

# Cds Nanoparticles Decorated 1D CeO<sub>2</sub> Nanorods for Enhanced Photocatalytic Desulfurization Performance

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**Abstract:** The CdS nanoparticles were constructed on one-dimensional (1D) CeO<sub>2</sub> nanorods by two-step hydrothermal method. The X-ray diffraction (XRD), transmission electron microscopy (TEM), Raman spectra, X-ray photoelectron spectra (XPS) and UV-vis diffuse reflection spectroscopy (DRS) techniques were used to characterize these CdS/CeO<sub>2</sub> nanocomposites. It is concluded that when the molar ratio of CdS and CeO<sub>2</sub> was 1:1, the nanocomposites exhibited the best photocatalytic desulfurization activity, reaching 92 % in 3 hours. Meanwhile, transient photocurrent (PT) measurement, photoluminescence (PL) spectra and electrochemical impedance spectroscopy (EIS) measurement indicated that the modification of CeO<sub>2</sub> nanorods by CdS nanoparticles could significantly inhibit the recombination of photogenerated electrons and holes. In addition, the possible mechanism of photocatalytic oxidation desulfurization of the nanocomposites was proposed. This study may provide an effective CeO<sub>2</sub>-based photocatalysts for photocatalytic desulfurization applications.

**Keywords:** CdS; CeO<sub>2</sub>; Nanocomposite; Heterojunction; Photocatalytic desulfurization

## 1. Introduction

Sulfur oxides (SO<sub>x</sub>) emitted from vehicle fuel combustion easily cause acid rain and haze, which has become a serious environmental pollution problem. Therefore, it is urgent to remove sulfur containing organic compounds from fuel to reduce sulfur content [1,2]. Subsequently, a series of desulfurization technologies are developed, such as hydrodesulfurization [3], oxidative desulfurization [4], adsorptive desulfurization [5], biodesulfurization [6]. Among them, hydrodesulfurization is a predominant technology currently used in industry, which requires hydrogen consumption to achieve high pressure and high temperature. In addition, it is difficult to remove dibenzothiophene (DBT) and its derivatives from fuel. Alternatively, photocatalytic desulfurization is a new desulfurization technology using semiconductor photocatalyst for catalytic oxidation desulfurization, which has the advantages of mild reaction conditions, low energy consumption and environmental friendliness. In the process of photocatalytic desulfurization, DBT and its derivatives can be oxidized to corresponding sulfones, which have polarity and can be easily removed by solvent extraction [7,8]. In recent years, a series of photocatalytic desulfurization catalysts have been developed, such as TiO<sub>2</sub>-based photocatalyst [9,10], bismuth series material [11,12], g-C<sub>3</sub>N<sub>4</sub> framework material [13,14], metal organic framework material [15], etc.

CeO<sub>2</sub> is an important rare earth oxide semiconductor material, which is commonly used as a photocatalyst for pollutant degradation and energy conversion. However, CeO<sub>2</sub> is a wide band gap semiconductor, which usually responds in the ultraviolet region, and the ultraviolet light only accounts for 5% of the sunlight, which greatly hinders its application [16-18]. Therefore, the heterojunction of CeO<sub>2</sub> and another narrow band gap semiconductor is expected to improve the photocatalytic performance. Moreover, one-dimensional (1D) nanomaterials have attracted much attention in recent years

due to their high length-to-diameter ratio, which facilitates the rapid charge transfer along the axial direction [19,20].

CdS is a narrow band gap semiconductor, which can effectively use visible light, and it is a promising material. Nevertheless, the rapid recombination of photogenerated carriers and severe photocorrosion hinder the further application of CdS [21,22]. Thus, the effective combination of CdS and CeO<sub>2</sub> to form a heterojunction is expected to overcome these disadvantages.

Herein, in this work, we used CdS nanoparticles to decorate 1D CeO<sub>2</sub> nanorods to prepare well-defined interfacial heterojunction composite. And then the photocatalytic performance of prepared photocatalysts was investigated by photocatalytic degradation of dibenzothiophene (DBT) under visible irradiation. Finally, the enhancement mechanism of photocatalytic desulfurization was studied.

## 2. Results

### 2.1 Preparation of samples

#### 2.1.1 Synthesis of CeO<sub>2</sub> nanorods

0.02 mol Ce (NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was dissolved in 5 mL deionized water, then 35 mL 10 M NaOH solution was added. After being fully stirring, the mixture was transferred to a 50 mL Teflon hydrothermal reactor and heated to 110 ° C for 10 hours, the obtained products were centrifugally washed and dried, and then calcined at 400 ° C for 2 hours to obtain CeO<sub>2</sub> nanorods.

#### 2.1.2 Synthesis of CdS/CeO<sub>2</sub> composite

A certain amount of prepared CeO<sub>2</sub> nanorods powders were ultrasonic dispersed in 20 mL of deionized water, and then 20 mL of 0.1M CdCl<sub>2</sub>·2.5H<sub>2</sub>O solution was added. After full stirring, 20 mL of 0.1M Na<sub>2</sub>S solution is slowly added, then the mixture was transferred to a Teflon hydrothermal reactor and heated to 160 ° C for 24 hours, and then filter, wash and dry the suspension to finally obtain CdS/CeO<sub>2</sub> composite. The molar ratios of CdS to CeO<sub>2</sub> in the prepared samples were 1:2, 1:1, 2:1, respectively.

