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Article

Synergistic effects in N-K₂Ti₄O₉/UiO-66-NH₂ composites and their photocatalysis degradation of cationic dyes

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ABSTRACT

N-K₂Ti₄O₉/UiO-66-NH₂ composites synthesized by a facile solvothermal method have a core-shell structure with UiO-66-NH₂ forming the shell around a N-K₂Ti₄O₉ core. Their photocatalytic activities in the degradation of dyes under visible light irradiation were investigated. The N-K₂Ti₄O₉/UiO-66-NH₂ composites exhibited higher photocatalytic activity than the pure components. This synergistic effect was due to the high adsorption capacity of UiO-66-NH₂ and that the two components together induced an enhanced separation efficiency of photogenerated electron-hole pairs. The mass ratio of N-K₂Ti₄O₉ to ZrCl₄ of 3:7 in the composite exhibited the highest photocatalytic activity. Due to the electrostatic attraction between the negatively charged backbone of UiO-66-NH₂ with the positively charged groups of cationic dyes, the composites were more photocatalytically active for cationic dyes than for anionic dyes.

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1. Introduction

Dyes are widely used in the textile, paper and printing industries, so the treatment of dye-containing wastewater is a crucial problem to solve [1–3]. Semiconductor (SC) photocatalysis for the degradation of organic dyes in water has emerged as a renewable technology [4–6]. Potassium titanate (K₂Ti₄O₉) is a potential material for the photocatalytic reaction due to its nontoxicity, low cost, physical and chemical stability, availability, and unique electronic and optical properties [7–9]. However, because its band gap is 3.2–3.4 eV [10], K₂Ti₄O₉ can only be used under ultraviolet light. It is of great interest to try to take advantage of the visible light in solar energy by reducing its band gap to widen its practical applications. Doping N

element into K₂Ti₄O₉ (N-K₂Ti₄O₉) is a common method of reducing the band gap [11,12].

Recent research has been focused on metal-organic frameworks (MOFs), which are made of metal clusters linked by organic ligands [13–17]. Due to their uniform but tunable pore size and high specific surface area, MOFs are considered for adsorption [18], storage [19–21], and health care applications [22]. A group at Valencia [23] first synthesized a Zr(IV)-based MOF (UiO-66-NH₂), which is based on a Zr₆O₄(OH)₄ octahedron and a lattice formed by 12-fold connection through a 2-amino-1,4-benzene-dicarboxylate linker. The UiO-66-NH₂ framework is robust and can undergo isorecticular functionalization without losing its high hydrothermal and chemical stability. Shen et al. [24] have shown that UiO-66-NH₂ has high

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visible light photocatalytic activity for reducing Cr(VI).

It has been found that the combination of two different semiconductors can yield an enhanced photocatalytic activity via a synergistic effect such as more efficient charge separation [25–27]. In this work, N-K₂Ti₄O₉/UiO-66-NH₂ composites were prepared by a facile solvothermal method and shown to exhibit enhanced photocatalytic activity for dye degradation under visible light by its comparison with the two pure component materials. Moreover, the composites exhibited better photocatalytic activity for cationic dyes than anionic dyes.

2. Experimental

2.1. Materials

Potassium carbonate, titanium dioxide, urea, zirconium tetrachloride, *N,N*-dimethyl formamide (DMF), and chloroform were obtained from Sinopharm Chemical Reagent Co., Ltd. 2-Amino-1,4-benzenedicarboxylic acid was purchased from Tokyo Chemical Industry Co., Ltd. All chemicals were used as received without further purification.

2.2. Preparation of catalysts

K₂Ti₄O₉ was produced by the direct calcination of K₂CO₃ and TiO₂ [28]. Then the K₂Ti₄O₉ (1.0000 g) and urea (2.0000 g) were suspended in ethanol (15 mL) by stirring. The mixture was heated to completely evaporate the solvent, followed by calcination in air at 400 °C for 4 h to yield N-K₂Ti₄O₉ [29].

The N-K₂Ti₄O₉/UiO-66-NH₂ composites were synthesized as UiO-66-NH₂ with different N-K₂Ti₄O₉/ZrCl₄ ratios [23]. A typical method is as follows. ZrCl₄ (0.0848 g), 2-amino-1,4-benzenedicarboxylic acid (0.0656 g), and benzoic acid (0.984 g) were dissolved in DMF (42 mL). N-K₂Ti₄O₉ (0.0371 g) was added into the solution under ultrasonic vibration for 30 min. The mixture was transferred to a stainless steel Teflon-lined autoclave of 50 mL capacity and maintained at 120 °C for 24 h. Then, the autoclave was cooled in air to room temperature and the resulting solid was filtered, repeatedly washed with CHCl₃ and dried at room temperature. The prepared composite was called N-K₂Ti₄O₉/UiO-66-NH₂(3:7) where the mass ratio of N-K₂Ti₄O₉ to ZrCl₄ was 3:7. Similarly, when the molar ratio of N-K₂Ti₄O₉ to ZrCl₄ was *x*:*y*, the composite was named N-K₂Ti₄O₉/UiO-66-NH₂(*x*:*y*).

