near-infrared (NIR) range for better photocatalytic performance [32-34]. When CDs were loaded on the surface of CdS-based composites, the CDs could absorb visible light and emit short wavelength light through upconversion, which in turn excited CdS to form electron-hole pairs. Meanwhile, CDs could also act as electron reservoirs to trap electrons emitted from CdS, resulting in hindrance of the recombination of electron-hole (e^{-} -h⁺) pairs, which was important for the continuous formation of •OH and $•O_2^-$ radicals [34].

In the present work, we combined the advantages of introducing CDs and CdS to design an effective photocatalyst to improve the catalysis activity of TiO₂. In the developed system, the CDs were synthesized by one-pot hydrothermal treatment of milk, and the ternary nano-composites of CDs/CdS-TiO₂ were prepared by a simple approach. The as-prepared photocatalysts were examined by characterizing the structure, morphology, and optical properties. The photocatalytic activity of the composites was investigated for the degradation of benzene and toluene under visible light illumination. The results demonstrate that when the optimal mass ratio of CdS

QDs to CDs was 3:1, the degradation efficiency for benzene and toluene within 2 h was both above 90%. We also extensively investigated the molecular-level pathway of benzene and toluene based on trapping experiments, and all the intermediates have been analyzed by LC-MS.

2. Experimental

2.1. Materials

All reagents were analytical grade and used without further purification. CdCl₂·2.5H₂O (99%), Na₂S·9H₂O, sodium sulfite (Na₂SO₃), and mercaptoacetic acid (MAA) were purchased from J&K Chemical Ltd. (Beijing, China). Sodium borohydride (NaBH₄), disodium salt of ethylenediaminetetraacetic acid (EDTA-2Na), ammonium oxalate (AO) were obtained from the Fengchuan Chemical Reagent Co. Ltd. (Tianjin, China). Sodium hydroxide (NaOH), *p*-benzoquinone (*p*-BQ), isopropyl alcohol (IPA), cetyltrimethylammonium bromide (CTAB) and benzene were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Commercial TiO₂ (P25) was kindly supplied by Macklin Company (Shanghai, China). The milk was purchased from the local supermarket of Kunming, China. All experiments were carried out using double distilled water (DDW).

2.2. Instruments

X-ray power diffraction (XRD, Bruker, Germany) analysis was carried out to determine the crystal pattern of catalyst using Cu $K\alpha$ radiation operated at 40 mA and 40 kV with 2 θ collection range from 5° to 90°. Morphologies of the catalyst were

measured using field emission scanning electron microscopy (FESEM, JEOL 7006F) and high-resolution transmission electron microscope (HR-TEM, FEI Tecnai G2 TF30). The fluorescence spectra were recorded using a G9800A fluorescence spectrophotometer (Agilent, USA). UV-Vis diffuse reflection spectroscopy (DRS) was performed on a SHIMADZU UV-2550 spectrophotometer using BaSO₄ as the reference. And X-ray photoelectron spectra (XPS) were investigated on an Axis Ultra spectrometer (Kratos) to observe the elemental compositions and the chemical oxidation state using Mg K α radiation excitation source

- 2.3. Preparation of catalyst
- 2.3.1 Synthesis of CDs

The CDs were synthesized by one-pot hydrothermal treatment of milk as the carbon source according to follows [35, 36]. First, 50 mL of the fresh milk was added into 50 mL of deionized water. Then, the solution was transferred into a teflon-lined stainless steelautoclave and heated at 180 °C for 6 h. After naturally cooling to room temperature, the CDs solution was centrifuged 10000 rpm for 10 min to remove weight precipitate and any impurities. The product was filtered through the 0.22 μ m filter membrane.

2.3.2. Synthesis of CdS quantum dots

MAA-stabilized CdS quantum dots (CdS QDs) were synthesized according to the literature [37]. Typically, 250 μ L of MAA was added to 50 mL of 1.0×10^{-2} mol/L CdCl₂ aqueous solution, the pH was adjusted to 9.0 with a 1.0 mol/L NaOH solution. During the above process, N₂ was bubbled throughout the solution to remove O₂ for

30 min. Then, 5.0 mL of 0.1 mol/L Na₂S aqueous solution was injected into this solution to obtain MAA-capped water-soluble CdS QDs and the reaction mixture was refluxed under N_2 atmosphere for 4 h. This procedure produced CdS QDs with a Cd to S (Cd/S) ratio of 1.0.

