Nb₂O₅/ZnAl–LDH composites and its calcined products for photocatalytic degradation of congo red under visible light irradiation

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Abstract: We demonstrate novel Nb₂O₅·nH₂O/LDH composites that were firstly fabricated *via* hydrothermal synthesis of Nb₂O₅ microspheres followed by *in situ* growth of ZnAl–LDH shell. The structure of the Nb₂O₅·nH₂O/LDH was investigated, and the results showed that the ZnAl–LDH had grown inside the slit of burr–surface of Nb₂O₅·nH₂O microspheres. Its calcined product Nb₂O₅/LDO shows a high adsorption capacity of the congo red (abbr. CR). The photocatalytic experiment results indicate that the Nb₂O₅/LDO displays obviously photoactivity and the degradation of CR could reach a ratio of 85% under visible–light irradiation, but the Nb₂O₅ alone exhibits no photocatalytic activity for CR. The ·OH radicals may be predominant oxidative species responsible.

Key words: Semiconductors; Nb₂O₅; layered double hydroxides; composite materials; degradation under visible light irradiation;

1. Introduction

The dye-contaminated wastewater has been one of the most serious environmental pollution problems [1]. Various treatment technologies have been applied for dyes treatment, including adsorption, filtration, biological treatment, photocatalytic degradation, and so on. Photocatalytic degradation under visible light irradiation has gained widespread attention because of its rapid, high efficiency, economical and no secondary pollution [2, 3]. Now, a number of photocatalytic materials such as TiO_2 [4], Nb_2O_5 [5], CuO [6], ZnS [7], have been developed. Among these photocatalysts, niobium oxide (Nb_2O_5) with excellent chemical stability and environmental friendly behaviour has been considered as a promising material.

As we know, Nb_2O_5 is a photosensitive catalyst, and the degradation process of dyes contains three steps [5, 8, 9]: (1) dyes adsorbed onto Nb_2O_5 surface; (2) dye adsorbing photons and then excited; (3) excited dye transfers electrons to the conduction band of the semiconductor. Obviously, the first step of the adsorption is a very important link. Prado *et al.* [9] had investigated the surface charge properties of Nb_2O_5 in detail, and pointed out that the surface charge of Nb_2O_5 took on negative charge (MO^-) in weak acid, neutral or alkaline condition. So, Nb_2O_5 catalyst can absorb cationic dyes and degrade them, such as Rhodamine [10], and Methylene blue [11]. However, because the anionic dyes cannot be adsorbed onto surface of Nb_2O_5 in the above conditions, so there are few reports of single Nb_2O_5 degradation anionic dyes, such as Congo red (CR). The application prospect of Nb_2O_5 in wastewater treatment is very limited.

Recently, layered double oxides (LDO), which are the calcined products of layered double hydroxides, are widely studied and reported as adsorbent materials for removing anionic dyes due to their high surface area [12] and unique memory effect [13, 14]. Taking advantage of the “memory effect”, anionic dyes such as CR, have been easily adsorbed onto surface and interlayer of as-formed LDH. Herein, $\text{ZnAl}-\text{CO}_3$ -LDH had grown firstly inside the slit of burr-surface of the $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$

microspheres *via* hydrothermal method. The obtained $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}/\text{LDH}$ was calcined to prepare $\text{Nb}_2\text{O}_5/\text{LDO}$ catalyst. Compared with the Nb_2O_5 catalyst alone with no degradation effect for CR, the $\text{Nb}_2\text{O}_5/\text{LDO}$ composite shows good photo degradation under visible light irradiation, exhibiting a high degradation rate of 85% for CR

2 . Experimental

Synthesis of $\text{Nb}_2\text{O}_5/\text{LDO}$ composite

Firstly, $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ microspheres were prepared through the hydrothermal synthesis, and detailed process can be found in the (supporting information). Next, 0.5 g of obtained $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ microspheres were dispersed into 200 mL deionized water, and then scattered for 60 min using ultrasonic mill. The white suspension was then transferred into three-neck round-bottomed flask, and 0.298 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.005 mol/L), 0.188 g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.0025 mol/L) and 0.210 g urea (0.018 mol/L) were also added into the suspension, and then heated to 100 °C under reflux for 24 h with magnetic stirring. The product was washed, dried and denoted $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}/\text{LDH}$. Finally, $\text{Nb}_2\text{O}_5/\text{LDO}$ was prepared by calcining $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}/\text{LDH}$ product at 400 °C for 4 h. Photocatalytic activity of $\text{Nb}_2\text{O}_5/\text{LDO}$ was investigated, and detailed process can be found in the (supporting information). Catalysts characterization can be found in the (supporting information).

