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Hydrothermal synthesis of $\text{CeO}_2/\text{NaNbO}_3$ composites with enhanced photocatalytic performance

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ABSTRACT

A highly active photocatalyst $\text{CeO}_2/\text{NaNbO}_3$ is fabricated by a simple and facile hydrothermal method. The obtained photocatalyst composites are characterized by X-ray powder diffraction, scanning electron microscopy, transmission electron microscopy and ultraviolet-visible diffuse reflectance spectroscopy. The photocatalytic activity of the obtained samples is demonstrated by the photocatalytic degradation of the colorless antibiotic agent ciprofloxacin and the dye rhodamine B. The results reveal that $\text{CeO}_2/\text{NaNbO}_3$ composites exhibit a higher photocatalytic property than pure NaNbO_3 under both UV and visible light irradiation. Furthermore, the optimum mass ratio of CeO_2 in the $\text{CeO}_2/\text{NaNbO}_3$ composites is 2.0 wt%. The improved photocatalytic activity is attributed to the higher separation rate of the photo-induced electrons and holes, and the higher migration rate of the photogenerated charge in the interfacial region. Furthermore, the photoluminescence spectra, photocurrent, electrochemical impedance spectroscopy and trapping experiment are applied to demonstrate the photocatalytic reaction mechanism of the as-prepared samples. The result of the trapping experiment indicates that $\cdot\text{OH}$ radicals, $\cdot\text{O}_2^-$ radicals and holes are all involved in the photocatalytic degradation process of RhB. Furthermore, a possible mechanism for the enhancement of the photocatalytic activity is also proposed.

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1. Introduction

Owing to the urgent need to minimize the depletion of resources and ecological environmental deterioration, the photocatalysis technique based on semiconductors has attracted tremendous attention since the discovery of the Fujishima–Honda effect in 1972 [1–10]. To date, titanium dioxide (TiO_2) has been studied the most extensively among the variety

of photocatalysts [11–13]. Unfortunately, a low quantum efficiency and high recombination rate have limited the practical application of TiO_2 . In the photocatalysis field, the development of new semiconductor photocatalysts, which possess a simultaneous high photooxidation and photoreduction performance, remains a hot topic.

Recently, perovskite-type NaNbO_3 has attracted much attention owing to its excellent properties, such as nonlinear

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optical characteristics, ferroelectricity, ionic conductivity, high sound velocity, photorefractive effect, photocatalytic performance and so on [14–17]. In photocatalytic reactions, the wide band gap (≈ 3.24 eV) endows NaNbO_3 with a high conductor band minimum (CBM) and low valence band maximum (VBM). Therefore, NaNbO_3 exhibits a strong photooxidation and photoreduction capacity [18,19]. The enhanced photoelectron excitation and transfer of a perovskite photocatalyst have been attributed to its high degree of symmetry [20]. Thus, the cubic NaNbO_3 with high symmetry should be beneficial for electron excitation and transfer. Unfortunately, some inherent drawbacks, including the inefficient charge separation, poor quantum yield, poor photocatalytic activity and so on, limit its practical application in the photocatalysis field. To address these issues, an effective way is to couple NaNbO_3 with another semiconductor to form a heterojunction composite with improved photocatalytic activity. To date, many semiconductors have been applied to modify NaNbO_3 , such as ZnO [21], Bi_2O_3 [22], WO_3 [23], CdS [24] and In_2O_3 [25]. These composites all exhibit a much higher photocatalytic performance than that of a single-phase semiconductor. Therefore, it is beneficial to find an excellent semiconductor to modify NaNbO_3 .

CeO_2 , as a conventional catalyst, has been widely investigated in various fields including photocatalysis [26]. CeO_2 , with the features of stability and non-toxicity, is an n-type semiconductor [27]. Investigators have shown an enhanced photocatalytic activity by coupling CeO_2 with different semiconductors, such as $\text{CeO}_2\text{-TiO}_2$ [28,29], $\text{CeO}_2\text{/Bi}_2\text{O}_3$ [30], RGO/CeO_2 [31], and $\text{CeO}_2\text{/Cu}_2\text{O}$ [32]. These results revealed that the combination of CeO_2 with other semiconductors could dramatically improve the photocatalytic efficiency, which was attributed to the suitable matching of the energy band levels [33,34]. Therefore, it is expected that combining NaNbO_3 with CeO_2 to form a heterojunction nanocomposite will enhance the photocatalytic property. To the best of our knowledge, the composite photocatalyst $\text{CeO}_2\text{/NaNbO}_3$ has not been studied to date.

