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Cds Nanoparticles Decorated 1D CeO₂ Nanorods for Enhanced Photocatalytic Desulfurization Performance

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Abstract: The CdS nanoparticles were constructed on one-dimensional (1D) CeO₂ nanorods by two-step hydrothermal method. The X-ray diffraction (XRD), transmission electron microscopy (TEM), Raman spectra, X-ray photoelectron spectra (XPS) and VU-vis diffuse reflection spectroscopy (DRS) techniques were used to characterize these CdS/CeO₂ nanocomposites. It is concluded that when the molar ratio of CdS and CeO₂ 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 CeO₂ 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 CeO₂-based photocatalysts for photocatalytic desulfurization applications.

Keywords: CdS; CeO₂; Nanocomposite; Heterojunction; Photocatalytic desulfurization

1. Introduction

Sulfur oxides (SO_x) 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 TiO₂-based photocatalyst [9,10], bismuth series material [11,12], g-C₃N₄ framework material [13,14], metal organic framework material [15], etc.

CeO₂ is an important rare earth oxide semiconductor material, which is commonly used as a photocatalyst for pollutant degradation and energy conversion. However, CeO₂ 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 CeO₂ 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 CeO₂ to form a heterojunction is expected to overcome these disadvantages.

Herein, in this work, we used CdS nanoparticles to decorate 1D CeO₂ 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 CeO₂ nanorods

0.02 mol Ce (NO₃)₃·6H₂O 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 CeO₂ nanorods.

2.1.2 Synthesis of CdS/CeO₂ composite

A certain amount of prepared CeO₂ nanorods powders were ultrasonic dispersed in 20 mL of deionized water, and then 20 mL of 0.1M CdCl₂·2.5H₂O solution was added. After full stirring, 20 mL of 0.1M Na₂S 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/CeO₂ composite. The molar ratios of CdS to CeO₂ 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 Ka 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 election 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 α 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 Na₂SO₄ 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 K₃Fe(CN)₆/K₄Fe(CN)₆ (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 temperatur.

2.4 Photocatalytic desulfurization measurement

0.08 g DBT was dissolved in 200 mL n-octane as model oil, subsequently, 0.1 g photocatalysts were added under constant stirring, and then appropriate H₂O₂ 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°, 33.1°, 47.4°, and 56.2° correspond to the (111), (200), (220) and (311) different crystal planes of cubic fluorite CeO₂ respectively (JCPDS 34-0394). And the diffraction peaks at 24.6°, 26.4°, 28.0°, 36.5°, 43.6°, 47.7° and 51.7° are indexed to the (100), (002), (101), (102), (110), (103) and (112) crystal planes of hexagonal structure CdS respectively (JCPDS:41-1049). In addition, when CdS nanoparticles are deposited on CeO₂ nanorods, the characteristic peaks of both cubic fluorite CeO₂ and hexagonal CdS are observed in the composites. It is worth noting that with increasing the molar ratio of CdS to CeO₂, the intensity of the characteristic peaks of CdS enhance in the composites. The results demonstrate that the CdS are successfully loaded on the surface of CeO₂.

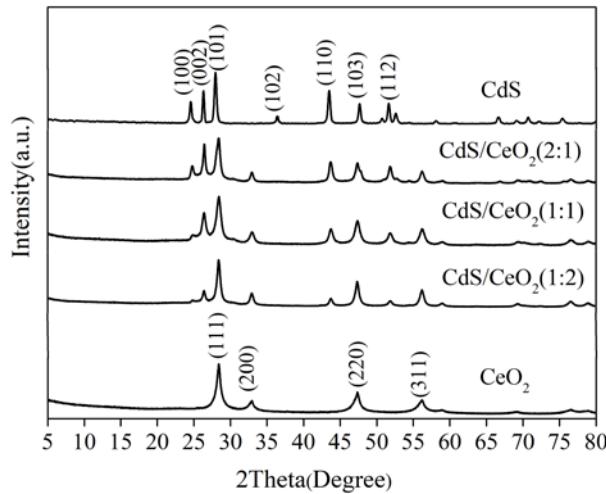


Figure 1. XRD patterns of CdS, CeO₂ and the various CdS/CeO₂ composites.