3. Results and discussion

Fig. 1a shows the XRD pattern of the $\text{CO}_3\text{-LDH}$, $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}/\text{LDH}$ and $\text{Nb}_2\text{O}_5/\text{LDO}$. For $\text{CO}_3\text{-LDH}$, a series of strong (*00l*) reflections at $2\theta = 11.6^\circ$, 23.5° , and 34.5° observed are characteristics of a layered phase, which shows a basal spacing $d_{(003)}$ of 0.76 nm meaning CO_3^{2-} in the interlayer region. The typical diffraction peaks at $2\theta = 22.7^\circ$ and 46.4° can be indexed to the (001) and (002) reflections of $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ (JCPDS: 28-0371), and the broad peaks (▼) at $2\theta = 26^\circ$ are relative to the hydrated niobium oxides[15]. In the case of $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}/\text{LDH}$ precursor, superimposition XRD patterns of LDH and $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ were observed, which meant the combination of the two compositions. After 400 °C calcination, the

series of (00 l) reflections of CO₃-LDH disappear, indicating the formation of LDO, the same as reported in the literature[16].

The FT-IR spectra of the as-prepared samples are shown in Fig. 1b. For the CO₃-LDH sample, the peak at 1356 cm⁻¹ is due to the vibration of CO₃²⁻ anion in LDH interlayer [17]. The Nb₂O₅·nH₂O microspheres show the intense broad band centered at around 655 cm⁻¹ due to the stretching vibration of Nb-O groups accompanying a shoulder near 860 cm⁻¹ [5]. Obviously, the FT-IR spectrum of Nb₂O₅·nH₂O/LDH composite displays the existence of characteristic bands of Nb₂O₅·nH₂O and CO₃-LDH samples, further confirming the formation of Nb₂O₅·nH₂O/LDH heterostructure. In addition, the band at 1356 cm⁻¹ attributed to CO₃²⁻ disappeared after the calcination of Nb₂O₅·nH₂O/LDH under 400 °C, meaning the collapse of the layered structure and the formation of Nb₂O₅/LDO

Fig. 1. (a) XRD patterns and (b) FT-IR spectra of CO₃-LDH, Nb₂O₅·nH₂O, Nb₂O₅·nH₂O/ LDH and Nb₂O₅/ LDO.

The morphologies of the as-prepared samples were characterized by scanning electron microscopy (SEM). As shown in Fig. 2a, the obtained Nb₂O₅·nH₂O sample is in the form of uniform microspheres with burr-surface and the average size of ~1 μm. After the in situ growth of CO₃-LDH shell, the burr-surface morphology was covered by many rod-like particles inside the slit of burr-surface of Nb₂O₅·nH₂O microspheres, which also were observed in the corresponding HRTEM image (Fig.

2b). These rod-like particles were determined to be $\text{CO}_3\text{-LDH}$, because a typical lattice of 0.76 nm was observed (Fig. 2b). Combining with the XRD, FT-IR, SEM and TEM results, it can be confirmed that the $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}/\text{LDH}$ composite was synthesized. In addition, the morphologies are retained after $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}/\text{LDH}$ calcined to be $\text{Nb}_2\text{O}_5/\text{LDO}$. SEM-EDX is carried out for clarifying the composition of $\text{Nb}_2\text{O}_5/\text{LDO}$ (Fig. 2c) and the results reveal that Zn and Al elements are found besides Nb and O, and Zn/Al molar ratio is about 2. The UV-Vis DRS spectra of Nb_2O_5 microsphere and $\text{Nb}_2\text{O}_5/\text{LDO}$ are shown in Fig. 2d. Compared with single Nb_2O_5 , the absorption edges of $\text{Nb}_2\text{O}_5/\text{LDO}$ just had small change, and were still retained in the ultraviolet region, indicating that the $\text{Nb}_2\text{O}_5/\text{LDO}$ was photosensitive catalyst in the degradation of CR.