2.3.3. Synthesis of CDs/CdS-TiO₂ ternary nanocomposites

The ternary nano-composite of CDs/CdS-TiO₂ was synthesized as follows: initially, 5.0 g of commercial TiO₂ (P25) powder and 0.5 g CTAB were added into 100 mL DDW and stirred for 4 h. After that, the precipitated TiO₂ powder was separated by centrifugation, further dried in vacuum at 60 °C. The powder was calcined at 450 °C for 5 h in the muffle furnace. 1.0 g of above TiO₂ powder was added into the mixture solution of 24 mL 0,5 mg/mL CdS QDs and 1 mL 4 mg/mL CDs, and stirred for 24 h at room temperature. The final products were centrifuged and washed with deionized water and ethanol for several times, and finally dried in vacuum at 60 °C for several hours. To investigate the effect of the content of CDs and CdS QDs on the photocatalytic activity, different mass ratio of CDs to CdS QDs modified TiO₂ nano-composites were prepared. In our study, the optimal mass ratio of CdS QDs to CDs was 3:1.

2.4. Catalytic degradation experiment

The photocatalytic activity of the synthesized photocatalysts were evaluated at ambient temperature under a commercial 300 W Xe-arc lamp (GXH-300, Shanghai, China, Jiguang Special lamp Co. Ltd.) as a source of visible-light irradiation. In a typical photocatalytic experiment, 40 mg the as-prepared CDs/CdS-TiO₂ ternary

nano-composites were suspended in 50 mL of aqueous solution containing benzene (30 µg/mL) and toluene (30 µg/mL), separately. Prior to photocatalytic experiments, the suspension was stirred for 2 h to achieve adsorption-desorption equilibrium state of the solution, which was kept in the dark before light irradiation. The reaction mixture was irradiated with stirring under the Xe-arc lamp while the system was cooled by fan to maintain the reaction mixture at room temperature. After the specified time interval 5 mL of solution was drawn and centrifuged at 5000 rpm for 5 min to remove the catalyst. The concentrations of benzene and toluene in the solution were measured using UV-Vis spectrophotometer (UV-2550, SHIMADZU, Japan) at wavelength 254 and 260 nm, respectively. The same experiments were done for bare TiO₂, CdS QDs-TiO₂, and CDs-TiO₂ for comparison purpose. The photodegradation percentage was calculated using the following equation: $D_{(%)} = (C_0 - C_t)/C_0 \times 100$, where C_0 and C_t are the concentrations of target analytes at time 0 and t (s), respectively, and t is the irradiation time.

2.5. Detection of active species

On the basis of the previously reported method [38], in order to determine and reveal the role of various kinds of photocatalytic-dependent radicals and reaction mechanisms, a series of scavenger test experiments were conducted. Herein, isopropyl alcohol (IPA), ammonium oxalate (AO), *p*-benzoquinone (*p*-BQ) and Na₂EDTA were used for hydroxyl radicals (•OH), holes (h⁺), superoxide radicals (•O₂⁻) and H₂O₂ scavengers, respectively.

2.6. Identification of degradation pathway

The degradation intermediates of benzene and toluene were detected by an ACQUITY UHPLC/MS (Waters, America). The mixture solution of 90% acetonitrile and 10% formic acid (0.1% by volume) was used as the mobile phase. The flow rate was 0.2 mL/min. The mass spectrometry analysis was conducted by electrospray ionization (ESI) in positive ionization mode. The mass spectra with a scan range m/z 10-110 were recorded. The temperature of drying gas heater was 500 °C. The drying gas (N₂) flow rate was 1000 L/h, and the capillary voltage was 600 V. The data were analyzed by Waters MasslynxTM 4.1 System.