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 CeO₂, the peak at 465 cm⁻¹ can be attributed to the F2g Raman active interior phonon mode of fluorite cubic structure. As for pure CdS, the two dominant peaks at 300 cm⁻¹ and 600 cm⁻¹ are attributed to the first-order longitudinal optical (1LO) and the second-order longitudinal optical (2LO) phonon modes of CdS, respectively[24]. Moreover, It is observed that all the composites have the peaks corresponding to the both CeO₂ and CdS with varying intensities. The Raman peak intensity of CdS / CeO₂ composites is lower than that of pure CeO₂ or pure CdS. This may be attributed to the scattering loss caused by defects in the heterojunction[25,26]. With the increase of CeO₂ content, the

characteristic peak intensity of CeO_2 in the CdS/CeO_2 composite gradually increases. Therefore, The Raman measurement results further demonstrate the existence of CdS and CeO_2 in the composite.

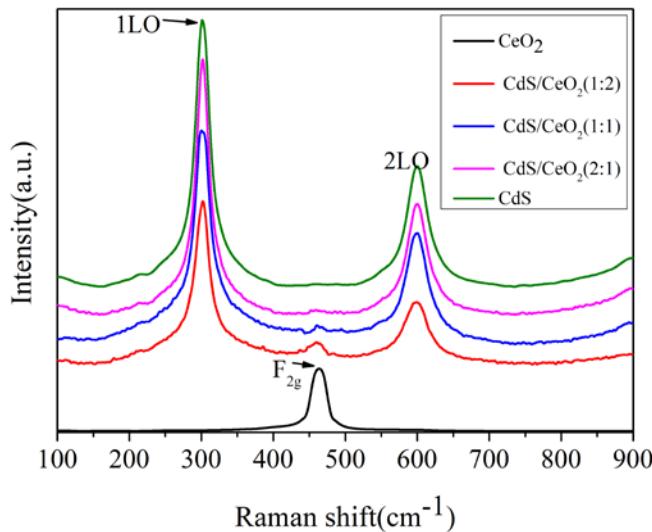


Figure 2. Raman spectra of CdS , CeO_2 and various CdS/CeO_2 samples

3.3 Morphological analysis

Figure 3 shows TEM and HRTEM images of CeO_2 nanorods and $\text{CdS}/\text{CeO}_2(1:1)$ composite. It can be seen from Figure 3a that the prepared 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 CeO_2 . As shown in Figure 3c, CdS nanoparticles are deposited on the surface of CeO_2 nanorods, and the structure of 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 CdS and the (111) crystal plane of cubic fluorite CeO_2 . The well-defined heterojunction structure may facilitate the separation of photogenerated electrons and holes, improving the photocatalytic efficiency.