### 2.2 Characterization

X-ray diffraction (XRD) measurement was performed on an X-ray diffractometer with Cu K $\alpha$  radiation (Rigaku, D/max-RB,  $\lambda$ =0.15406 nm); Raman spectra were measured by a Thermo Fisher Scientific DXR Raman spectrophotometer and the excitation laser wave length was 532 nm; The morphology was observed by a JEOL JEM-2100 transmission electron microscope (TEM) equipped with Gatan 832 CCD operating at a voltage of 200 kV; X-ray photoelectron spectroscopy (XPS) analysis was carried out using a Thermo Fisher Scientific ESCALAB 250 spectrometer with the mono Al K $\alpha$  radiation (1486.6 eV); Photoluminescence (PL) spectra were collected on a PerkinElmer LS45 fluorescence spectrometer with an excitation wavelength of 400 nm; Ultraviolet visible diffuse reflectance spectra (UV-Vis DRS) were measured by a Shimadzu UV-2450 spectrophotometer equipped with an integrating sphere.

### 2.3 Photoelectrochemical measurements

The photoelectrochemical tests were carried out on a LK5600 photoelectrochemical workstation. For the photocurrent measurement, the prepared sample deposited on the surface of FTO glass as the working electrode, the Ag/AgCl electrode as the reference electrode, the Pt plate as the counter electrode and the 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution as the supporting electrolyte, and the 300 W xenon lamp as the light source. And for electrochemical impedance spectroscopy (EIS) measurements, the three electrode system was also used; The electrolyte solution is 0.5 M KCl solution containing 0.01 M K<sub>3</sub>Fe(CN)<sub>6</sub>/K<sub>4</sub>Fe(CN)<sub>6</sub> (molar ratio 1:1), performed at bias voltages 0.5 V, in the frequency range of 0.1 Hz - 100 kHz with oscillation potential amplitudes of 0.01 V at room temperature.

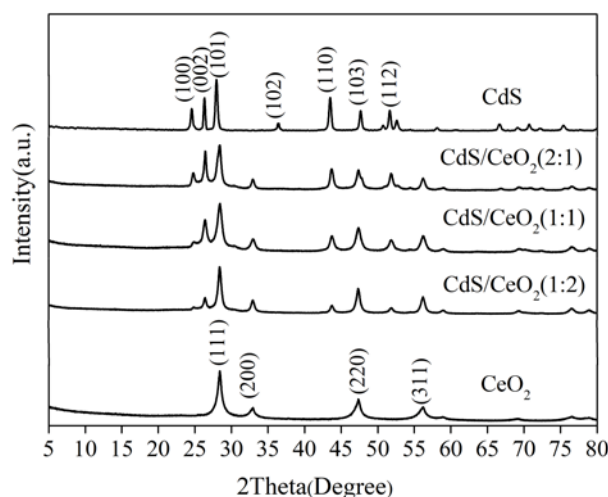
### 2.4 Photocatalytic desulfurization measurement

0.08 g DBT was dissolved in 200 mL n-octane as model oil, subsequently, 0.1 g photocatalyst was added under constant stirring, and then appropriate  $\text{H}_2\text{O}_2$  was added (molar ratio of O/S = 4:1). After dark adsorption for 30 minutes, the photocatalytic desulfurization process is carried out in a photochemical reaction instrument with a xenon lamp (300 W, with ultraviolet cut-off filter ( $\lambda > 420$  nm)). The dispersion was collected every 30 minutes and extracted with acetonitrile, and the sulfur content was determined on a UV fluorescent sulfur analyzer. The desulfurization rate  $D$  (%) was obtained according to the following formula:  $D = (1 - C_t/C_0) \times 100\%$ , where  $C_0$  is the initial sulfur content and  $C_t$  is the Sulphur content of the solution at reaction time  $t$ .

## 3. Discussion

### 3.1 XRD patterns analysis

The structures of the samples are confirmed by XRD analysis in Figure 1. The characteristic diffraction peaks at  $28.6^\circ$ ,  $33.1^\circ$ ,  $47.4^\circ$ , and  $56.2^\circ$  correspond to the (111), (200), (220) and (311) different crystal planes of cubic fluorite  $\text{CeO}_2$  respectively (JCPDS 34-0394). And the diffraction peaks at  $24.6^\circ$ ,  $26.4^\circ$ ,  $28.0^\circ$ ,  $36.5^\circ$ ,  $43.6^\circ$ ,  $47.7^\circ$  and  $51.7^\circ$  are index to the (100), (002), (101), (102), (110), (103) and (112) crystal planes of hexagonal structure  $\text{CdS}$  respectively (JCPDS:41-1049). In addition, when  $\text{CdS}$  nanoparticles are deposited on  $\text{CeO}_2$  nanorods, the characteristic peaks of both cubic fluorite  $\text{CeO}_2$  and hexagonal  $\text{CdS}$  are observed in the composites. It is worth noting that with increasing the molar ratio of  $\text{CdS}$  to  $\text{CeO}_2$ , the intensity of the characteristic peaks of  $\text{CdS}$  enhance in the composites. The results demonstrate that the  $\text{CdS}$  are successfully loaded on the surface of  $\text{CeO}_2$ .