3 Results and discussion

3.1 Structural characterization and surface composition

3.1.1 XRD analysis

A systematic X-ray diffraction measurement (XRD) study was carried out to investigate the crystalline phase and the structure. Fig. 1 showed the XRD pattern of the pure TiO₂ (P25), CdS QDs-TiO₂, CDs-TiO₂ and CDs/CdS-TiO₂ nano-composites, respectively. It was found that the samples were all well-crystallized. The XRD patterns displayed diffraction peaks centered at around 20 values of 25.3° 37.8°, 48.0°, 53.9°, 55.1° and 62.7° could be assigned to the (1 0 1), (0 0 4), (2 0 0), (1 0 5), (2 1 1) and (2 0 4) crystallographic planes of anatase TiO₂ (JCPDS 21-1272) [39,40]. The peak at around 20 value of 27.4° could be attributed to the (1 1 0) crystallographic plane of rutile TiO₂ (JCPDS 21-1276). CdS QDs-TiO₂, CDs-TiO₂ and CDs/CdS-TiO₂ nano-composites also exhibited the similar characteristic diffraction peaks of anatase TiO₂, suggesting that the existence of CdS QDs and CDs could hardly affect the

crystalline structure of TiO₂ nano-particles.

3.1.2 TEM analysis

The morphology and detailed microstructures features of prepared catalysts were further explored using TEM and high resolution TEM (HRTEM). As was shown in Fig. 2a, it could be seen that the average diameters of those spherical shape particles CdS QDs and CDs both were about 2-5 nm along, which were uniformly dispersed on the surface of larger TiO_2 (with an average diameter of about 20-50 nm). It confirmed that these samples were both composed by a mass of irregular nano-particles, which meant that the addition of CdS QDs and CDs could not change the morphologies of TiO₂ nano-particles obviously. The corresponding high magnification TEM image reflected that most of the particles possessed well-resolved lattice fringes. As displayed in the HRTEM images (Fig. 2b), the lattice distances shown that the inter planar spacing of 0.35 nm and 0.308 nm were corresponded well with (1 0 1) and (2 2 0) plane of anatase TiO₂ and CdS QDs, while the lattice spacing of CDs was 0.24 nm which well agreed with the plane (0 0 4) spacing of carbon. Again, the structures of CdS QDs-TiO₂, CDs-TiO₂ and CDs/CdS-TiO₂ nano-composites were confirmed, which was also consistent with the XRD results.

The textural properties of as-prepared bare, binary and ternary samples also were investigated using Brunauer-Emmett-Teller (BET) surface analysis. The BET specific surface areas of the as-prepared samples calculated from the linear part of the BET plot are summarized in Table 1. Compared with the as-prepared samples, the ternary CDs/CdS-TiO₂ has a BET surface area of 160.76 m²/g, which is higher than those of

pure CdS, CDs and TiO₂. The higher specific surface areas may beneficial for the photocatalytic degradation because there being more reactive radical species and oxidative intermediates for the oxidation and mineralization of pollutants, ease of transportation of them through the interconnected networks, and enhanced harvesting of light [41].

3.1.3 XPS analysis

To investigate surface chemical composition and bonding configuration of the as-prepared pure ODs-TiO₂. CDs-TiO₂ CDs/CdS-TiO₂ TiO₂. CdS and nano-composites, the X-ray photoelectron spectroscopy (XPS) analysis was employed and the results were shown in Fig. 3. The full-scale XPS pattern observed in Fig. 3a showed the coexistence elements of Ti, O, C, Cd and S in the as-prepared pure TiO₂, CdS QDs-TiO2, CDs-TiO2 and CDs/CdS-TiO2 nano-composites. Fig. 3b-f illustrated the high-resolution XPS spectra of Ti 2p, Cd 3d, S 2p, C 1s and O 1s, respectively. The Cd 3d and S 2p signals came from CdS and the presence of C 1s and O 1s signals again confirmed the existence of CDs in the composite nano-particles. Ti 2p XPS peaks were located at 458.8 eV and 464.4 eV (Fig. 3b) with a spin-orbital doublet splitting (Ti 2p_{3/2}-Ti 2p_{1/2}) of 6.6 eV in as-prepared composite sample, which implied an oxidation state of Ti⁴⁺. As presented in Fig. 3c, the deconvoluted peaks of the Cd $3d_{5/2}$ and Cd $3d_{3/2}$ located at 405.4 and 412.2 eV finely indicate the Cd²⁺ in CdS. The core level S 2p spectrum was shown in Fig. 3d, which could be fitted into two individual peaks S 2p_{3/2} and S 2p_{1/2} at 162.0 and 164.1 eV with a splitting energy of 2.1 eV, corresponding to the valence state of S^{2-} in CdS. The C 1s XPS spectrum in

Fig. 3e could be fitted by two main peaks at 284.5 and 285.6 eV, which could be attributed to the C–C/C=C and C–O groups, respectively. To further investigate the oxide state, O 1s was measured (Fig. 3f). The main peak were observed at the binding energie of 530.2 eV, which might be assigned to C–Ti–O, indicating that photo-generated electrons should transfer from valence band (VB) of the TiO₂ to CDs through C–Ti–O bond formed between TiO₂ microsphere interface and CDs.