Herein, we successfully synthesized $\text{CeO}_2\text{/NaNbO}_3$ heterostructure composites through a simple and facile process. The morphology, crystalline phase, and optical properties of the as-prepared samples were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM, HRTEM), X-ray powder diffraction (XRD), and ultraviolet-visible (UV-vis) diffuse reflectance spectroscopy (DRS). The essential characteristics of the different samples were obtained. Then the photocatalytic performance of all samples was investigated by the degradation of the dye rhodamine B (RhB) and the colorless antibiotic agent Ciprofloxacin (CIP). The results indicated that the $\text{CeO}_2\text{/NaNbO}_3$ composites possessed a higher photocatalytic activity compared with the pure NaNbO_3 under both UV and visible light irradiation. An optimum mass ratio of CeO_2 in the $\text{CeO}_2\text{/NaNbO}_3$ composites was obtained. Furthermore, radicals trapping experiments were used to confirm the active species that were participating in the photocatalytic activity reaction process. Moreover, the properties and the possible photocatalytic mechanism of the $\text{CeO}_2\text{/NaNbO}_3$ heterojunction composites in relation to the band positions of the two semiconductors are discussed in detail.

2. Experimental

2.1. Preparation of NaNbO_3

The perovskite-type NaNbO_3 was fabricated by a hydrothermal method [35]. First, a certain amount of NaOH was weighed to form a NaOH solution (10 mol/L), then the obtained NaOH solution (120 mL) was added into a 200-mL teflon-lined stainless steel autoclave. Next, Nb_2O_5 (2 g) was added into the NaOH solution. The mixture solution was stirred for 2 h. After stirring, the stir-rotor was removed and the autoclave was covered with a lid and jacket, then heat-treated at 150 °C for 48 h. After cooling, the obtained sample was filtered and washed using a large amount of ultrapure water. Finally, the sample was dried at 60 °C.

2.2. Preparation of $\text{CeO}_2\text{/NaNbO}_3$ nanocomposites

For the $\text{CeO}_2\text{/NaNbO}_3$ nanocomposites, a certain amount of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was dissolved in ultrapure water (10 mL), then the as-prepared NaNbO_3 (0.3 g) was added into the $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ solution. The mixture solution was continuously stirred for 1 h after ultrasonic treatment for 5 min. The mixture solution was heat-treated at 80 °C until the water was completely evaporated under stirring. Then the dried sample at 60 °C was ground. Finally, the ground sample was calcined at 400 °C for 4 h. A series of $\text{CeO}_2\text{/NaNbO}_3$ nanocomposites were prepared by simply adjusting the amounts of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ while using the same method. The as-prepared NaNbO_3 underwent the same procedure in the absence of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ to form a pure NaNbO_3 photocatalyst. The obtained composites were defined as $\text{CeO}_2\text{/NaNbO}_3\text{-1}$, $\text{CeO}_2\text{/NaNbO}_3\text{-2}$, $\text{CeO}_2\text{/NaNbO}_3\text{-3}$, for the samples with 1%, 2% and 5 wt% of CeO_2 , respectively.

2.3. Characterization

XRD was applied to illustrate the crystalline phase of the as-prepared samples. XRD patterns of the composites were measured on a SmartLab X-ray diffractometer with monochromatic $\text{Cu } K_\alpha$ radiation of $2\theta = 10^\circ\text{--}80^\circ$ at a scan rate of $10^\circ/\text{min}$. The obtained samples were characterized by SEM and TEM using a Hitachi S-4800 and a JEOL JEM-2100 microscope, respectively. In addition, UV-vis DRS of the as-prepared samples was performed on a UV-Vis spectrophotometer (Shimadzu, UV3600). Photoluminescence (PL) spectrometry was carried out on a fluorescence spectrophotometer (Hitachi F-7000) with an excitation wavelength of 290 nm. The photocurrent measurement and electrochemical impedance spectroscopy (EIS) were performed on a CHI660D electrochemical workstation (Chenhua Instruments).

2.4. Photocatalytic degradation of CIP and RhB

The photocatalytic activities of the different samples were determined by measuring the degradation of the colorless antibiotic agent CIP and the dye RhB under both UV and visible

light irradiation. A 300 W high-pressure Hg lamp, with a light filter cutting off the visible and near infrared light, was used as the UV light source (300–400 nm) (Zhongjiaojinyuan, CEL-HXUV300), while the visible light source was a xenon lamp with a 400-nm longpass filter. The typical photocatalytic degradation process was as follows: The initial concentration of the synthetic aqueous CIP was 10 mg/L. CIP (100 mL) and the photocatalyst (40 mg) were placed in a glass beaker. Prior to light illumination, the aqueous suspension was sonicated for 2 min and then magnetically stirred in the dark for 60 min to reach desorption–adsorption equilibrium. After irradiation, the suspension (approximately 1.5 mL) was extracted at two-minute intervals, then centrifuged and analyzed. The UV-vis spectrophotometer served to evaluate the concentration changes of CIP. The photocatalytic degradation procedure of RhB was the same as that of CIP. The initial concentrations of RhB and CIP were both 5 mg/L under visible irradiation.