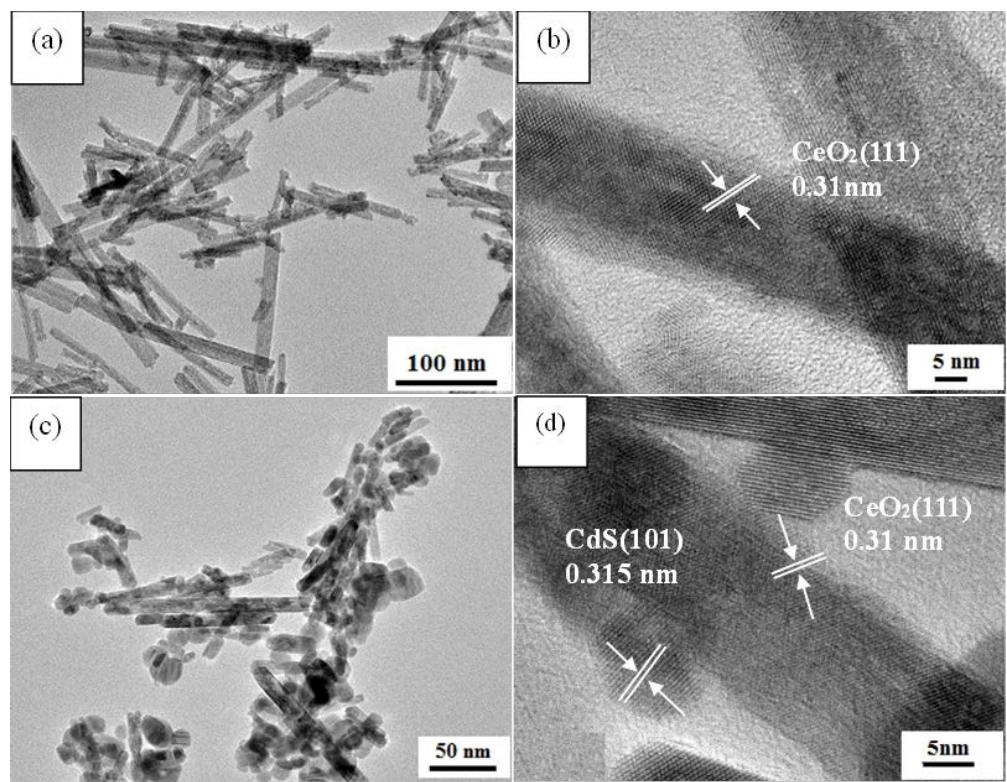


Figure 3. TEM and HRTEM images of CeO₂(a, b) and CdS/CeO₂(1:1) composite (c, d).

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, v₂, v₃, u, u₂, and u₃ represent Ce⁴⁺, and the other two peaks labeled as v₁ and u₁ correspond to Ce³⁺, which indicates the presence of mixed Ce⁴⁺ and Ce³⁺ states in the samples [27]. According to charge neutrality condition, the appearance of Ce³⁺ is an indicator of oxygen vacancies in CeO₂. The binding energy peaks labeled at 529.6 eV 530.6 eV and 531.7 eV correspond to lattice oxygen (OL), oxygen vacancies (V_O) and chemisorbed oxygen (OA) in CeO₂ nanorods, respectively (Figure 4b). Therefore, it indicates that there is a certain amount of V_O in CeO₂. When CdS is loaded, all Ce 3d and O₁s peaks shift slightly, indicating that there is charge transfer between CeO₂ and CdS[28,29]. As can be seen in Figure 4 c, the peaks at 404.7 eV and 411.6 eV are corresponded to the Cd 3d_{5/2} and Cd 3d_{3/2} 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_{3/2} and S 2p_{1/2}, 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/CeO₂(1:1) compared with pure CeO₂ nanorods and CdS, indicating that a heterojunction is formed between CdS nanoparticles and CeO₂ nanorods, which is conducive to the effective separation of photogenerated electrons and holes.