2.3. Characterization

X-ray diffraction (XRD) patterns of the samples were determined in the range of $2\theta = 4^\circ$ – 60° on a Rigaku D/max-2500V X-ray diffractometer using Cu-K α ($\lambda = 0.154$ nm) radiation. The morphological analysis of the samples was done using a JEM-2100F field emission transmission electron microscopy (FETEM) equipped with an energy dispersive X-ray spectrometer (EDS). Thermogravimetric analysis (TGA) of samples was carried out on a Perkin-Elmer Diamond TG thermal analyzer at a rate of 10 °C/min. X-ray photoelectron spectroscopy (XPS) was conducted using an ESCALAB250 spectrometer. The tran-

sient photocurrent responses were measured on an electrochemical system (CHI-660D). Ultraviolet-visible (UV-vis) spectra were recorded on a DUV-3700 spectrometer.

2.4. Adsorption experiments

The adsorption of dye was measured at ambient pressure and 25 °C in the dark. The photocatalyst (20 mg) was added into 100 mL dye aqueous solution (20 mg/L) with continuous stirring. Samples were taken at a fixed times and were filtered by a 0.22 μ m filter. The absorbance of the filtrate was measured using a Shimadzu UV-240 spectrophotometer.

2.5. Photocatalytic experiments

The photocatalytic degradation of dye was measured at ambient pressure and 25 °C in a homemade photochemical reaction equipment. The light source was a PHILIPS 70 W metal halidelamp ($\lambda < 380$ nm was filtered out by a cutoff filter). A 20 mg photocatalyst was added into 100 mL dye aqueous solution (5 mg/L). Before irradiation, the suspension was continuously stirred for 24 h in the dark in order to reach adsorption-desorption equilibrium between dye and the photocata-

Fig. 1. FETEM images of (a) UiO-66-NH₂, (b) N-K₂Ti₄O₉ and (c) N-K₂Ti₄O₉/UiO-66-NH₂(3:7); (d) EDS spectrum and (e) HRTEM image of N-K₂Ti₄O₉/UiO-66-NH₂(3:7).

lyst. The supernatant liquid was obtained by filtration by 0.22 μm filter and examined using a Shimadzu UV-240 spectrophotometer. For comparison, the photocatalytic activities of UiO-66-NH₂ and N-K₂Ti₄O₉ were also tested under the same conditions.

3. Results and discussion

3.1. Morphology and composition of N-K₂Ti₄O₉/UiO-66-NH₂ photocatalysts

It can be seen from Fig. 1(a) that pure UiO-66-NH₂ comprised disc-like particles with the particle size in the range of 30–40 nm. In contrast, pure N-K₂Ti₄O₉ in Fig. 1(b) comprised rod-like microcrystallites with diameters between 100 and 350 nm, and length of a few micrometers. Fig. 1(c) displays that the N-K₂Ti₄O₉ rod-like microcrystallites were covered by UiO-66-NH₂ in the N-K₂Ti₄O₉/UiO-66-NH₂ composite, which exhibited a core-shell structure. As shown in Fig. 1(e), the lattice fringes of the (512) and (403) planes of N-K₂Ti₄O₉ can be clearly seen. Although the crystal structure of UiO-66-NH₂ was destroyed by electron beam bombardment, the clear heterojunction interfaces of N-K₂Ti₄O₉/UiO-66-NH₂ can be observed in Fig. 1(e). These suggest that the N-K₂Ti₄O₉ rod-like microcrystallites were in intimate contact with UiO-66-NH₂.

The EDS spectra of N-K₂Ti₄O₉/UiO-66-NH₂(3:7) indicated that N, K, Ti, O, and Zr were the major chemical elements in the composite. Moreover, the approximate K/Ti atomic ratio of 1:2 was in good agreement with the nominal value for N-K₂Ti₄O₉. It can be seen from Fig. 2 that N-K₂Ti₄O₉ and UiO-66-NH₂ existed with different configurations in the composite. The K and Ti distributions by EDS mapping (Fig. 2(b) and (c)) showed that N-K₂Ti₄O₉ was a core rod in the composite. However, the Zr

Fig. 2. (a) Zr, (b) Ti, (c) K, and (d) N distribution of N-K₂Ti₄O₉/UiO-66-NH₂(3:7) by EDS mapping.