2.5. Photocurrent and EIS test

The photocurrent and EIS of different samples were investigated using a standard three-electrode system. In the system, $\text{CeO}_2/\text{NaNbO}_3$ and NaNbO_3 electrodes served as the working electrode, and the counter electrode and reference electrode were platinum wire and Ag/AgCl , respectively [36]. The electrolyte for the photocurrent and EIS testing was 0.1 mol/L Na_2SO_4 . For the photocurrent measurement, the photocurrent responses of the different samples were recorded for the 20 s between light and dark, where the light source was a 250-W mercury lamp. For the EIS measurement, the EIS of the composites was measured under an open circuit potential with a 10-mV amplitude of the sinusoidal wave (frequency was 0.05 Hz–100 kHz). In addition, the UV light source was identical with that used in the photocurrent experiment.

3. Results and discussion

3.1. Characterization of the samples

Fig. 1 shows the crystal phase of the as-prepared composites that were examined by XRD. Fig. 1(a) shows that the distinct peaks at $2\theta = 22.78^\circ, 32.41^\circ, 46.55^\circ, 52.35^\circ, 57.79^\circ, 67.91^\circ, 72.67^\circ$ and 77.17° could be indexed to the (100), (110), (200), (210), (211), (220), (300) and (310) planes of the cube NaNbO_3 (JCPDS card no. 19-1221), which verified the high purity of the obtained NaNbO_3 [24]. After forming a composite of NaNbO_3 with CeO_2 , only the diffraction peak at $2\theta = 28.7^\circ$ was added when the mass ratio of CeO_2 was from 2% to 5% (Fig. 1(c), (d)). This was indexed to the (111) planes of CeO_2 (JCPDS card no. 34-0394) [37]. This result could be ascribed to the small crystallization of CeO_2 . Furthermore, the other peaks of CeO_2 were not observed because of the small content of CeO_2 in the composites. The coincidence of the planes of NaNbO_3 and CeO_2 was also a reason. No characteristic peaks of any impurities were observed in the $\text{CeO}_2/\text{NaNbO}_3$ nanocomposites.

Fig. 2 shows the sizes and morphologies of the synthesized pure NaNbO_3 and $\text{CeO}_2/\text{NaNbO}_3$ composites that were obtained

Fig. 1. XRD patterns of NaNbO_3 (a), $\text{CeO}_2/\text{NaNbO}_3$ -1 (b), $\text{CeO}_2/\text{NaNbO}_3$ -2 (c), and $\text{CeO}_2/\text{NaNbO}_3$ -3 (d).

by SEM. Obviously, the morphologies of the pure NaNbO_3 catalysts was made up of a cube with smooth surfaces, and the width of the cubic NaNbO_3 was approximately $1.8\ \mu\text{m}$ (Fig. 2(a)). Fig. 2(b)–(d) present the morphologies of $\text{CeO}_2/\text{NaNbO}_3$ -1, $\text{CeO}_2/\text{NaNbO}_3$ -2, $\text{CeO}_2/\text{NaNbO}_3$ -3, respectively. Fig. 2(b) shows that some CeO_2 particles were dispersed on the surface of the cubic NaNbO_3 catalyst for $\text{CeO}_2/\text{NaNbO}_3$ -1. Compared with Fig. 2(b), Fig. 2(c) shows that the amount of CeO_2 particles on the surface of the cubic NaNbO_3 increased for $\text{CeO}_2/\text{NaNbO}_3$ -2. In addition, the surface of NaNbO_3 was almost completely covered by CeO_2 particles for $\text{CeO}_2/\text{NaNbO}_3$ -3, as shown in Fig. 2(d). It was expected that more CeO_2 particles were loaded on the surface of NaNbO_3 as the content of CeO_2 in the composites was increased, which confirmed the successful deposition of CeO_2 on the surface of the cubic NaNbO_3 .

Fig. 3 shows the typical TEM and HRTEM images of the $\text{CeO}_2/\text{NaNbO}_3$ -2 nanocomposite that exhibited the best mass ratio of CeO_2 (2 wt%). Some small CeO_2 particles could be clearly seen at the boundary of the TEM image of NaNbO_3 in Fig. 3(a). In addition, two different gap fringes were observed,

Fig. 2. Typical SEM images of NaNbO_3 (a) and $\text{CeO}_2/\text{NaNbO}_3$ composites (b–d).

Fig. 3. TEM and HRTEM image of CeO₂/NaNbO₃-2 composite.

as shown in Fig. 3(b). This result further revealed that CeO₂ nanoparticles were dispersed on the surface of NaNbO₃. Furthermore, the two different gap fringes were roughly calculated to be 0.392 and 0.312 nm. The lattice spacing of 0.392 nm was in accordance with the (100) crystal plane of NaNbO₃ [38], while the lattice spacing of 0.312 nm was matched with the (111) crystal plane of CeO₂ [39]. This confirmed the formation of CeO₂/NaNbO₃ heterojunction composites [40], as shown by the red mark in Fig. 3(b). Therefore, it was expected that the formed heterojunction could facilitate the separation of photo-generated electrons and holes [41].