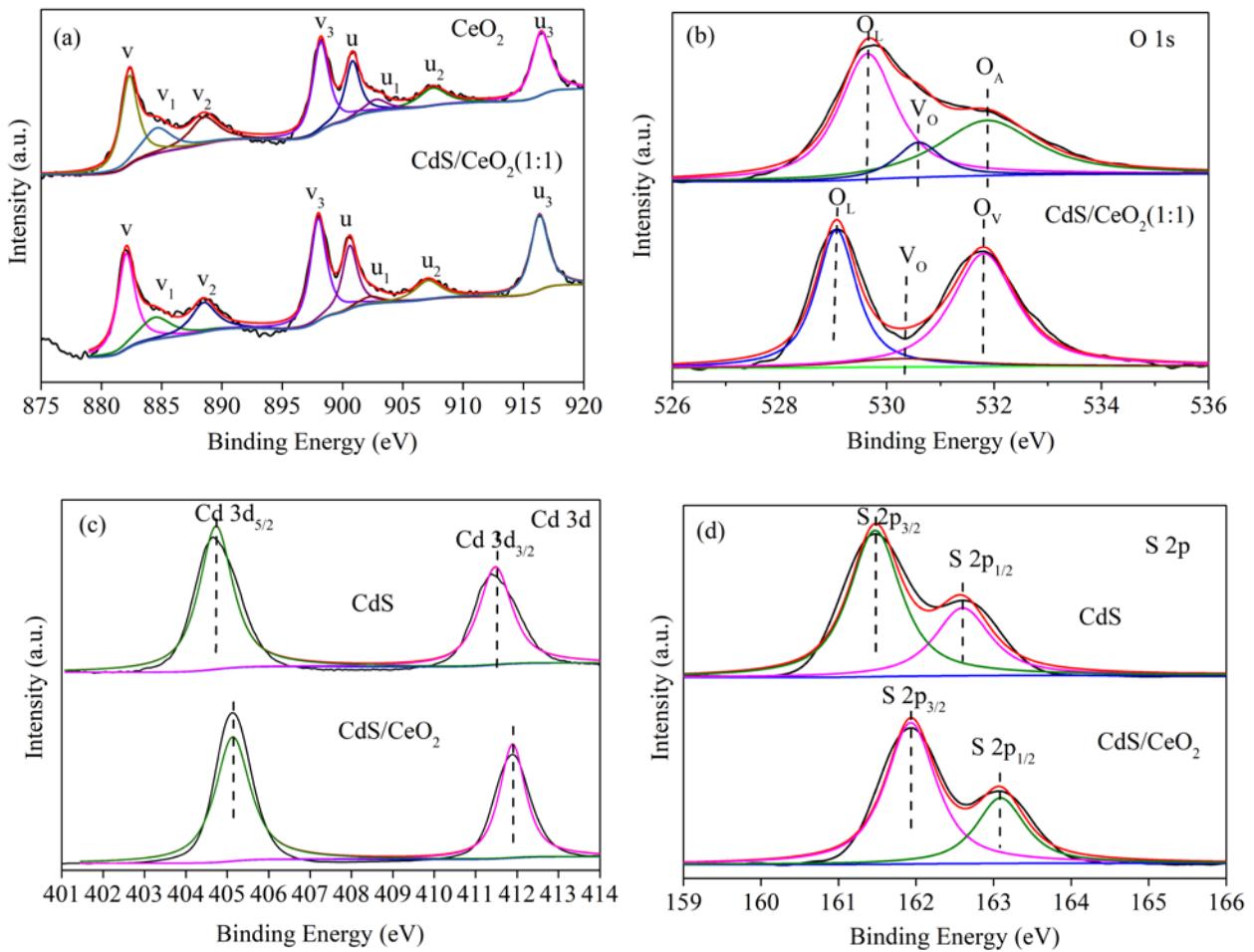


Figure 4. High-resolution XPS spectra (a) Ce 3d, (b) O 1s, (c) Cd 3d and (d) S 2p of the samples.

3.5 UV-vis DRS analysis

Figure 5 shows the ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) of CeO₂, CdS and CdS/CeO₂ composites. As shown in Figure 5a, the absorption band edge of CeO₂ is about 400 nm, and that of CdS is about 550 nm. For the CdS/CeO₂ 