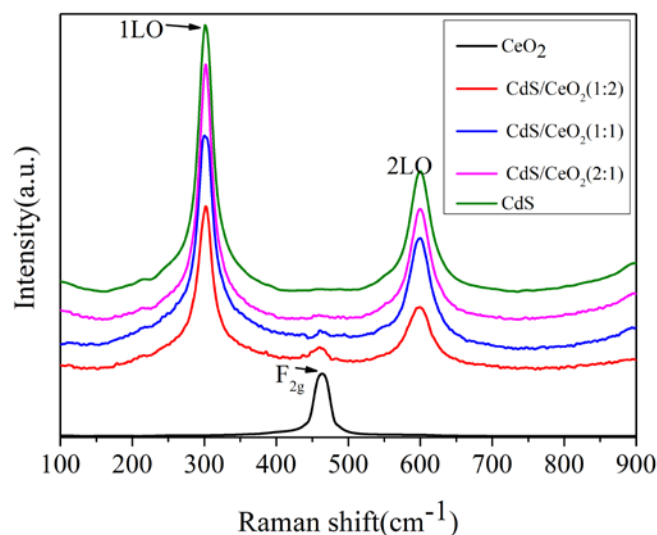


**Figure 1.** XRD patterns of  $\text{CdS}$ ,  $\text{CeO}_2$  and the various  $\text{CdS}/\text{CeO}_2$  composites.

### 3.2 Raman Spectroscopy analysis

Raman spectroscopy with an excitation wavelength of 532 nm were used to measure the structure and electronic properties of materials. As shown in Figure 2, For pure  $\text{CeO}_2$ , the peak at  $465\text{ cm}^{-1}$  can be attributed to the  $\text{F}_{2g}$  Raman active interior phonon mode of fluorite cubic structure. As for pure  $\text{CdS}$ , the two dominant peaks at  $300\text{ cm}^{-1}$  and  $600\text{ cm}^{-1}$  are attributed to the first-order longitudinal optical (1LO) and the second-order longitudinal optical (2LO) phonon modes of  $\text{CdS}$ , respectively[24]. Moreover, It is observed that all the composites have the peaks corresponding to the both  $\text{CeO}_2$  and  $\text{CdS}$  with varying intensities. The Raman peak intensity of  $\text{CdS} / \text{CeO}_2$  composites is lower than that of pure  $\text{CeO}_2$  or pure  $\text{CdS}$ . This may be attributed to the scattering loss caused by defects in the heterojunction[25,26]. With the increase of  $\text{CeO}_2$  content, the

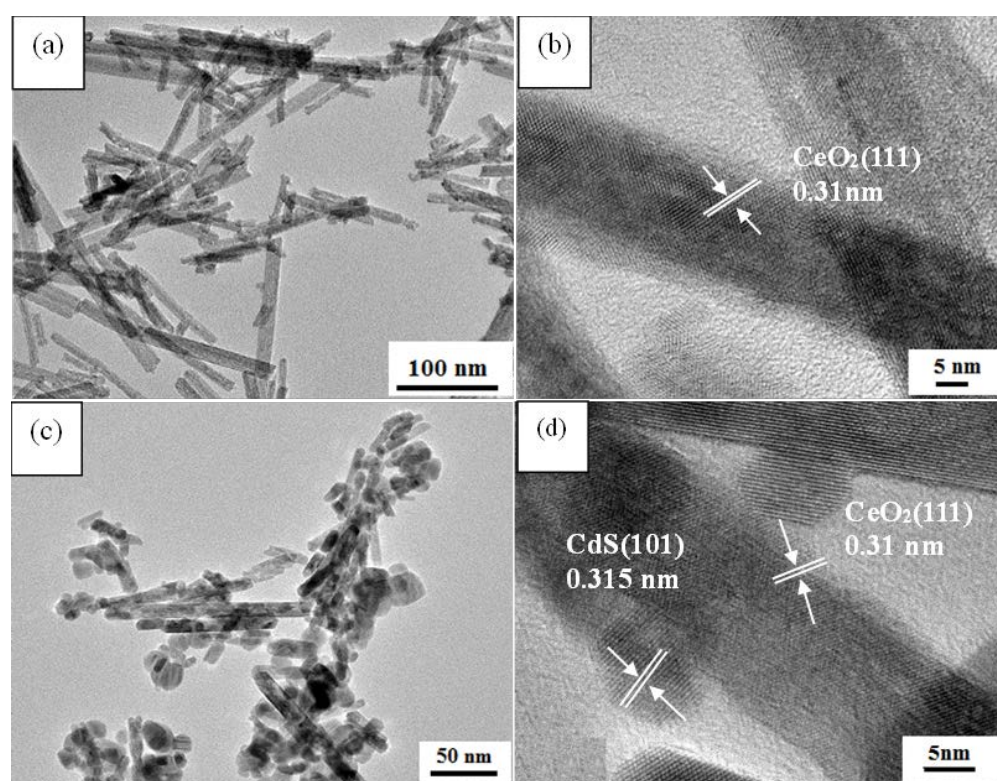
characteristic peak intensity of  $\text{CeO}_2$  in the  $\text{CdS}/\text{CeO}_2$  composite gradually increases. Therefore, The Raman measurement results further demonstrate the existence of  $\text{CdS}$  and  $\text{CeO}_2$  in the composite.