Fig. 4 displays the optical properties and band gap of the as-obtained samples that were investigated by DRS. Obviously, Fig. 4(a) shows that pure NaNbO₃ exhibited a strong absorption in the UV range, while the absorption capacity for visible light was poor. This results from the wide band gap of NaNbO₃. In addition, the optical absorption edge of pure NaNbO₃ was at approximately 380 nm. Obvious red shifts of the photo absorption edge were obtained for the CeO₂/NaNbO₃ composites. These shifts were ascribed to the influence of CeO₂ with a narrow band gap. Furthermore, this result indicated that CeO₂/NaNbO₃ composites might be able to decompose organic pollutants under visible light irradiation. Additionally, the visible light absorption intensity of CeO₂/NaNbO₃ composites gradually increased with the increased mass ratio of CeO₂, which revealed that more CeO₂ nanoparticles existed in the composites. According to a previous report, the band gap (E_g) of a semiconductor can be determined from the DRS plots. The E_g of the as-prepared samples was obtained through the plots of $(ah\nu)^2$ versus $(h\nu)$ [42–44]. As is shown in Fig. 4(b), E_g of NaNbO₃ was estimated to be approximately 3.28 eV, and E_g was estimated to be 3.13, 3.05, and 2.9 eV for CeO₂/NaNbO₃-1,

CeO₂/NaNbO₃-2, and CeO₂/NaNbO₃-3, respectively.

The band edge values of the conduction band and valence band of semiconductors can be roughly estimated with a simple approach [45,46]. The E_{VB} and E_{CB} of the photocatalyst can be predicted by the following equations [47]: $E_{CB} = X_{\text{photocatalyst}} - E^e - 0.5E_g$, and $E_{VB} = E_{CB} + E_g$, where X is the absolute electronegativity of the semiconductor, E^e is the energy of free electrons where the value of E^e is generally replaced by 4.5 eV, and E_g is the band gap energy of the semiconductor. According to previous reports, the X value of NaNbO₃ was 5.44 eV [23,48], and the E_g of NaNbO₃ was 3.28 eV, as was mentioned above. It was easy to calculate the E_{VB} and E_{CB} of NaNbO₃ from the above equilibrium formulae. E_{CB} and E_{VB} of NaNbO₃ were -0.7 and 2.58 eV, respectively. For the CeO₂ nanoparticles, the X value and E_g of CeO₂ from a previous report were 5.56 and 2.72 eV, respectively [49], hence the E_{CB} and E_{VB} of CeO₂ were calculated to be -0.28 and 2.42 eV, respectively.

3.2. Photocatalytic activity

The photocatalytic activity of the as-obtained samples was investigated by the degradation of the model polluted with the dye RhB and colorless antibiotic agent CIP under both UV and visible light irradiation. The photocatalytic degradation percentage of RhB and CIP without any photocatalysts could be ignored because of their very low degradation percentage that has been previously illustrated by our groups [50]. The adsorption percentages of RhB were 3.6%, 4.8%, 5.5% and 7.4% for NaNbO₃, CeO₂/NaNbO₃-1, CeO₂/NaNbO₃-2, and CeO₂/NaNbO₃-3, respectively. The composites all exhibited a higher adsorption activity than that of pure NaNbO₃. Therefore, the addition of CeO₂ would assist the photocatalytic activity although the enhanced adsorption activity was limited. The photocatalytic activities of the different samples are displayed in Fig. 5. Fig. 5(a) shows that almost 50% of RhB was degraded by pure NaNbO₃ after 30 min under UV light irradiation. Along with the increasing contents of CeO₂ in the composites, the photocatalytic property of CeO₂/NaNbO₃ was gradually enhanced. When the mass ratio of CeO₂ exceeded 2 wt%, the photocatalytic degradation capacity of CeO₂/NaNbO₃ declined. Therefore, the highest photocatalytic activity with the optimum

Fig. 4. (a) Diffuse reflectance spectra for different samples and (b) energy gap of different samples.

Fig. 5. The photocatalytic degradation of (a) RhB and (b) CIP under UV light irradiation, and the photocatalytic degradation of (c) RhB and (d) CIP under visible light irradiation by the samples.

mass ratio of CeO_2 was obtained, that is, the best mass ratio of CeO_2 was 2 wt%. Two reasons can be used to explain the results. First, in a certain range, the increased contents of CeO_2 lead to the formation of more heterojunctions in the $\text{CeO}_2/\text{NaNbO}_3$ composites. The effect of the heterojunctions is that the separation and migration rate of photogenerated charge carriers can be enhanced. As a result, the probability of the recombination of electrons and holes can be reduced [51]. Therefore, $\text{CeO}_2/\text{NaNbO}_3$ composites exhibit a higher photocatalytic property compared with pure NaNbO_3 . Second, when the mass ratio of CeO_2 exceeds 2 wt%, the number of active sites of NaNbO_3 is constant, so more heterojunctions are not formed with a further increase in CeO_2 , and the redundant CeO_2 can easily aggregate. Therefore, the aggregated CeO_2 cannot contact with NaNbO_3 to form efficient heterojunctions, which leads to the decline of the degradation capacity.