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 CeO₂, CdS/CeO₂ (1:2), CdS/CeO₂ (1:1), CdS/CeO₂ (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, CeO₂ nanorods can only absorb UV light, the increase of the CdS nanoparticles would result in the increase of light adsorption in the visible region.

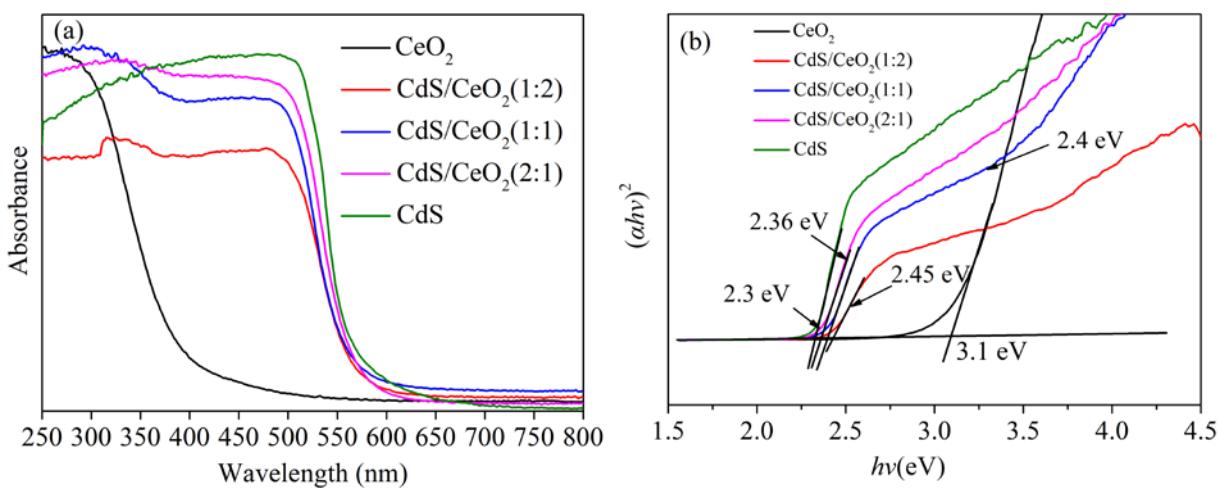


Figure 5. (a) UV-vis DRS of the photocatalysts; (b) Plots of $(ahv)^2$ vs photon energy (hv) .