**Figure 2.** Raman spectra of  $\text{CdS}$ ,  $\text{CeO}_2$  and various  $\text{CdS}/\text{CeO}_2$  samples

### 3.3 Morphological analysis

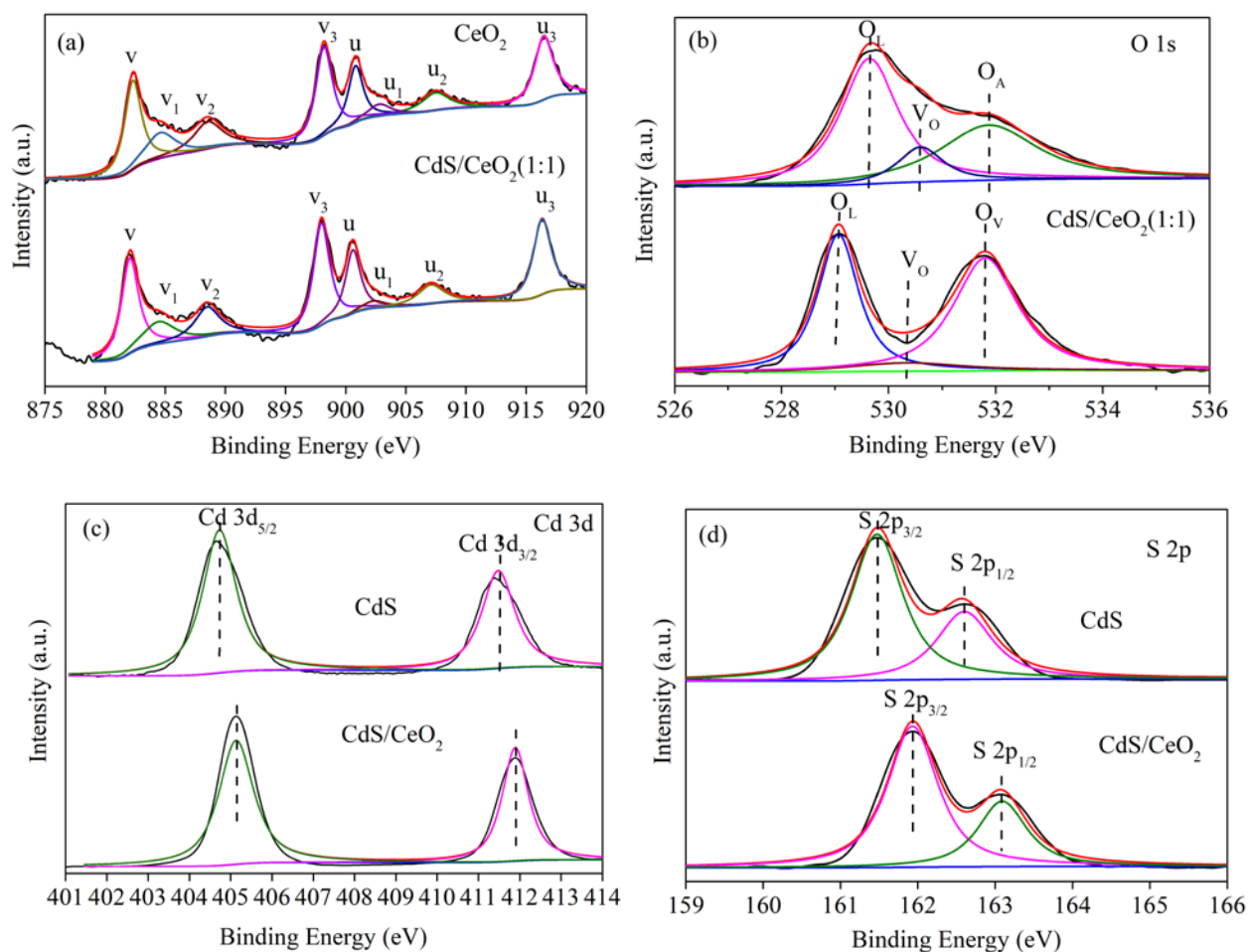
Figure 3 shows TEM and HRTEM images of  $\text{CeO}_2$  nanorods and  $\text{CdS}/\text{CeO}_2(1:1)$  composite. It can be seen from Figure 3a that the prepared  $\text{CeO}_2$  presents a rod like structure, with a diameter of 20-30 nm and a length of 50-100 nm. Moreover, the corresponding HRTEM image (Figure 3b) shows that the crystal plane spacing  $d=0.31\text{nm}$  corresponds to the (111) crystal plane of cubic fluorite  $\text{CeO}_2$ . As shown in Figure 3c,  $\text{CdS}$  nanoparticles are deposited on the surface of  $\text{CeO}_2$  nanorods, and the structure of  $\text{CeO}_2$  nanorods is not destroyed in the composite. It can be seen from the Figure 3d that the two different crystal plane spacings are  $d=0.315\text{ nm}$  and  $d=0.31\text{ nm}$ , which respectively correspond to the (101) crystal plane of hexagonal  $\text{CdS}$  and the (111) crystal plane of cubic fluorite  $\text{CeO}_2$ . The well-defined heterojunction structure may facilitate the separation of photogenerated electrons and holes, improving the photocatalytic efficiency.