The environmental problems arising from the wide spread use of the antibiotic agent CIP and the lack of treatment processes have increasingly become more evident [52,53]. Therefore, it is of great importance to remove CIP from the environment. The adsorption percentages of CIP (initial concentration was 10 mg/L) were 1.1%, 1.7%, 2.5% and 2.8% for NaNbO_3 , $\text{CeO}_2/\text{NaNbO}_3$ -1, $\text{CeO}_2/\text{NaNbO}_3$ -2, and $\text{CeO}_2/\text{NaNbO}_3$ -3, respectively. Fig. 5(b) shows that the change of the photocatalytic degradation percentage of CIP for the different samples was

not drastic. The photocatalytic degradation percentage of CIP by NaNbO_3 was 49% under UV light irradiation after 12 min, while the $\text{CeO}_2/\text{NaNbO}_3$ -2 composite decomposed 58% of CIP. Compared with pure NaNbO_3 , $\text{CeO}_2/\text{NaNbO}_3$ composites could decompose more CIP. The degradation tendency of CIP by the as-prepared samples was the same with that of RhB under UV light irradiation.

For the results of the photocatalytic performance under the visible light irradiation, Fig. 5(c) and (d) display the degradation percentages of RhB and CIP for the different samples. After 180 min, 50% of RhB was decomposed by $\text{CeO}_2/\text{NaNbO}_3$ -2, while the degradation percentage of CIP reached approximately 50% with $\text{CeO}_2/\text{NaNbO}_3$ -2 after 60 min. This revealed that the composites decomposed CIP easier than RhB. In Fig. 5(c), a part of RhB can be decomposed by pure NaNbO_3 , which was attributed to the sensitized effect of the RhB. Furthermore, the degradation tendency of RhB by the composites under visible light irradiation was identical with that under UV light irradiation. In Fig. 5(d), the CIP was almost not decomposed by the pure NaNbO_3 under visible light irradiation owing to the wide band gap of NaNbO_3 . The degradation percentage of CIP by $\text{CeO}_2/\text{NaNbO}_3$ composites first increased then decreased with an increasing content of CeO_2 . The result was in good agreement with the above mentioned photocatalytic results. Therefore, the results of the photocatalytic degradation of the two

different kinds of pollutants revealed that CeO_2 -decorated NaNbO_3 heterojunction composites possess a high photocatalytic property under both UV and visible light irradiation.

Moreover, apart from the above explanation for the photocatalytic performance, the reaction kinetics of the degradation process of RhB and CIP were used to demonstrate the photocatalytic activity of the as-obtained samples. The result were obtained generally from an apparent pseudo-first-order model, as expressed by the following equation [54]: $\ln(C_0/C) = kt$. Fig. 6 displays the reaction kinetics of the degradation process of RhB and CIP under both UV and visible light irradiation, and the k values of the different samples are shown in Table 1 (K_a and K_b was used to express the apparent rate constant of the RhB and CIP under UV light irradiation, respectively; K_c and K_d relate to the reaction kinetics of RhB and CIP under visible light irradiation, respectively). According to the fitted plot of the data, the obtained R^2 reached approximately 0.99, which suggested that the pseudo-first-order kinetics model was valid to illustrate the photocatalytic property [55]. Herein, as is shown in Fig. 6, the results of the reaction kinetics of different samples all indicated that the degradation capacity of the composites for different pollutants first increased then decreased along with the increased contents of CeO_2 under both UV and visible light irradiation. The results are consistent with those of the above section. In addition, the K values of the different samples (Table 1) revealed that $\text{CeO}_2/\text{NaNbO}_3$ -2 exhibited a maximum rate

Table 1

The apparent rate constants for different samples.

Sample	K_a	K_b	K_c	K_d
NaNbO_3	0.023	0.055	0.00088	0.0011
$\text{CeO}_2/\text{NaNbO}_3$ -1	0.046	0.059	0.0061	0.0018
$\text{CeO}_2/\text{NaNbO}_3$ -2	0.061	0.073	0.012	0.0037
$\text{CeO}_2/\text{NaNbO}_3$ -3	0.054	0.069	0.008	0.0021

constant, which was almost 2.65 times and 1.34 times higher than that of pure NaNbO_3 under UV light irradiation for the degradation of RhB and CIP, respectively. Under visible light irradiation, the K value of $\text{CeO}_2/\text{NaNbO}_3$ -2 was approximately 3.36 times and 141 times higher than that of pure NaNbO_3 for the degradation of RhB and CIP, respectively.