3.2 UV-vis diffuse reflectance spectra analysis

The optical properties of as-prepared binary composites pure TiO2, CdS QDs-TiO₂, CDs-TiO₂ and CDs/CdS-TiO₂ nano-composites were investigated using UV-vis diffuse reflectance spectroscopy (UV-vis DRS) and the results were shown in Fig.4a. It was clearly that the spectrum of the pure TiO₂ (P25) showed a significantly absorption edge at wavelength shorter than 380 nm, which could be assigned to its intrinsic band gap absorption. For CDs/CdS-TiO₂ nano-composites, the absorption edge slightly shifted to the visible region with enhanced absorption intensity. The band gap narrowing of CDs/CdS-TiO₂ nano-composites was mainly attributed to the C atoms occupying the interstitial sites in the TiO₂ lattice, which led to a decrease in optical band gap energy [34]. It could be also found that the deposition of CdS improved obviously the absorption intensity of TiO₂ narrow band gaps in visible light region ($\lambda > 420$ nm) and the absorption edge appeared an obvious red shift which might be ascribed to the narrow band gap of CdS QDs. It was a direct proof that the loading of CdS QDs and CDs on the surface of TiO₂ both would enhance the absorption intensity in visible light region and improved the light harvest and was also

beneficial to its photocatalytic performance.

The energy band gap (Eg) of the as-synthesized photocatalysts was calculated according to the UV-vis absorption spectra. In semiconductor physics, the formula $(\alpha hv)^{m} = A(hv - Eg)$ was used to relate the absorption coefficient to the energy band gap, where α , h, v, A, and Eg corresponded to the absorption coefficient, Planck constant, light vibration frequency, proportional constant and band gap energy, respectively. The m value depended on the nature of the electronic transition, when m = 2, the semiconductor had a direct band gap, while when m = 1/2, the semiconductor had an indirect band gap [32, 42]. TiO₂ was an indirect semiconductor, the switched tauc plots of the $(\alpha hv)^{1/2}$ versus photon energy (hv) were displayed in Fig. 4b, where the two intersections of the tangent lines and the baseline denoted the band gap energies. The band gap energies of CDs/CdS-TiO2, CdS QDs-TiO2, CDs-TiO2 and pure TiO₂ nano-composites determined from the intercepts were approximately 2.28, 2.56, 2.79 and 3.10 eV, respectively. Obviously, the modification of CdS QDs and CDs with TiO₂ could reduce the corresponding band gap energy, indicating an easier trend for CDs/CdS-TiO₂ nano-composites to generate the electron-hole pairs by absorbing wider wavelength of light.

3.3 Photoluminescence spectra analysis

It is well known that photoluminescence (PL) emission is important to disclose the fate of electron-hole pairs in semiconductor because PL emission is resulted from the recombination of photogenerated electrons and holes for some semiconductors [41]. PL spectra were taken to understand the recombination rate of electron/hole of

charge carrier trapping, migration and transfer. The higher intensity corresponds to the faster recombination. Fig. 5 showed the typical PL spectra of pure TiO₂ (P25), CdS QDs-TiO₂, CDs-TiO₂, CDs/CdS-TiO₂ nano-composites excited in 300 nm. The main emission peak of these composites was centered at 602 nm, which could be contributed to the band-band PL phenomenon with the energy of Iight approximately equal to the band energy of TiO₂. The results showed that the modification of CdS QDs and CDs onto TiO₂ drastically decreased the PL intensity of pristine TiO₂. When both of CdS QDs and CDs were decorated onto the surface of TiO₂, the peak intensity further decreased for CDs/CdS-TiO₂ and CDs-TiO₂. These results suggest that the hetero structure among TiO₂, CdS QDs and CDs and CDs can effectively diminish the electron/hole recombination rate. The PL intensity has strong effect on the photocatalytic activity of the corresponding photocatalysts.