**Figure 3.** TEM and HRTEM images of CeO<sub>2</sub> (a, b) and CdS/CeO<sub>2</sub>(1:1) composite (c, d).

### 3.4 XPS spectra analysis

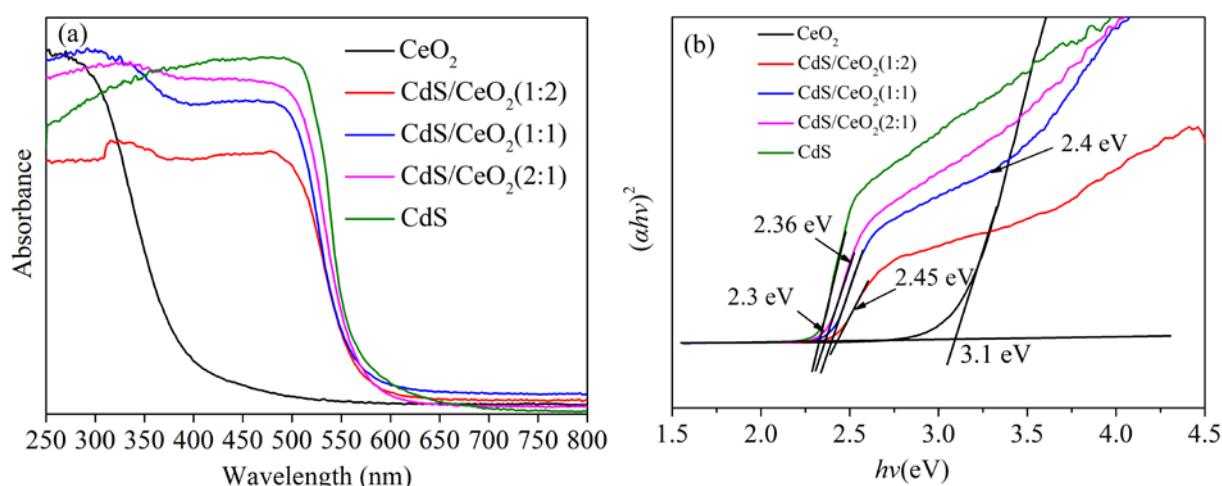
The surface chemical states of the prepared samples are studied by XPS spectroscopy. The high-resolution XPS spectra of Ce 3d, O 1s, Cd 3d and S 2p are shown in Figure 4a-d, respectively. In Figure 4a, the characteristic peaks of Ce 3d are divided into eight fitting peaks. The six peaks labeled as  $v_1$ ,  $v_2$ ,  $v_3$ ,  $u_1$ ,  $u_2$ , and  $u_3$  represent Ce<sup>4+</sup>, and the other two peaks labeled as  $v_1$  and  $u_1$  correspond to Ce<sup>3+</sup>, which indicates the presence of mixed Ce<sup>4+</sup> and Ce<sup>3+</sup> states in the samples [27]. According to charge neutrality condition, the appearance of Ce<sup>3+</sup> is an indicator of oxygen vacancies in CeO<sub>2</sub>. The binding energy peaks labeled at 529.6 eV, 530.6 eV and 531.7 eV correspond to lattice oxygen (OL), oxygen vacancies (Vo) and chemisorbed oxygen (OA) in CeO<sub>2</sub> nanorods, respectively (Figure 4b). Therefore, it indicates that there is a certain amount of Vo in CeO<sub>2</sub>. When CdS is loaded, all Ce 3d and O<sub>L</sub> peaks shift slightly, indicating that there is charge transfer between CeO<sub>2</sub> and CdS [28,29]. As can be seen in Figure 4c, the peaks at 404.7 eV and 411.6 eV are corresponded to the Cd 3d<sub>5/2</sub> and Cd 3d<sub>3/2</sub> of Cd (II) states in CdS sample. As shown in Figure 4d, the XPS spectrum of S 2p exhibits two peaks at 161.5 and 162.6 eV, which are attributed to S 2p<sub>3/2</sub> and S 2p<sub>1/2</sub>, respectively [30,31]. It is worth noting that the peaks of Ce 3d, O 1s, Cd 3d and S 2p are shifted slightly in CdS/CeO<sub>2</sub>(1:1) compared with pure CeO<sub>2</sub> nanorods and CdS, indicating that a heterojunction is formed between CdS nanoparticles and CeO<sub>2</sub> nanorods, which is conducive to the effective separation of photogenerated electrons and holes.