Fig. 3. XRD patterns of (1) N-K₂Ti₄O₉, (2) UiO-66-NH₂, and (3) N-K₂Ti₄O₉/UiO-66-NH₂(3:7).

elements were distributed around the core rod as a shell (Fig. 2(a)). These confirmed that the composite possesses a core-shell structure with UiO-66-NH₂ forming the shell around the N-K₂Ti₄O₉ core.

The XRD patterns of N-K₂Ti₄O₉ and UiO-66-NH₂ are shown in Fig. 3, which were in accordance with the reference patterns [23,24,28]. It can be seen that the N-K₂Ti₄O₉/UiO-66-NH₂(3:7) composite displayed the characteristic peaks of both N-K₂Ti₄O₉ and UiO-66-NH₂, and the intensity and location of the peaks were changed somewhat. That is, the composite is not a simple physical mixture, and there existed interfacial interactions between N-K₂Ti₄O₉ and UiO-66-NH₂. This may be due to the formation of N-K₂Ti₄O₉/UiO-66-NH₂ heterojunctions.

To further understand the UiO-66-NH₂ content in the composites, the thermogravimetric analysis (TGA) of UiO-66-NH₂ and the composites were studied. From Fig. 4, we can see that all the curves showed three steps. The first step was assigned to the loss of adsorbed water molecules during heating to 100 °C. The second in range of 100–350 °C was related to the removal of the residual hydroxyl groups on the surface of UiO-66-NH₂. The third above 350 °C was attributed to the decomposition of the organic linkers. As there was no change in N-K₂Ti₄O₉ during the TGA, the mass percent of UiO-66-NH₂ and

Fig. 4. TGA curves of UiO-66-NH₂ and N-K₂Ti₄O₉/UiO-66-NH₂(x:y) composites.

Table 1N-K₂Ti₄O₉ and UiO-66-NH₂ content in the composites.

Sample	<i>r</i> * (%)	Content (%)	
		UiO-66-NH ₂	N-K ₂ Ti ₄ O ₉
N-K ₂ Ti ₄ O ₉	100	0	100
UiO-66-NH ₂	41	100	0
N-K ₂ Ti ₄ O ₉ /UiO-66-NH ₂ (1:9)	44	95	5
N-K ₂ Ti ₄ O ₉ /UiO-66-NH ₂ (2:8)	46	91	9
N-K ₂ Ti ₄ O ₉ /UiO-66-NH ₂ (3:7)	52	82	18
N-K ₂ Ti ₄ O ₉ /UiO-66-NH ₂ (4:6)	59	69	31
N-K ₂ Ti ₄ O ₉ /UiO-66-NH ₂ (5:5)	67	56	44
N-K ₂ Ti ₄ O ₉ /UiO-66-NH ₂ (6:4)	74	43	57

* Residual mass fraction.

N-K₂Ti₄O₉ in the composites can be determined by the following equations:

$$m_1 \times r_1 = m_2 \times r_2 + m_3 \times r_3 \quad (1)$$

$$m_1 = m_2 + m_3 \quad (2)$$

where m_1 , m_2 , m_3 , r_1 , r_2 , and r_3 are the mass and residual mass fraction (%) of N-K₂Ti₄O₉/UiO-66-NH₂($x:y$), N-K₂Ti₄O₉, and UiO-66-NH₂, respectively (Table 1). As shown, from the TGA, the UiO-66-NH₂ content decreased with increasing mass ratio of N-K₂Ti₄O₉ to ZrCl₄ in the preparation of the composites.

The broad scan XPS spectra gave the chemical compositions of N-K₂Ti₄O₉, UiO-66-NH₂, and N-K₂Ti₄O₉/UiO-66-NH₂(3:7) (Fig. 5(a)), which agreed with the EDS spectra (Fig. 1(d)). From Fig. 5(b), the peak at 398.6 eV was from N-K₂Ti₄O₉ and was due to an interaction between the metal ions (K, Ti) and N, while the N 1s spectrum of UiO-66-NH₂ can be deconvoluted into two curves. One peak at 399.2 eV was assigned to PhNH₂ N [30], and the other at 400.2 eV may be due to the interaction between amidogen and proton (Fig. 5(c)) [31,32]. For the

N-K₂Ti₄O₉/UiO-66-NH₂(3:7) composite, the N 1s spectra of the two components can be both observed as expected (Fig. 5(d)).

3.2. Adsorption activity of the N-K₂Ti₄O₉/UiO-66-NH₂ photocatalysts

The adsorption by the pure component materials and composites of the various dyes, such as rhodamine B (RhB), methylene blue (MB), neutral red (NR), methyl orange (MO), and congo red (CR) was studied (Fig. 6). RhB, MB, and NR are cationic dyes with positively charged groups on their molecular structure. In contrast, MO and CR are anionic dyes and have negatively charged groups. The adsorbed quantity, q_e , was calculated using the following equation:

$$q_e = V(C_0 - C_e)/M \quad (3)$$

where q_e (mg/g) is the amount of dye adsorbed at equilibrium, with C_0 and C_e (mg/L) denoting the liquid phase concentrations of dye at initial time and equilibrium, and V (L) and M (g) are the volume of the dye solution and mass of adsorbent, respectively.