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 H_2O_2 exists without any catalyst, the desulfurization percentage is only about 7.5 %, indicating that H_2O_2 has a certain oxidation capacity, but the efficiency is relatively low. The photocatalytic desulfurization activities of different samples are as follows: $\text{CdS}/\text{CeO}_2(1:1) > \text{CdS}/\text{CeO}_2(2:1) > \text{CdS} > \text{CdS}/\text{CeO}_2(1:2) > \text{CeO}_2$, indicating that the heterojunction formed by CdS and CeO_2 can significantly improve the photocatalytic desulfurization activity. When the molar ratio of 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 h^{-1} , 0.27446 h^{-1} , 0.22957 h^{-1} , 0.57659 h^{-1} and 0.39763 h^{-1} for the CeO_2 , CdS , $\text{CdS}/\text{CeO}_2(1:2)$, $\text{CdS}/\text{CeO}_2(1:1)$ and $\text{CdS}/\text{CeO}_2(2:1)$. It is clear that the photocatalyst $\text{CdS}/\text{CeO}_2(1:1)$ displays the best photocatalytic activity among these prepared photocatalysts. The reusability of $\text{CdS}/\text{CeO}_2(1:1)$ 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].

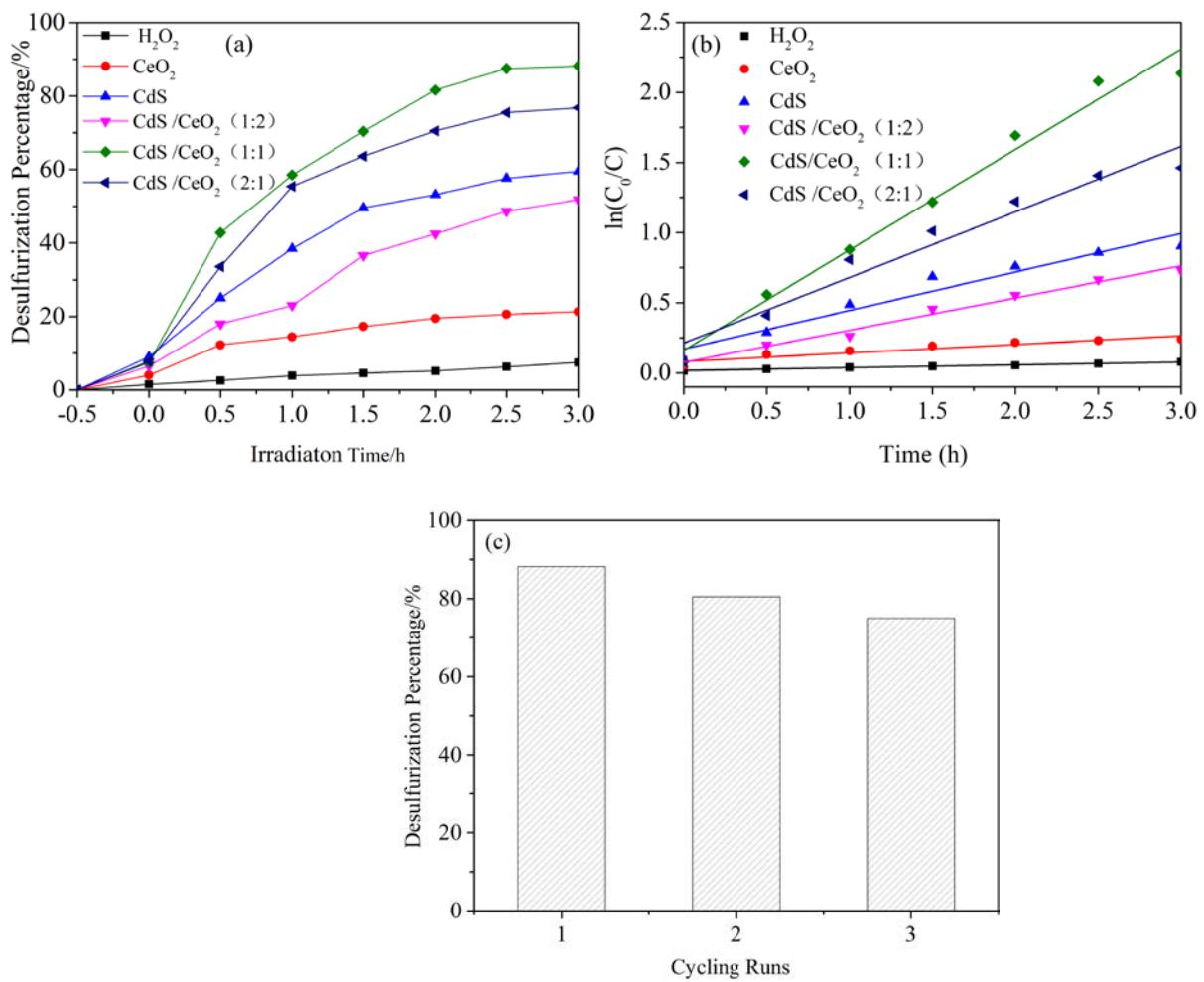


Figure 6. Photocatalytic desulfurization rate of model oil by different photocatalysts; (b) kinetic curves for photocatalytic desulfurization over the prepared photocatalysts, (c) Cycling runs of CdS/CeO_2 (1:1) composite on the desulfurization rate.

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 CdS/CeO_2 composite sample is significantly higher than that of the pure CeO_2 and CdS , indicating a higher charge separation efficiency [34,36]. The EIS Nyquist plots are displayed in Figure 7b, the arc radius of CdS/CeO_2 composite sample is obviously smaller than that of CeO_2 and CdS samples, indicating that the charge transfer resistance of CdS/CeO_2 composite is lower [37,38]. The PL spectra of CeO_2 , CdS and CdS/CeO_2 (1:1) are shown in Figure 7c, CdS/CeO_2 composite exhibits weaker PL intensity than that of pure CeO_2 and CdS , which indicates that the combination of CeO_2 and 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.