**Figure 4.** High-resolution XPS spectra (a) Ce 3d, (b) O 1s, (c) Cd 3d and (d) S 2p of the samples.

### 3.5 UV-vis DRS analysis

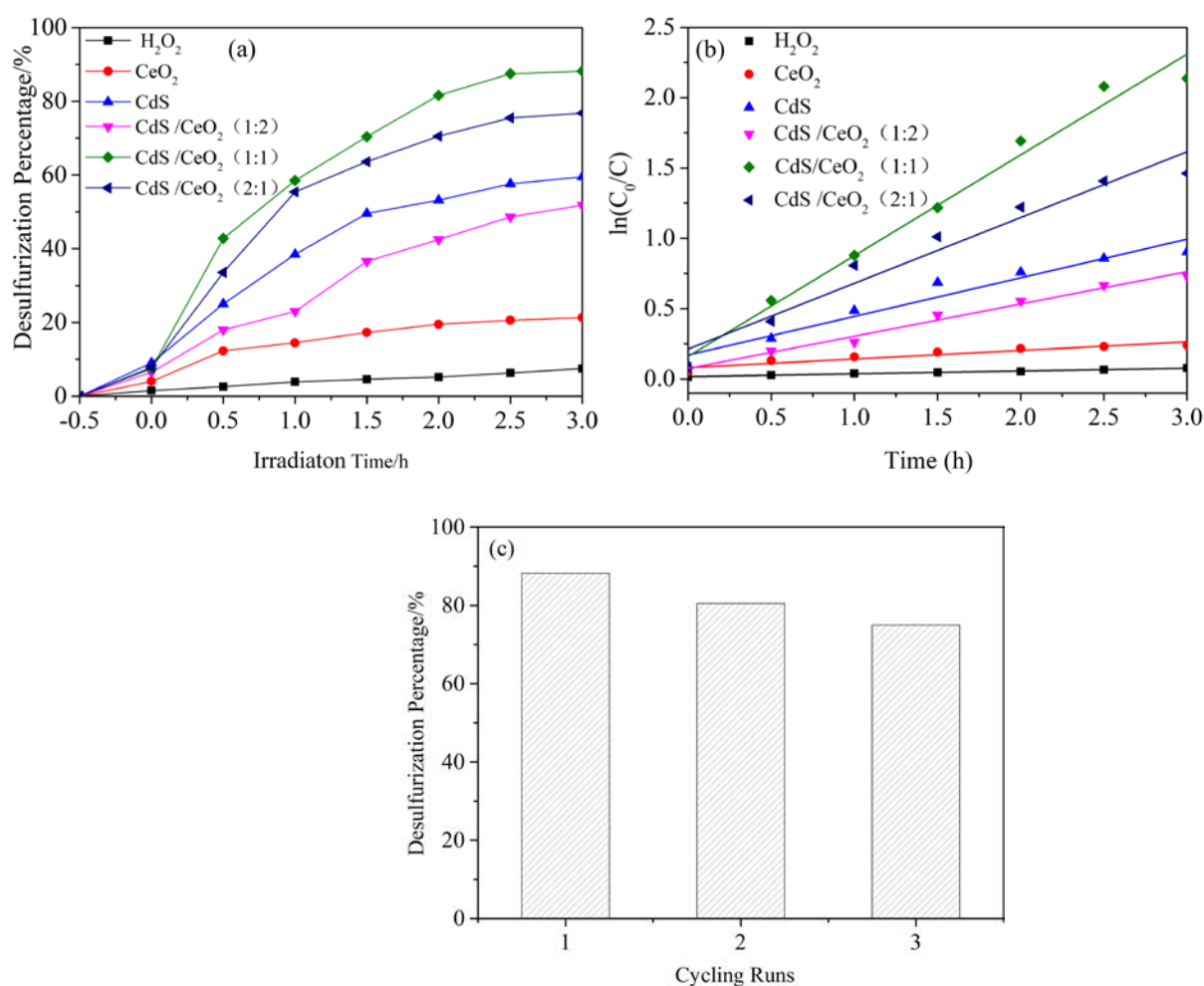
Figure 5 shows the ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) of CeO<sub>2</sub>, CdS and CdS/CeO<sub>2</sub> composites. As shown in Figure 5a, the absorption band edge of CeO<sub>2</sub> is about 400 nm, and that of CdS is about 550 nm. For the CdS/CeO<sub>2</sub> composites, the absorption edge is red shifted with the increase of the molar ratio of CdS. According to the Tauc plot of  $(\alpha h\nu)^2$  vs  $(h\nu)$ , the band gap energy ( $E_g$ ) values of CeO<sub>2</sub>, CdS/CeO<sub>2</sub> (1:2), CdS/CeO<sub>2</sub> (1:1), CdS/CeO<sub>2</sub> (2:1) and CdS are estimated to be 3.1 eV, 2.45 eV, 2.4 eV, 2.36 eV and 2.3 eV (Figure 5b), respectively [32,33]. Therefore, CeO<sub>2</sub> nanorods can only absorb UV light, the increase of the CdS nanoparticles would result in the increase of light adsorption in the visible region.