Fig. 7(a)–(c) shows the variation of adsorption capacity q_t with time t in the presence of N-K₂Ti₄O₉, UiO-66-NH₂, and N-K₂Ti₄O₉/UiO-66-NH₂(3:7). There was no obvious adsorption or obvious difference for all the dyes on N-K₂Ti₄O₉. However, obvious adsorption was observed for the cationic dyes on UiO-66-NH₂ and the composites. This was due to the fact that UiO-66-NH₂ has a large surface area, and the positively charged groups of the dyes were attracted to the negatively charged backbone of UiO-66-NH₂ [33]. In contrast, UiO-66-NH₂ exhibited poor adsorption capacity for the anionic dyes because there existed electrostatic repulsion between them.

Fig. 5. (a) Broad scan XPS spectra of (1) N-K₂Ti₄O₉, (2) UiO-66-NH₂, and (3) N-K₂Ti₄O₉/UiO-66-NH₂(3:7); N 1s spectra of (b) N-K₂Ti₄O₉, (c) UiO-66-NH₂, and (d) N-K₂Ti₄O₉/UiO-66-NH₂(3:7).

Fig. 6. Molecular structure of the dyes.

In order to find the rate controlling step in the adsorption of these dyes on N-K₂Ti₄O₉, UiO-66-NH₂, and the composites, pseudo-first order [34,35] and second order [36,37] kinetic models were used to fit the experimental data as represented by Eqs. (4) and (5), respectively:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \quad (5)$$

where q_e and q_t are the amounts of dye adsorbed on the adsorbent (mg/g) at equilibrium and time t , respectively, and k_1 and

k_2 denote the rate constants of the first order (h⁻¹) and second order adsorption (g mg⁻¹ h⁻¹) kinetics. We calculated the values of q_e , k_1 , and the correlation coefficient R^2 from the linear plot of $\ln(q_e - q_t)$ against t (Fig. 7(e)) for the pseudo-first order model. Similarly, q_e , k_2 , and R^2 for the pseudo second order model were obtained from the slope and intercept of the plot of t/q_t against t (Fig. 7(f)). The coefficients of the pseudo-first order and second order models are summarized in Table 2.

For N-K₂Ti₄O₉, the correlation coefficients R^2 of the pseudo-first order and second order models were both higher than 0.99, but $q_{e,cal}$ calculated by the pseudo-first order model was much closer to the experimental $q_{e,exp}$ as compared with those by the pseudo-second order model. Thus, the adsorption of these dyes on N-K₂Ti₄O₉ followed the pseudo-first order model. However, we found that the pseudo-second order adsorption model was more suitable for fitting the kinetics of adsorption on UiO-66-NH₂, which was based on the correlation coefficient R^2 and $q_{e,cal}$. Due to the fact that the adsorption quantity of UiO-66-NH₂ was much higher than that of N-K₂Ti₄O₉, the adsorption on the composites also followed the pseudo-second order model.

We chose one cationic dye, RhB, to study the adsorption performance of the composites. Fig. 7(d) shows that the adsorption activity of the composites was between those of N-K₂Ti₄O₉ and UiO-66-NH₂, and increased with increasing UiO-66-NH₂ content. Thus, loading UiO-66-NH₂ on the N-K₂Ti₄O₉ surface facilitates the transfer of cationic dye from solution to the composites surface, which would benefit the heterogeneous reactions.

Fig. 7. Adsorption capacity of the various dyes on (a) N-K₂Ti₄O₉, (b) UiO-66-NH₂, and (c) N-K₂Ti₄O₉/UiO-66-NH₂(3:7); (d) Adsorption capacity of RhB on N-K₂Ti₄O₉/UiO-66-NH₂ composites; (e) Pseudo-first order and (f) pseudo-second order kinetic plots of dye adsorption on N-K₂Ti₄O₉/UiO-66-NH₂(3:7).

Table 2

Coefficients of pseudo-first order and second order models.