3.3. Possible mechanism of the enhanced photocatalytic activity for $\text{CeO}_2/\text{NaNbO}_3$ samples

Some reactive species, such as h^+ , $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ radicals, are known to exist during the photocatalytic degradation process and can induce the degradation of pollutants. Therefore, a trapping experiment was carried out in an attempt to elucidate the reaction mechanism. Tert-butanol, EDTA- Na_2 and p -benzoquinone served as the scavengers of $\bullet\text{OH}$, h^+ and $\bullet\text{O}_2^-$ radicals, respectively [56]. If the activity was suppressed after the addition of the scavengers, the corresponding radical spe-

Fig. 6. The kinetic constants of RhB (a) and CIP (b) degradation under UV light irradiation, CIP (c) and RhB (d) degradation under visible light irradiation by different samples.

Fig. 7. Effect of scavengers on the photocatalytic degradation of RhB by CeO₂/NaNbO₃-2 under UV light irradiation.

cies could be designated to play an important role in the photocatalytic degradation reaction [23,57,58]. The obtained results of the trapping experiment of RhB degradation by CeO₂/NaNbO₃-2 under UV light irradiation are shown in Fig. 7. The addition of *p*-benzoquinone decreased the decomposition of RhB seriously (only 8.2% was decomposed), which indicated that $\bullet\text{O}_2^-$ radicals played an important role in the photocatalytic degradation of RhB. When tert-butanol and EDTA-Na₂ were added, the degradation percentage of RhB decreased to 22.6% and 15%, respectively. The degradation percentages of RhB after adding the above three scavengers were much lower than the situation without any scavenger. The results illustrated that $\bullet\text{OH}$, $\bullet\text{O}_2^-$ radicals and h^+ all participated in the photocatalytic degradation reaction of RhB.

The efficient photocatalysts exhibit an important feature where they can achieve a high separation rate of electrons and holes [53]. To probe the recombination of the charge carriers for different samples, the PL spectra were measured and the results are shown in Fig. 8. The emission peak of pure NaNbO₃ centered at around 405 nm was stronger compared with the other peaks. With the increasing mass ratio of CeO₂, the CeO₂/NaNbO₃ composites displayed a stronger emission peak

Fig. 8. Photoluminescence spectra of NaNbO₃, CeO₂/NaNbO₃ composites.

centered at around 470 nm rather than around 405 nm. This may result from the emission peak of pure CeO₂ possibly being centered around 470 nm. The weaker the intensity of PL, the lower the recombination probability of photoexcited electron and hole pairs [59,60]. The PL intensity of the different samples followed the following order: NaNbO₃ > CeO₂/NaNbO₃-1 > CeO₂/NaNbO₃-3 > CeO₂/NaNbO₃-2. Therefore, we could conclude that the CeO₂/NaNbO₃ composites exhibited a higher separation rate of the charge carriers compared with pure NaNbO₃. In addition, CeO₂/NaNbO₃-2 composite possessed the lowest recombination rate among all of the composites, which meant that more electrons and holes could participate in the redox reaction, and thus induced the highest photocatalytic activity for the degradation of different pollutants. This result further illustrates that the photocatalytic performance of the heterojunction system was enhanced because of this inbuilt ability to separate the photogenerated charge carriers.

According to the reaction principle of photocatalysts, after the separation of photoexcited charge carriers, the migration rate and the charge consumption of electrons and holes will act as key factors to determine the photocatalytic property [61]. Photocurrent and EIS were used to investigate the transfer rate

Fig. 9. Photocurrent responses of CeO₂/NaNbO₃-2 (a), CeO₂/NaNbO₃-3 (b), CeO₂/NaNbO₃-1(c), and NaNbO₃ (d); (B) EIS property of the as-prepared samples.

of electrons, and the obtained results are displayed in Fig. 9. For the results of the photocurrent, the intensity directly expressed the efficiency of the photocurrent. Fig. 9(a) shows that the photocurrent intensity of $\text{CeO}_2/\text{NaNbO}_3\text{-2}$ was the highest, which was followed by $\text{CeO}_2/\text{NaNbO}_3\text{-3}$ and $\text{CeO}_2/\text{NaNbO}_3\text{-1}$. Pure NaNbO_3 exhibited the lowest photocurrent intensity compared with the composites. This result indicated that composites possessed a higher transfer rate of charge carriers than pure NaNbO_3 . Nyquist plots were used to express the result of EIS. The smaller the radius of the Nyquist circle, the lower the charge-transfer resistance [62]. As is shown in Fig. 9(b), pure NaNbO_3 exhibited the largest radius, and with an increasing content of CeO_2 , the radius of the composites first decreased then increased. The $\text{CeO}_2/\text{NaNbO}_3\text{-2}$ composite exhibited the smallest radius compared with the other samples. This revealed that the charge-transfer resistance of the composites was lower than that of pure NaNbO_3 . Hence, the $\text{CeO}_2/\text{NaNbO}_3$ composites possessed a higher charge-transfer rate compared with pure NaNbO_3 . Therefore, the low recombination possibility of the photogenerated electron and hole pairs and the high transfer rate of the charge carriers acted in the function of a heterojunction to improve the photocatalytic performance.