Fig.2. (a) SEM and (b) TEM images of $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}/\text{LDH}$ and $\text{Nb}_2\text{O}_5/\text{LDO}$, and (c) EDX of $\text{Nb}_2\text{O}_5/\text{LDO}$ and (d) UV–Vis DRS spectra of Nb_2O_5 and $\text{Nb}_2\text{O}_5/\text{LDO}$.

The photocatalytic activity of the $\text{Nb}_2\text{O}_5/\text{LDO}$ sample was evaluated for CR photodegradation under visible light irradiation, and the results were compared with those of CR photolysis (without photocatalyst) and with Nb_2O_5 alone (Fig. 3a). It was observed that the photolysis of CR itself was negligible, confirming its photo stabilization under visible light. Using Nb_2O_5 itself as a catalyst, CR was not degraded under visible–light irradiation, because the surface charge of Nb_2O_5 took to be electronegative (MO^-) at pH 6.5 [8], so Nb_2O_5 cannot adsorb the negatively charged CR and degrade it. Moreover, using corresponding amount of LDO, there is no degradation for CR (Figure S1). Using $\text{Nb}_2\text{O}_5/\text{LDO}$ as a catalyst, about 35% of CR can be absorbed to $\text{Nb}_2\text{O}_5/\text{LDO}$ in the dark as shown in Fig. 3(a), indicating that $\text{Nb}_2\text{O}_5/\text{LDO}$ possesses a high adsorption capacity for CR, beneficial for photocatalytic degradation of it on the surface of the photocatalyst under visible–light irradiation. With 390 min of visible–light irradiation, the concentration of CR decreased to 15%, suggesting that the degradation of CR could reach 85% in the presence of $\text{Nb}_2\text{O}_5/\text{LDO}$. The photocatalytic experimental data were found to fit pseudo-first-order kinetics (Figure S2), and the degradation constant of the sample was 0.003. Fig. 3b shows absorption variation of CR over $\text{Nb}_2\text{O}_5/\text{LDO}$ photocatalyst, which again confirm that CR degrades obviously with the increase in the time interval. In order to prove that the removal of CR is a degradation process rather than adsorption, the removal percentages with time increasing under dark adsorption and visible light irradiation was compared in Fig. 3c. Adsorption equilibrium time of CR on $\text{LDO}/\text{Nb}_2\text{O}_5$ is about 30 min, and the removal percentage is almost unchanged over time under dark, which is consistent with the results of the literature [1]. However, it is obvious that the removal percentage has been decreasing over time under visible light irradiation. Therefore, the $\text{Nb}_2\text{O}_5/\text{LDO}$ is indeed able to degrade the anionic dye of CR under visible light irradiation. The photocatalytic degradation processs of $\text{Nb}_2\text{O}_5/\text{LDO}$ is investigated by using isopropanol and KI as $\cdot\text{OH}$ radicals and hole

scavengers, respectively. As shown in Fig. 3d, the photodegradation rate of CR is slightly prevented in $\text{Nb}_2\text{O}_5/\text{LDO}$ –KI system, whereas it is obviously inhibited in $\text{Nb}_2\text{O}_5/\text{LDO}$ –isopropanol system, inferring the $\cdot\text{OH}$ radicals may be predominant oxidative species responsible.

Fig. 3. Photocatalytic activity under visible-light irradiation. (a) the curve of C_0/C versus time interval, (b) Absorption variation of CR over $\text{Nb}_2\text{O}_5/\text{LDO}$ and (c) the curve of removal percentages versus time under dark adsorption and visible light irradiation and (d) photodegradation of CR by $\text{Nb}_2\text{O}_5/\text{LDO}$ under various solutions.

4. Conclusions

$\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}/\text{LDH}$ composites, CO_3 -LDH grown inside the slit of burr-surface of the $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ microspheres *via* hydrothermal method, are successfully designed and synthesized. Its calcined products show a high adsorption capacity for CR due to outside LDO. The $\text{Nb}_2\text{O}_5/\text{LDO}$ catalyst shows good photo degradation under visible light irradiation compared with single Nb_2O_5 catalyst no degradation effect of CR. Thus, $\text{Nb}_2\text{O}_5/\text{LDO}$ can be applied as photocatalyst to degrade CR.

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