3.4 Photocatalytic activity evaluations

The degradation efficiencies of benzene and toluene over pure TiO₂ (P25), CdS QDs-TiO₂, CDs-TiO₂, CDs/CdS-TiO₂ nano-composites under simulated sunlight irradiation within 3 h were displayed in Fig. 6a. All CDs/CdS-TiO₂ nano-composites, which were prepared with different mass ratios mixture of CdS QDs to CDs, exhibited much higher photocatalytic activities compared to the as-prepared photocatalysts like pure TiO₂ (P25), CdS QDs-TiO₂ and CDs-TiO₂. The maximum photocatalytic degradation efficiency of benzene and toluene was obtained with a 3:1 mass ratio of CDs to CdS QDs modified TiO₂ nano-composites (90%), while that of pure TiO₂

(P25), CdS QDs-TiO₂, CDs-TiO₂ nano-composites was around 15%. When the proportion of CdS QDs arrived to a large amount, it would lead to stability concerns raised by photocorrosion and the CdS electron transfer center was likely to be the electron recombination center in the process of photocatalytic reaction, and the efficiency of the electron hole separation was decreased [43]. Besides, both CdS QDs and CDs modified TiO₂ nano-composites could effectively hinder the electron/hole (e^- - h^+) recombination and enhance more absorbance of light, which was important for the continuous formation of •OH and •O₂⁻ radicals, CDs/CdS-TiO₂ nano-composites improved the photocatalytic property owing to the synergistic effect between CDs and CdS QDs. It should be noted that the best-performing system CDs/CdS-TiO₂ nano-composites, which were prepared with 3:1 mass ratios mixture of CdS QDs to CDs, was selected as a model for the follow-up study.

In addition, photocatalytic degradations of benzene and toluene were studied by as-prepared CDs/CdS-TiO₂ nanocomposites under simulated sunlight irradiation. The curves of degradation efficiency versus reaction time for samples were shown in Fig. 6b. From these figures, it was clear that the time taken for 90% degradation of the benzene was 1 h, whereas 90% degradation of the toluene was 2 h. As a contrast on the correctness of the results, the benzene and toluene concentrations of the same samples before and after degradation were analyzed simultaneously by the HPLC method. The results showed that photocatalytic degradation rates of benzene and toluene were fairly close to the results of HPLC-VWD. Besides, photocatalytic degradation of p-xylene was also studied for contradistinction, and the results showed

only 33% degradation of the *p*-xylene was obtained even after 3 h. Those results indicated that CDs/CdS-TiO₂ nano-composites showed better photocatalytic activity towards benzene and toluene compared to *p*-xylene. It can be explained as follows: in this system, the degradation is started by addition of superoxide radicals (\cdot O₂⁻), hydroxyl radicals (\cdot OH) and positive holes (h⁺) to benzene and toluene, which yield some by-products such as phenol, benzaldehyde and benzoic acid. Eventually, the reaction mineralizes these benzene and toluene to end products such as carbon dioxide and H₂O. From molecular structure, owing to the symmetric structure and conjugation of methyl with benzene ring of toluene and *p*-xylene [44], the more superoxide radicals (\cdot O₂⁻), hydroxyl radicals (\cdot OH) and positive holes (h⁺) they need, the more difficult it is to photocatalytic degrade, especially *p*-xylene.

3.5 Photocatalysis degradation mechanism analysis

To speculate on the photocatalytic mechanism and reveal the contribution of each active radical species in the photo-degradation system, a series of the radical trapping experiments were carried out further, including *p*-benzoquinone (*p*-BQ) as a superoxide radical ($\cdot O_2^-$) scavenger, isopropyl (IPA) as a hydroxyl radical ($\cdot OH$) scavenger, Na₂EDTA as an H₂O₂ scavenger and ammonium oxalate (AO) as hole (h⁺) scavenger [45-48]. As displayed in Fig. 7, without the addition of scavengers, the photocatalytic conversion ratio of benzene and toluene degradations were 93.8% and 90.2% after 3 h of visible light irradiation, respectively. The degradation ratio of benzene and toluene decreased slightly when Na₂EDTA was added into the photoreaction system, while *p*-BQ, IPA and AO both decreased obviously. Based on

the above analysis, it clearly suggested that the $\cdot O_2^-$, h^+ and $\cdot OH$ should be the major radicals for benzene and toluene degradation in the photodegradation process. Meanwhile, H_2O_2 also promoted the process of photocatalytic reaction.