During the photocatalytic degradation processes, the reuse and stability of the photocatalyst are a factor to evaluate the quality of the photocatalyst. To evaluate the reusability and stability of the $\text{CeO}_2/\text{NaNbO}_3$ nanocomposites, recycling reactions were performed, where the sample with the highest photocatalytic activity was used to degrade RhB under UV light irradiation, and the results are displayed in Fig. 10. The specific procedure of the recycling reactions was as follows. First, after completion of the photocatalytic degradation reaction, the photocatalyst was washed with a large amount of water and dried at 60 °C. Second, the obtained sample was attired with the dye to conduct the same photocatalytic reaction. Finally, the obtained photocatalyst was reused for the next cycle. After three cycles, it could be clearly seen that the photocatalytic activity of photocatalysts exhibited no apparent change. Therefore, this showed that the photocatalysts exhibited excellent reusability and stability.

Fig. 10. Cycling runs for the photodegradation of RhB by $\text{CeO}_2/\text{NaNbO}_3\text{-2}$ under UV light irradiation.

The band gap structures of NaNbO_3 and CeO_2 were obtained in the above section. Furthermore, it was observed that the $\cdot\text{OH}$, $\cdot\text{O}_2^-$ radicals and h^+ all participated in the photocatalytic degradation reaction of pollutants, so a possible reaction mechanism of $\text{CeO}_2/\text{NaNbO}_3$ is proposed. The schematic is shown in Fig. 11. According to the E_g of NaNbO_3 and CeO_2 , we could determine that the n-n type heterojunction structure belongs to the type-I [63]. As is shown in Fig. 11(a), under UV light irradiation, after the samples are irradiated, NaNbO_3 and CeO_2 both generate charge carriers. First, the photoexcited electrons in the CB of NaNbO_3 transfer to the CB of CeO_2 because of the higher CB position of NaNbO_3 , and the holes in the VB of NaNbO_3 migrate to the VB of CeO_2 owing to the higher VB position of NaNbO_3 . During the process, it should be noted that the transfer rate of electrons is faster than that of holes, and the difference of migration rate between electrons and holes leads to a greater separation. Then, the electrons in the CB of NaNbO_3 can react with oxygen to form $\cdot\text{O}_2^-$ radicals. In this way, the CB edge potential of CeO_2 (-0.28 eV vs. NHE) is more positive than the standard redox potential $E^\theta(\text{O}_2/\cdot\text{O}_2^-)$ (-0.33 eV vs. NHE), thus the electrons in the CB of CeO_2 cannot reduce O_2 to yield $\cdot\text{O}_2^-$ [64]. Furthermore, $E^\theta(\text{O}_2/\cdot\text{HO}_2)$ (-0.05 eV vs. NHE) and $E^\theta(\text{O}_2/\text{H}_2\text{O}_2)$ (0.695 eV vs. NHE) are more positive than the CB edge potential of CeO_2 and NaNbO_3 , respectively. Meanwhile, the h^+ in the VB of CeO_2 and NaNbO_3 not only oxidize OH^- or H_2O to $\cdot\text{OH}$ but also directly decompose the RhB. Therefore, the photocatalytic activity is significantly promoted.

However, only the CeO_2 can be excited to generate charge carriers after the samples are irradiated by visible light. The above mentioned reaction mechanism of the $\text{CeO}_2/\text{NaNbO}_3$ is not appropriate to explain the high photocatalytic activity of the composites under visible light irradiation. For the n-n type heterojunction with type-I, the possible reaction mechanism has been reported previously [65]. First, before the irradiation, for the n-n type heterojunction $\text{CeO}_2/\text{NaNbO}_3$, the electrons of NaNbO_3 transfer to the CeO_2 because of the higher CB position of NaNbO_3 . This results in a positive region on NaNbO_3 and a negatively charged region on CeO_2 . Next, a built-in electric field is established in the junction area until the Fermi level reaches

Fig. 11. Schematic diagram of the possible photocatalytic mechanism over $\text{CeO}_2/\text{NaNbO}_3$ under UV and visible light irradiation.

equilibrium. Under visible light irradiation, as is shown in Fig. 11(b), the built-in electric field not only promotes the separation of electrons and holes in CeO_2 but also facilitates the electrons flowing towards NaNbO_3 [66]. However, the electrons cannot migrate to NaNbO_3 , which leads to the electrons accumulating at the interface. These electrons and holes on the valence band of CeO_2 both take part in the redox reaction to degrade the pollutants. Hence, under UV light irradiation, the improvement of photocatalytic activity is attributed to the effect of the heterojunction, while under visible light, the built-in electric field acts as the dominating factor to enhance the photocatalytic performance of $\text{CeO}_2/\text{NaNbO}_3$. The heterojunction and the built-in electric field both improve the separation of charge carries and enhance the transfer rate of electrons.