Adsorbent	Dye	$q_{e,exp}$ (mg/g)	Pseudo-first order model			Pseudo-second order model		
			k_1 (h ⁻¹)	$q_{e,cal}$ (mg/g)	R^2 (%)	k_2 (g mg ⁻¹ h ⁻¹)	$q_{e,cal}$ (mg/g)	R^2 (%)
N-K ₂ Ti ₄ O ₉	RhB	3.901	1.026	3.708	99.71	0.341	4.423	99.17
	MB	4.697	1.046	3.821	99.39	0.284	5.325	99.27
	NR	4.149	1.045	4.062	99.58	0.321	4.704	99.13
	MO	3.539	1.046	3.467	99.79	0.377	4.013	99.23
	CR	3.921	1.046	3.840	99.48	0.340	4.445	99.18
UiO-66-NH ₂	RhB	22.446	3.230	39.500	92.22	0.399	22.957	99.95
	MB	23.636	1.687	12.316	93.94	0.499	24.021	99.99
	NR	22.810	1.443	13.101	93.87	0.340	23.332	99.99
	MO	8.780	1.516	4.999	94.48	0.963	8.972	99.99
	CR	6.739	1.296	4.232	94.64	0.807	6.957	99.98
N-K ₂ Ti ₄ O ₉ /UiO-66-NH ₂ (3:7)	RhB	19.629	2.502	16.163	88.77	0.815	19.861	99.99
	MB	21.970	1.862	10.037	92.83	0.801	22.217	99.99
	NR	20.463	1.507	9.818	90.10	0.547	20.786	99.99
	MO	8.244	1.571	4.274	93.12	1.283	8.389	99.99
	CR	6.309	1.304	3.683	93.04	0.991	6.484	99.98
N-K ₂ Ti ₄ O ₉ /UiO-66-NH ₂ (1:9)	RhB	22.020	2.078	10.072	93.96	1.023	22.217	99.99
N-K ₂ Ti ₄ O ₉ /UiO-66-NH ₂ (2:8)	RhB	20.915	2.289	10.037	95.65	0.800	21.164	99.99
N-K ₂ Ti ₄ O ₉ /UiO-66-NH ₂ (4:6)	RhB	17.385	1.792	10.270	94.15	0.663	17.665	99.99
N-K ₂ Ti ₄ O ₉ /UiO-66-NH ₂ (5:5)	RhB	14.927	1.822	10.324	92.35	0.627	15.216	99.98
N-K ₂ Ti ₄ O ₉ /UiO-66-NH ₂ (6:4)	RhB	12.444	1.739	7.989	96.89	0.743	12.700	99.98

3.3. Photocatalytic activities of N-K₂Ti₄O₉/UiO-66-NH₂ photocatalysts

The photocatalytic activities of N-K₂Ti₄O₉, UiO-66-NH₂, and the composites were evaluated using the degradation of RhB under visible light irradiation. As shown in Fig. 8(a), N-K₂Ti₄O₉ showed poor photocatalytic activity. By comparison, UiO-66-NH₂ exhibited a little higher visible light photocatalytic activity. This may be due to the small BET surface area of N-K₂Ti₄O₉ and poor separation efficiency of photogenerated electron-hole pairs of UiO-66-NH₂. However, the N-K₂Ti₄O₉/UiO-66-NH₂ composites exhibited a greatly enhanced photocatalytic activity, which may be the result of the combination of two different semiconductors.

The photocatalytic activities of N-K₂Ti₄O₉/UiO-66-NH₂ with different N-K₂Ti₄O₉/ZrCl₄ ratios were studied, and the results are displayed in Fig. 8(b). All the composites exhibited a higher photocatalytic activity than N-K₂Ti₄O₉ and UiO-66-NH₂. In particular, the composite with the N-K₂Ti₄O₉/ZrCl₄ ratio of 3:7 displayed the highest photocatalytic activity, which indicated that the synergistic effect between N-K₂Ti₄O₉ and UiO-66-NH₂ was the best.

The photodegradation of the various dyes on N-K₂Ti₄O₉/UiO-66-NH₂(3:7) was further studied under visible light irradiation. From Fig. 8(c), it can be seen that N-K₂Ti₄O₉/UiO-66-NH₂(3:7) exhibited an obviously better photocatalytic activity for the cationic dyes (RhB, MB, and NR) than for anionic dyes (MO and CR). The insets of Fig. 8(d) showed that the initial RhB solution had a deep red color before photocatalysis, and it became nearly colorless after 3 h. However, the photographs of the MO solution did not reveal obvious changes in the color

before and after the photocatalysis.

In order to confirm that RhB was not photodegraded by itself, a control experiment was carried out. The result showed that there was no noticeable change in RhB concentration after 3 h stirring under visible light irradiation but without a photocatalyst (Fig. 8(e)). Another control experiment also showed that RhB was not degraded on the photocatalyst after 3 h without visible light irradiation (Fig. 8(e)). These phenomena indicated that the photocatalytic reaction only happened with the existence of both irradiation and photocatalyst.