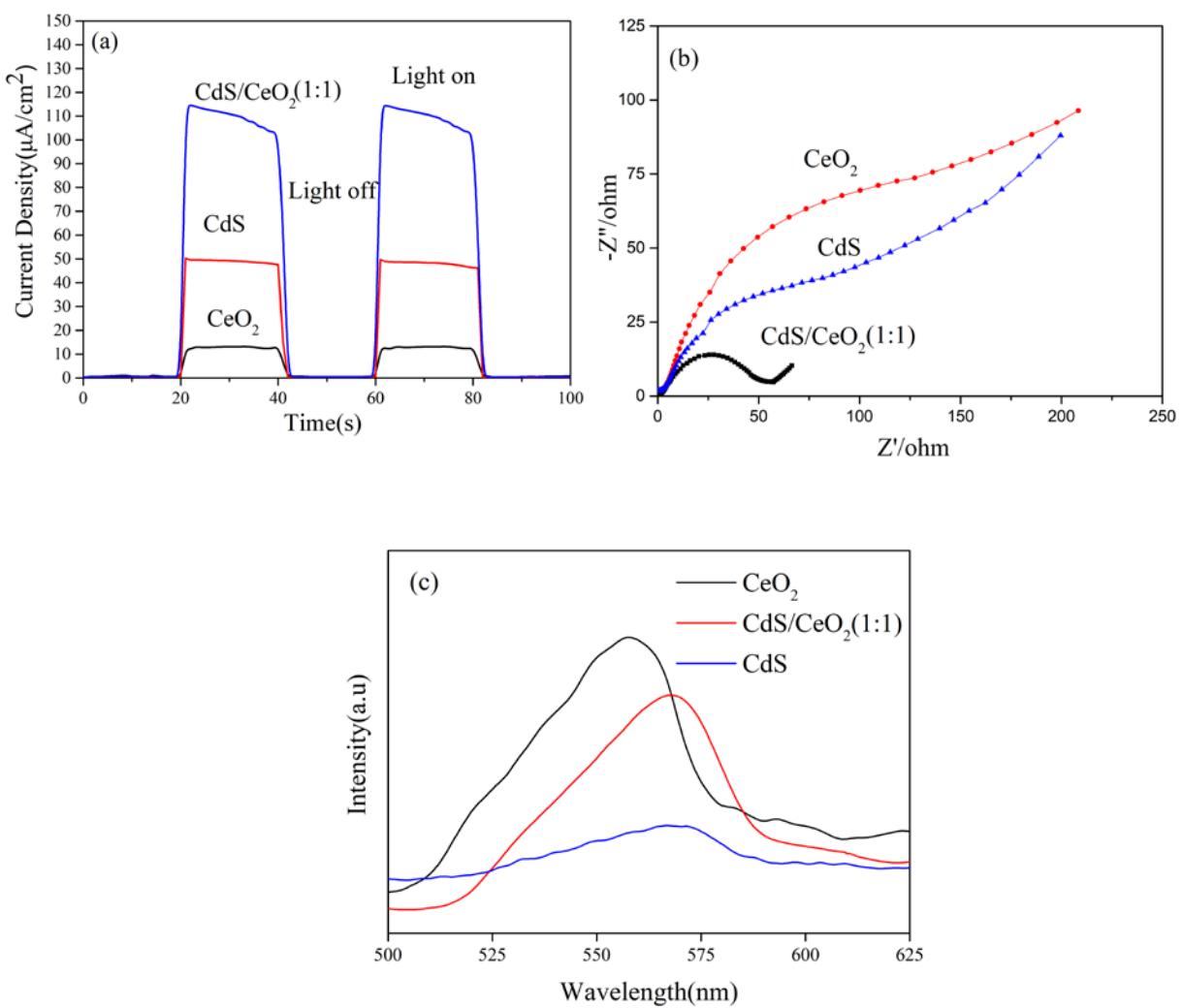


Figure 7. (a) photocurrent response;(b) Nyquist impedance plots and (c) Photoluminescence spectra of CeO_2 , CdS and CdS/CeO_2 (1:1).

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]: $E_{\text{CB}} = \chi - E_0 - 0.5E_g$, where χ is the electronegativity of a semiconductor, 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_2 and CdS are 3.1 and 2.3 eV, respectively. The calculated CB positions of CeO_2 and CdS are -0.49 and -0.65 eV, respectively. And the calculated VB positions of CeO_2 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_2 (-0.49 eV), the excited electrons in CdS are transferred to the CB of CeO_2 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_2O_2 to generate hydroxyl radicals ($\bullet\text{OH}$) and hydroxyl (-OH). However, since the VB potential of CdS (1.65 eV) is lower than the redox potential of -OH/ $\bullet\text{OH}$

(1.99 eV), holes cannot react with hydroxyl (-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 DBTO₂. Finally, due to the strong polarity of DBTO₂, it can be removed by extraction separation to achieve the purpose of desulfurization[2,7,43]. In addition, the surface V_{O} of CeO₂ 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 H₂O/-OH[29,44]. Figure 8 illustrates the possible photocatalytic desulfurization mechanism.

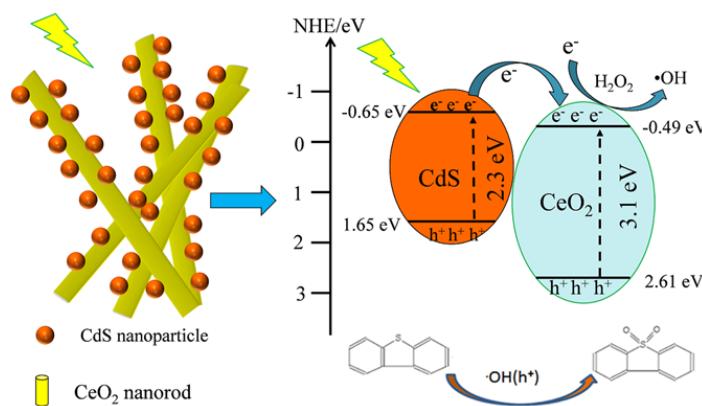


Figure 8. Schematic illustration of photocatalytic desulfurization mechanism of CdS/CeO₂ composite

4. Conclusions

In conclusion, one-dimensional CeO₂ nanorods were modified by CdS nanoparticles to form heterojunction photocatalyst. The nanocomposites show great enhanced photocatalytic activity for photocatalytic desulfurization, and CdS/CeO₂ (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 CeO₂ nanorods, which effectively inhibits the photocorrosion of CdS with narrow band gap and improves the light trapping ability of CeO₂ 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 funding 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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