4. Conclusions

In summary, $\text{CeO}_2/\text{NaNbO}_3$ heterostructure composites were successfully synthesized by a simple and flexible method. The photocatalytic performance of the composites was improved compared with pure NaNbO_3 under both UV and visible light irradiation, and the composites could degrade CIP easier than RhB. Furthermore, the amount of CeO_2 exhibited an apparent effect on the photocatalytic activity of the composites, where the optimum mass ratio of CeO_2 in the $\text{CeO}_2/\text{NaNbO}_3$ composites was 2.0%. The degradation ability of RhB and CIP by $\text{CeO}_2/\text{NaNbO}_3$ -2 was 1.4 times and 2.7 times higher than that of pure NaNbO_3 under UV light irradiation, while the decomposition capacity of RhB and CIP by $\text{CeO}_2/\text{NaNbO}_3$ -2 was 13.6 times and 3.4 times higher than that of pure NaNbO_3 under visible light irradiation. The significant improvement in the photocatalytic property under UV light irradiation was ascribed to the formation of heterojunctions, which could not only enhance the transfer rate of photogenerated charge in the internal field, but also reduce the recombination probability of electron and hole pairs. These advantages have been demonstrated by the results from the photocurrent, EIS and PL studies. Furthermore, holes, $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ all participate in decomposing contaminants. Under visible light irradiation, the improved

photocatalytic performance results from the built-in electric field, which also promotes the separation of electron and hole pairs.

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Graphical Abstract

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Hydrothermal synthesis of $\text{CeO}_2/\text{NaNbO}_3$ composites with enhanced photocatalytic performance

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The $\text{CeO}_2/\text{NaNbO}_3$ heterojunction composites were synthesized by a simple hydrothermal method. The formation of heterojunctions promoted the separation of photogenerated electrons and holes, thereby resulting in a higher the photocatalytic activity.

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CeO₂/NaNbO₃复合物的水热合成及其光催化性能的提高

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摘要: 钙钛矿型NaNbO₃由于其非线性光学、铁电、离子导电性、高声速、光催化性能和光折变等优良性能而备受关注。在光催化反应中, 宽禁带宽度(≈ 3.24 eV)使NaNbO₃具有较高的导带底(CBM)和较低的价带顶(VBM)。因此, 它表现出强烈的光氧化和光还原能力。众所周知, 钙钛矿型光催化剂光电子激发和传输能力的增强归因于其较高的对称性。因此, 具有高

对称性的立方 NaNbO_3 有利于电子激发和转移。但是,一些固有的缺点,包括电荷分离效率低、量子产率差和光催化活性差等,限制了其在光催化领域的实际应用。为了解决这些问题,一种有效的方法是与其他半导体结合,形成具有改善光催化活性的异质结复合物。 CeO_2 作为传统的催化剂在光催化领域得到了广泛研究。 CeO_2 具有稳定、无毒的特点,是一种n型半导体。目前,研究人员已经发现 CeO_2 与不同半导体的耦合可以提高 CeO_2 的光催化活性。这归因于能级水平的适当匹配。

本文通过简易水热法制备了高活性的 $\text{CeO}_2/\text{NaNbO}_3$ 异质结复合物,并采用X射线粉末衍射(XRD)、扫描电子显微镜(SEM)、透射电子显微镜(TEM, HRTEM)和紫外-可见漫反射光谱(DRS)等表征技术研究了所制光催化剂的物相结构、样品形貌和光学性能。所制样品的光催化活性通过光催化降解无色抗菌环丙沙星(CIP)和染料罗丹明B(RhB)证实。结果表明,在紫外和可见光照射, $\text{CeO}_2/\text{NaNbO}_3$ 复合物比纯 NaNbO_3 具有更高的光催化活性。此外, $\text{CeO}_2/\text{NaNbO}_3$ 复合物中 CeO_2 的最佳质量比为2.0 wt%。紫外光照射下光催化性能的显著提高是由于 $\text{CeO}_2/\text{NaNbO}_3$ 异质结的形成不仅提高了光生电荷在界面范围内的迁移速率,而且降低了光激发产生的电子和空穴的复合率。可见光照射下内置电场的存在促进了电子和空穴的分离,提高了光催化性能。此外,利用光致发光(PL)光谱、光电流、电化学阻抗谱和捕获实验证明了样品的光催化反应机理。捕获实验结果表明, $\cdot\text{OH}$ 自由基、 $\cdot\text{O}_2^-$ 自由基和空穴都参与了RhB的光催化降解过程。最后,探讨了提高光催化活性的可能机理。

关键词: 异质结; NaNbO_3 ; CeO_2 ; 光催化

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