The regeneration of the photocatalyst is one of the important steps for practical application. After each photocatalytic experiment, the photocatalyst was separated from the solution by centrifuging, washed with deionized water and CH₃Cl and dried. As shown in Fig. 8(f), after four cycles, the K value stabilized at 0.7301 h⁻¹, which was 96% of that for the first cycle. In addition, first order kinetic plots were made to determine the rate constant of the photocatalytic reaction. The results are shown in Table 3.

3.4. Photocatalytic mechanism of the N-K₂Ti₄O₉/UiO-66-NH₂ photocatalysts

By comparing the adsorption capacity and photocatalytic activities of the different dyes on N-K₂Ti₄O₉/UiO-66-NH₂(3:7) (Fig. 9(a)), we found that the adsorption capacity was an important factor that influenced the photocatalytic activity. As UiO-66-NH₂ has a negatively charged backbone that can adsorb cationic dyes more effectively, it also showed higher photocatalytic activity for the cationic dyes.

However, Fig. 9(b) shows another phenomenon. When the N-K₂Ti₄O₉/ZrCl₄ ratio was in the range of 10:0–3:7 (the ratio

Fig. 8. (a) Photodegradation of RhB on $\text{N-K}_2\text{Ti}_4\text{O}_9$, UiO-66-NH_2 , and $\text{N-K}_2\text{Ti}_4\text{O}_9/\text{UiO-66-NH}_2(3:7)$; (b) Photodegradation of RhB on $\text{N-K}_2\text{Ti}_4\text{O}_9/\text{UiO-66-NH}_2$ composites; (c) Photodegradation of various dyes on $\text{N-K}_2\text{Ti}_4\text{O}_9/\text{UiO-66-NH}_2(3:7)$; (d) Time evolution of the absorbance during the photodegradation process; (e) Photodegradation of RhB on $\text{N-K}_2\text{Ti}_4\text{O}_9/\text{UiO-66-NH}_2(3:7)$ with or without irradiation; (f) Photodegradation of RhB on the recycled $\text{N-K}_2\text{Ti}_4\text{O}_9/\text{UiO-66-NH}_2(3:7)$.

10:0 means pure $\text{N-K}_2\text{Ti}_4\text{O}_9$), the photocatalytic activity of the composites increased with increasing the adsorption capacity for RhB, whereas when the $\text{N-K}_2\text{Ti}_4\text{O}_9/\text{ZrCl}_4$ ratio was between 3:7–0:10, the photocatalytic activity decreased. This means that the adsorption capacity was not the only factor to determine a high photocatalytic activity.

It is well known that the mobility of the photogenerated carriers also plays an important role in the photocatalytic pro-

cess. So we recorded the transient photocurrent responses of $\text{N-K}_2\text{Ti}_4\text{O}_9$, UiO-66-NH_2 , and $\text{N-K}_2\text{Ti}_4\text{O}_9/\text{UiO-66-NH}_2(3:7)$ during several on-off cycles under visible light irradiation (Fig. 10(a)) [38–40]. As shown, $\text{N-K}_2\text{Ti}_4\text{O}_9/\text{UiO-66-NH}_2(3:7)$ displayed a higher photocurrent intensity than $\text{N-K}_2\text{Ti}_4\text{O}_9$ and UiO-66-NH_2 , thus showing a higher separation efficiency of the photogenerated electron-hole pairs. This means that the photogenerated carriers can transfer rapidly at the $\text{N-K}_2\text{Ti}_4\text{O}_9/\text{UiO-66-NH}_2$ het-

Table 3
Photocatalytic degradation kinetics of RhB.