According to the discussion above, the possible reaction mechanism schematic for the photocatalytic degradation of benzene and toluene has been illustrated in scheme 1. The CDs could absorb visible light and emit short wavelength light through upconversion, which in turn excited CdS to form electron-hole pairs. Meanwhile, CDs could also act as electron reservoirs to trap electrons emitted from CdS, resulting in hindrance of the recombination of the undesirable electron-hole $(e^{-}h^{+})$ pairs, and promote charge separation, resulting in a higher utilization ratio of energy [32]. Owing to their synergistic effect, the electrons trapped from those two paths could be transferred effectively to the adsorbed oxygen molecules to form superoxide radical $(\bullet O_2^{-})$. Simultaneously, superoxide radical $(\bullet O_2^{-})$ could further react with two protons to form hydrogen peroxide (H_2O_2) , which undergoes reaction with electrons to form more •OH radicals. Meanwhile, the holes could be consumed quickly by adsorbed hydroxyl ions or water molecule to produce more hydroxyl radicals (•OH). More importantly, the electron-hole pairs transferred to CDs could react with H₂O instead of CdS itself, especially the holes, hence making CDs/CdS-TiO₂ a stable photocatalyst without requirement for any sacrificial agents.

3.6 Degradation reaction pathway and intermediate products analysis

LC-MS was used to identify the intermediates and final degradation products of benzene and toluene. In this system, the main characteristic peaks of benzene (m/z =

78) and toluene (m/z = 91) were detected before light illumination and its intensity decreased gradually after visible light irradiation, respectively. Upon photocatalytic reaction, a reaction product such as CO₂ was detected and intermediate products such as phenol and benzoquinone (m/z = 93), benzaldehyde (m/z = 106), benzoic acid (m/z= 121), malonic acid (m/z = 104), oxalic acid (m/z = 89), glycolic acid (m/z = 76), acetaldehyde (m/z = 44), acetic acid (m/z = 59) and formaldehyde (m/z = 29) were identified. Based on the results of mass to charge ratio (m/z) and preliminary structures of intermediates products, the proposed reaction pathway describing the photodegradation mechanism can be suggested as shown in scheme 2. The degradation is started by addition of superoxide radicals ($\bullet O_2$), hydroxyl radicals (•OH) and positive holes (h^+) to benzene and toluene, which yield phenol or benzaldehyde. The subsequent cleavage of the phenol or benzaldehyde would result in the formation of malonic acid. The malonic acid is converted to lower molecular weight organic compounds such as formaldehyde and acetic acid, which will then be converted to carbon dioxide and H₂O as the end products through the subsequent reaction steps. Eventually, the reaction mineralizes benzene and toluene to end products such as carbon dioxide and H₂O.

4. Conclusion

In summary, an efficient $CDs/CdS-TiO_2$ ternary nano-composite was fabricated as a photocatalyst for visible light organic pollutants splitting without requirement for any sacrificial agents. These charge carriers generated on CdS would transfer to CDs due to a dual synergistic effect of sensitization between CDs and CdS QDs, leading to

a rapid separation of the electron-hole pairs (e⁻-h⁺). Besides, CDs, as efficient electron reservoirs, enhanced the absorption towards visible light and trapped electrons emitted, resulting in a higher utilization ratio of energy and significantly enhancing the photocatalytic activity of the system. The experimental results showed that when the optimal mass ratio of CdS QDs to CDs was 3:1, above 90% degradation efficiencies were achieved both benzene within 1 h and toluene within 2 h, respectively. The proposed system is a promising photocatalytic degradation pathway that has good potential for application to pollutant purification.

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Sample	CdS	CDs	TiO ₂	CdS-TiO ₂	CDs-TiO ₂	CDs/CdS-TiO ₂
BET (m^2/g)	23.70	57.12	130.14	165.62	198.09	160.76

Table 1 BET surface area of the as-prepared catalysts.

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Highlights:

1. An efficient cadmium sulfide quantum-dots and carbon dots modified TiO₂ photocatalyst (CdS/CDs-TiO₂) was successfully fabricated.

2. A dual synergistic effect of sensitization between CDs and CdS QDs effectively

hinder the electron/hole (e^-h^+) recombination and enhance more absorbance of light.

3. Above 90% degradation efficiencies were achieved for benzene and toluene within

2 h while the optimal mass ratio of CdS QDs to CDs was 3:1.

A Children and a standard and a standard a standar



Graphics Abstract



Figure 1





Figure 3





Figure 5