**Figure 5.** (a) UV-vis DRS of the photocatalysts; (b) Plots of  $(ahv)^2$  vs photon energy ( $h\nu$ ).

### 3.6. Performance of photocatalytic desulfurization

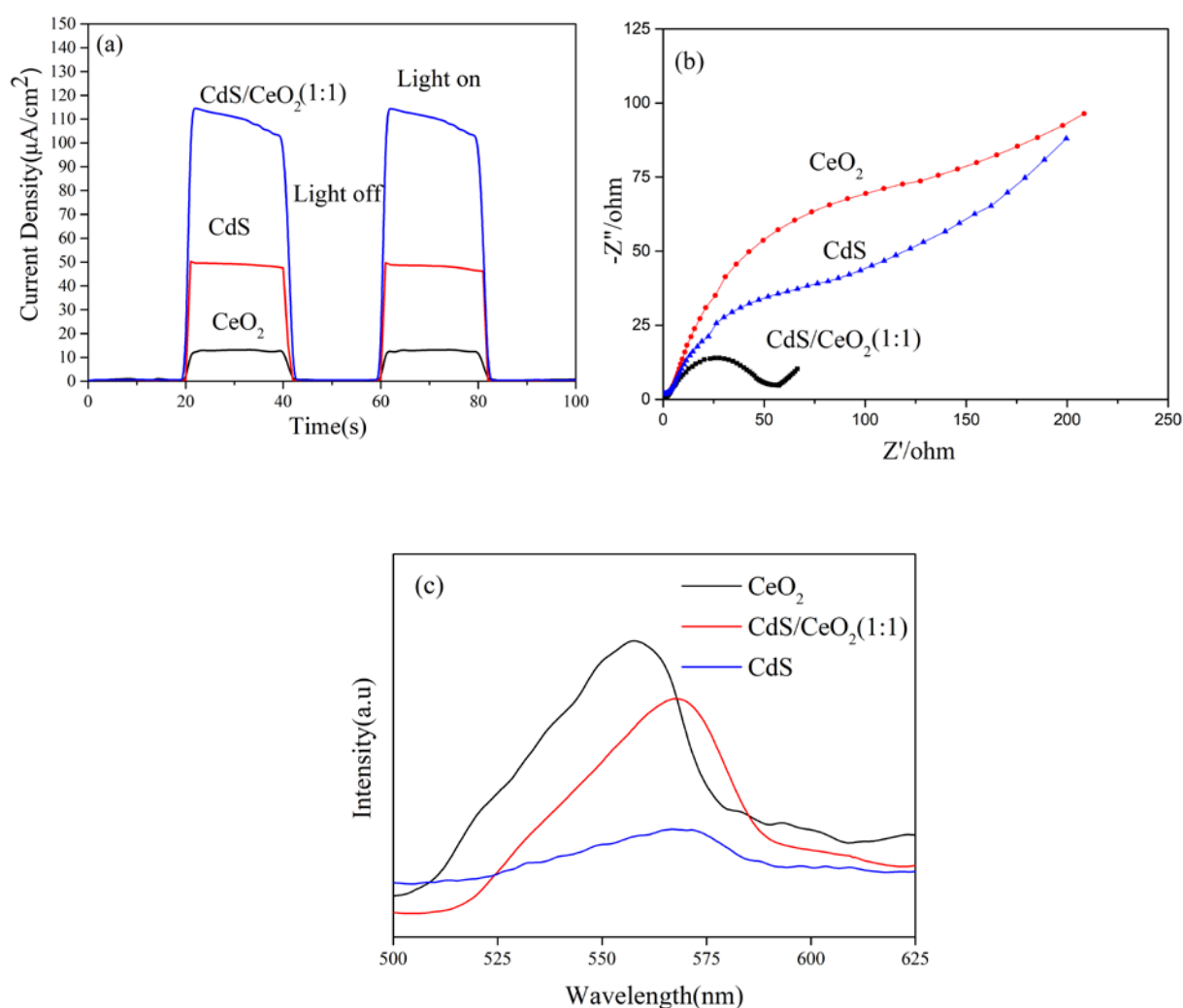
Figure 6a shows the photocatalytic removal of dibenzothiophene (DBT) from model oil with different photocatalysts. Under dark conditions, all photocatalysts have low desulfurization capacity for DBT. When only  $\text{H}_2\text{O}_2$  exists without any catalyst, the desulfurization percentage is only about 7.5 %, indicating that  $\text{H}_2\text{O}_2$  has a certain oxidation capacity, but the efficiency is relatively low. The photocatalytic desulfurization activities of different samples are as follows:  $\text{CdS/CeO}_2(1:1) > \text{CdS/CeO}_2(2:1) > \text{CdS} > \text{CdS/CeO}_2(1:2) > \text{CeO}_2$ , indicating that the heterojunction formed by CdS and  $\text{CeO}_2$  can significantly improve the photocatalytic desulfurization activity. When the molar ratio of  $\text{CeO}_2$  and CdS is 1:1, the highest desulfurization efficiency can reach 92 % in 3 hours. Meanwhile, the corresponding photocatalytic desulfurization kinetic curves over the prepared photocatalysts are shown in Figure 6c. The reaction data are fitted by a first-order model as depicted by the formula[33]:  $\ln(C_0/C) = kt + b$ , where  $k$  is the pseudo-first-order rate constant, and the relationship between  $\ln(C_0/C)$  and catalytic reaction time  $t$  is considered being linear. The corresponding desulfurization rate constants ( $k$ ) are estimated to be  $0.08109 \text{ h}^{-1}$ ,  $0.27446 \text{ h}^{-1}$ ,  $0.22957 \text{ h}^{-1}$ ,  $0.57659 \text{ h}^{-1}$  and  $0.39763 \text{ h}^{-1}$  for the  $\text{CeO}_2$ , CdS,  $\text{CdS/CeO}_2(1:2)$ ,  $\text{CdS/CeO}_2(1:1)$  and  $\text{CdS/CeO}_2(2:1)$ . It is clear that the photocatalyst  $\text{CdS/CeO}_2(1:1)$  displays the best photocatalytic activity among these prepared photocatalysts. The reusability of  $\text{CdS/CeO}_2(1:1)$  composite is also investigated. As shown in Figure 6c, after repeated use for three times, the desulfurization percentage is about 75 %, indicating that the prepared composite has relatively good stability. The desulfurization percentage decreases during the cycle may be attributed to the easy filling of oxygen vacancy in photocatalytic process[35].



**Figure 6.** Photocatalytic desulfurization rate of model oil by different photocatalysts; (b) kinetic curves for photocatalytic desulfurization over the prepared photocatalysts, (c) Cycling runs of  $\text{CdS/CeO}_2$  (1:1) composite on the desulfurization rate.

### 3.7. Photoelectrochemical and PL analysis

The photocurrent measurement (PM), electrochemical impedance spectroscopy (EIS), and photoluminescence spectroscopy (PL) are used to analyze photogenerated electrons and holes separation efficiency. As shown in Figure 7a, when the light is turned on, all samples generate photocurrent, indicating that all the samples have light response. It is worth noting that the photocurrent of  $\text{CdS/CeO}_2$  composite sample is significantly higher than that of the pure  $\text{CeO}_2$  and  $\text{CdS}$ , indicating a higher charge separation efficiency [34,36]. The EIS Nyquist plots are displayed in Figure 7b, the arc radius of  $\text{CdS/CeO}_2$  composite sample is obviously smaller than that of  $\text{CeO}_2$  and  $\text{CdS}$  samples, indicating that the charge transfer resistance of  $\text{CdS/CeO}_2$  composite is lower [37,38]. The PL spectra of  $\text{CeO}_2$ ,  $\text{CdS}$  and  $\text{CdS/CeO}_2$ (1:1) are shown in Figure 7c,  $\text{CdS/CeO}_2$  composite exhibits weaker PL intensity than that of pure  $\text{CeO}_2$  and  $\text{CdS}$ , which indicates that the combination of  $\text{CeO}_2$  and  $\text{CdS}$  can effectively inhibit the recombination of electrons and holes [39,40]. Therefore, the well-defined heterojunction structure is conducive to transportation and separation of photogenerated electrons-holes, and enhance the photocatalytic activity.