Sample	Dye	$K (\text{h}^{-1})$	$t_{1/2} (\text{h})$	$R^2 (\%)$
Control experiment	RhB	0.0015	462.10	92.21
$\text{N-K}_2\text{Ti}_4\text{O}_9$	RhB	0.1567	4.42	99.86
UiO-66-NH_2	RhB	0.2419	2.87	99.97
$\text{N-K}_2\text{Ti}_4\text{O}_9/\text{UiO-66-NH}_2(1:9)$	RhB	0.4033	1.72	99.93
$\text{N-K}_2\text{Ti}_4\text{O}_9/\text{UiO-66-NH}_2(2:8)$	RhB	0.6647	1.04	99.83
$\text{N-K}_2\text{Ti}_4\text{O}_9/\text{UiO-66-NH}_2(3:7)$	RhB	0.7583	0.91	99.91
$\text{N-K}_2\text{Ti}_4\text{O}_9/\text{UiO-66-NH}_2(4:6)$	RhB	0.4934	1.40	99.73
$\text{N-K}_2\text{Ti}_4\text{O}_9/\text{UiO-66-NH}_2(5:5)$	RhB	0.4169	1.66	99.88
$\text{N-K}_2\text{Ti}_4\text{O}_9/\text{UiO-66-NH}_2(6:4)$	RhB	0.2854	2.43	99.73
$\text{N-K}_2\text{Ti}_4\text{O}_9/\text{UiO-66-NH}_2(3:7)$ -2 cycle	RhB	0.7455	0.93	99.86
$\text{N-K}_2\text{Ti}_4\text{O}_9/\text{UiO-66-NH}_2(3:7)$ -3 cycle	RhB	0.7434	0.93	99.96
$\text{N-K}_2\text{Ti}_4\text{O}_9/\text{UiO-66-NH}_2(3:7)$ -4 cycle	RhB	0.7301	0.95	99.88
$\text{N-K}_2\text{Ti}_4\text{O}_9/\text{UiO-66-NH}_2(3:7)$ +1 mmol/L EDTA-2Na	RhB	0.1289	3.47	99.91
$\text{N-K}_2\text{Ti}_4\text{O}_9/\text{UiO-66-NH}_2(3:7)$ +1 mmol/L BuOH	RhB	0.5399	1.28	99.95
$\text{N-K}_2\text{Ti}_4\text{O}_9/\text{UiO-66-NH}_2(3:7)$ +1 mmol/L BQ	RhB	0.6039	1.15	99.80
$\text{N-K}_2\text{Ti}_4\text{O}_9/\text{UiO-66-NH}_2(3:7)$	MB	0.9376	0.74	99.54
	NR	0.7642	0.91	99.16
	MO	0.1485	4.67	99.85
	CR	0.1325	5.23	99.70

Fig. 9. The photocatalytic rate constant (K) and adsorption capacity of (a) different dyes on $N-K_2Ti_4O_9/Uio-66-NH_2(3:7)$ and (b) RhB on $N-K_2Ti_4O_9$, $Uio-66-NH_2$, and $N-K_2Ti_4O_9/Uio-66-NH_2$ composites.

Fig. 10. (a) Photocurrent transient responses of (1) $N-K_2Ti_4O_9$, (2) $Uio-66-NH_2$, and (3) $N-K_2Ti_4O_9/Uio-66-NH_2(3:7)$; (b) Valence band XPS spectra and (c) UV-vis absorption spectra of (1) $N-K_2Ti_4O_9$ and (2) $Uio-66-NH_2$; (d) Photodegradation of RhB on $N-K_2Ti_4O_9/Uio-66-NH_2(3:7)$ with different scavengers.

erojunction interface, which may be the reason why $N-K_2Ti_4O_9/Uio-66-NH_2(3:7)$ showed a higher photocatalytic activity than $Uio-66-NH_2$, although it exhibited a lower adsorption capacity.

Furthermore, we measured the valence bands of $N-K_2Ti_4O_9$ and $Uio-66-NH_2$ by valence band XPS [41]. As shown in Fig. 10(b), the valence bands (VB) of $N-K_2Ti_4O_9$ and $Uio-66-NH_2$ were at 2.57 and 1.65 eV, respectively. Thus, the holes from the VB of $N-K_2Ti_4O_9$ will transfer readily to that of $Uio-66-NH_2$.

However, as the standard redox potential of $\cdot OH/OH^-$ is 2.38 eV [42], the photogenerated holes cannot oxidize OH^- to yield $\cdot OH$.

The UV-vis absorption spectra of $N-K_2Ti_4O_9$ and $Uio-66-NH_2$ were also studied (Fig. 10(c)). $N-K_2Ti_4O_9$ clearly showed the characteristic absorption of $K_2Ti_4O_9$ in the UV region [43], and a new absorption shoulder at 400–500 nm (3.10–2.48 eV) that can be attributed to the N surface plasmon resonance with the $K_2Ti_4O_9$ interband transition. The steep rise that $Uio-66-NH_2$ showed in the range of 300–500 nm is due to the band gap

transition. Near the absorption band edge, the optical absorption has the following behavior:

$$\alpha h\nu = A(h\nu - E_g)^{n/2} \quad (6)$$

where α , ν , E_g , and A are absorption coefficient, light frequency, band gap, and a constant, respectively, and n depends on whether the transition is direct ($n = 1$) or indirect ($n = 4$) [44]. For N-K₂Ti₄O₉ and UiO-66-NH₂, the value of n was 1. The band gaps of N-K₂Ti₄O₉ and UiO-66-NH₂ estimated from the intercept of the tangents to the plots were 3.20 and 2.65 eV, respectively (inset in Fig. 10(c)). Thus, the conduction bands of N-K₂Ti₄O₉ and UiO-66-NH₂ were at −0.63 and −1.00 eV, respectively, which are more negative than the standard redox potential of O₂/O₂^{•−} (−0.33 eV) and O₂/HOO[•] (−0.037 eV) [45]. As a result, the photogenerated electrons in the CB of N-K₂Ti₄O₉ and UiO-66-NH₂ can reduce O₂ to give O₂^{•−} or HOO[•], and the •OH radical can be generated from HOO[•] [46].