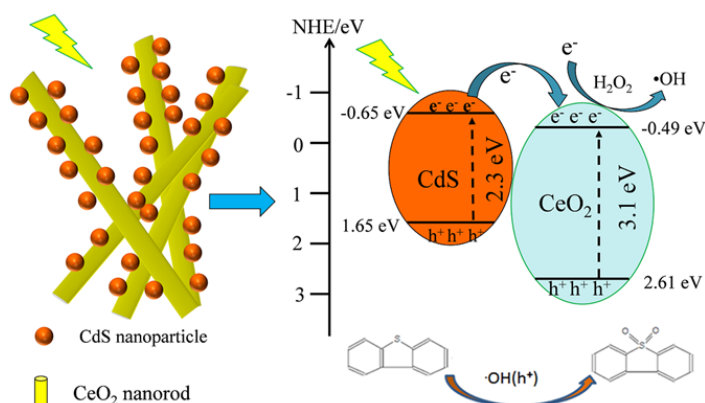


**Figure 7.** (a) photocurrent response; (b) Nyquist impedance plots and (c) Photoluminescence spectra of CeO<sub>2</sub>, CdS and CdS/CeO<sub>2</sub> (1:1).

### 3.8 Photocatalytic mechanism

In order to analyze the mechanism of photocatalytic desulfurization, it is necessary to determine the conduction band (CB) and valence band (VB) positions of semiconductors. The value of valence band (VB) and conduction band (CB) of semiconductor can be obtained according to the following formula [37,41]:  $E_{CB} = \chi - E_0 - 0.5E_g$ , where  $\chi$  is the electronegativity of a semiconductor, the geometric mean of the electronegativity of the constituent atoms,  $E_0$  is the energy of free electrons on the hydrogen scale (4.5 eV) and  $E_g$  is the band gap of the semiconductor. The DRS show that the band gaps ( $E_g$ ) of CeO<sub>2</sub> and CdS are 3.1 and 2.3 eV, respectively. The calculated CB positions of CeO<sub>2</sub> and CdS are -0.49 and -0.65 eV, respectively. And the calculated VB positions of CeO<sub>2</sub> and CdS are about 2.61 and 1.65 eV, respectively. When the composite is irradiated under visible light, CdS can be activated, and the electrons in the full VB of CdS can migrate to the empty CB, leaving a considerable number of positively charged holes at the corresponding position. Due to the CB potential of CdS (-0.65 eV) is lower than that of CeO<sub>2</sub> (-0.49 eV), the excited electrons in CdS are transferred to the CB of CeO<sub>2</sub> through the heterojunction interface, which makes the photogenerated electrons ( $e^-$ ) and holes ( $h^+$ ) effectively separated, inhibits the recombination of photocarriers, and improves the photocatalytic activity. At the same time, the photogenerated electrons react with H<sub>2</sub>O<sub>2</sub> to generate hydroxyl radicals ( $\bullet\text{OH}$ ) and hydroxyl ( $-\text{OH}$ ). However, since the VB potential of CdS (1.65 eV) is lower than the redox potential of  $-\text{OH}/\bullet\text{OH}$

(1.99 eV), holes cannot react with hydroxyl ( $-\text{OH}$ ) to form hydroxyl radicals ( $\bullet\text{OH}$ ) [42]. Hydroxyl radicals ( $\bullet\text{OH}$ ) and holes ( $h^+$ ) with strong oxidation can be oxidized DBT into  $\text{DBTO}_2$ . Finally, due to the strong polarity of  $\text{DBTO}_2$ , it can be removed by extraction separation to achieve the purpose of desulfurization [2,7,43]. In addition, the surface  $\text{V}_\text{O}$  of  $\text{CeO}_2$  plays an important role in the process of photocatalytic desulfurization. It not only serve as an electron reservoir to store the photogenerated electrons, inhibit the recombination of photogenerated electrons and holes, but also act as an active sites to promote the adsorption and activation of  $\text{H}_2\text{O}/\text{OH}$  [29,44]. Figure 8 illustrates the possible photocatalytic desulfurization mechanism.



**Figure 8.** Schematic illustration of photocatalytic desulfurization mechanism of CdS/CeO<sub>2</sub> composite

#### 4. Conclusions

In conclusion, one-dimensional  $\text{CeO}_2$  nanorods were modified by CdS nanoparticles to form heterojunction photocatalyst. The nanocomposites show great enhanced photocatalytic activity for photocatalytic desulfurization, and CdS/ $\text{CeO}_2$  (1:1) shows the highest desulfurization rate of 92 % in 3 hours under visible light. the nanocomposites demonstrate the outstanding photocatalytic activity, and the desulfurization rate reaches 92% for DBT in 3 hours. The excellent photocatalytic desulfurization performance is attributed to the transfer of visible light excited electrons on CdS nanoparticles to  $\text{CeO}_2$  nanorods, which effectively inhibits the photocorrosion of CdS with narrow band gap and improves the light trapping ability of  $\text{CeO}_2$  with broad band gap. This work may provide a new idea for the design and construction of photocatalytic deep desulfurization materials.

**Author Contributions:** Conceptualization, X.L. and H.H.; methodology, X.L. and J.Q.; validation, Z.L., X.Z. and H.H.; formal analysis, Z.L., W.X. and H.H.; investigation, X.L. and W.X.; resources, X.L.; data curation, X.Z. and W.X.; writing—original draft preparation, X.L. and Z.L.; writing—review and editing, H.H. and J.Q.; visualization, X.L. and X.Z.; supervision, X.L.; project administration, X.L.; funding acquisition, X.L. and H.H. All authors have read and agreed to the published version of the manuscript

**Funding:** This research was supported by Industry-University-Institute Cooperation Project of Jiangsu Province( BY2022428),China; and the Funding for school-level research projects of Yancheng Institute of Technology (xjr2019026).

**Conflicts of Interest:** The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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