In order to evaluate the role of these active oxidants, scavengers were added to the photocatalytic system. These were *tert*-butyl alcohol (*t*-BuOH) for •OH [47], benzoquinone (BQ) for O₂^{•−} [47,48], and disodium ethylenediaminetetraacetate dehydrate (EDTA-2Na) for the holes [38–40]. As shown in Fig. 10(d), the photodegradation of RhB was slightly inhibited by the addition of *t*-BuOH or BQ, while it was much suppressed when EDTA-2Na was included. This indicated that the dye degradation was mainly driven by the participation of the hole, and to a lesser extent by the contribution of •OH and O₂^{•−} radicals.

A photodegradation mechanism for the N-K₂Ti₄O₉/UiO-66-NH₂ composites under visible light irradiation is shown in Fig. 11. At the N-K₂Ti₄O₉/UiO-66-NH₂ heterojunction interface, the photogenerated electrons in the conduction band (CB) of UiO-66-NH₂ are transferred to the CB of N-K₂Ti₄O₉, and the holes from the valence band (VB) of N-K₂Ti₄O₉ are transferred to the VB of UiO-66-NH₂. The UiO-66-NH₂ shell can enhance the adsorption of cationic dyes from the solution, but repel anionic dyes. The photogenerated electrons in the CB of N-K₂Ti₄O₉ including those from the CB of UiO-66-NH₂ can be captured by dissolved O₂ to yield first the superoxide radical anion, O₂^{•−}, then the HOO[•] radical upon protonation, and finally the •OH radical via trapping the electron [46]. However, only small amount of the dye was oxidized by O₂^{•−} and •OH radical, and most of the dye was directly destroyed by the photogenerated holes in the VB of UiO-66-NH₂ including those from the VB of N-K₂Ti₄O₉. From Fig. 11, we can see that the electron-hole transfer at the N-K₂Ti₄O₉/UiO-66-NH₂ heterojunction interface

enhances the separation of the electron-hole pairs. Furthermore, after bringing together N-K₂Ti₄O₉ and UiO-66-NH₂, the resulting composites have the advantage of a high adsorption capacity especially for cationic dyes. These may be the reasons why the N-K₂Ti₄O₉/UiO-66-NH₂ composites have a synergistically enhanced photocatalytic performance as compared to the pure component materials.

4. Conclusions

N-K₂Ti₄O₉/UiO-66-NH₂ composites were synthesized by a facile solvothermal method. They possessed a core-shell structure with UiO-66 forming the shell around a N-K₂Ti₄O₉ core. The N-K₂Ti₄O₉/UiO-66-NH₂ composites showed selective adsorption of cationic dyes, which promoted the photodegradation of cationic dyes. A synergistic effect in the photocatalysis was due to the high separation efficiency of photogenerated electron-hole pairs at the interfaces of N-K₂Ti₄O₉ and UiO-66-NH₂. N-K₂Ti₄O₉/UiO-66-NH₂(3:7) exhibited the best photocatalytic activity among the composites.

References

- [1] A. S. Bhatt, P. L. Sakaria, M. Vasudevan, R. R. Pawar, N. Sudheesh, H. C. Bajaj, H. M. Mody, *RSC Adv.*, **2012**, 2, 8663–8671.
- [2] H. Chen, J. Zhao, *Adsorption*, **2009**, 15, 381–389.
- [3] V. K. Gupta, B. Gupta, A. Rastogi, S. Agarwal, A. Nayak, *J. Hazard. Mater.*, **2011**, 186, 891–901.
- [4] A. Dolbecq, P. Mialane, B. Keita, L. Nadjo, *J. Mater. Chem.*, **2012**, 22, 24509–24521.
- [5] A. Kubacka, M. Fernández-García, G. Colón, *Chem. Rev.*, **2012**, 112, 1555–1614.
- [6] W. Q. Fan, Q. H. Zhang, Y. Wang, *Phys. Chem. Chem. Phys.*, **2013**, 15, 2632–2649.
- [7] Y. Hosogi, H. Kato, A. Kudo, *J. Phys. Chem. C*, **2008**, 112, 17678–17682.
- [8] J. C. Cao, A. L. Wang, H. B. Yin, L. Q. Shen, M. Ren, S. Q. Han, Y. T. Shen, L. B. Yu, T. S. Jiang, *Ind. Eng. Chem. Res.*, **2010**, 49, 9128–9134.
- [9] W. Q. Cui, S. S. Ma, L. Liu, J. S. Hu, Y. H. Liang, J. G. McEvoy, *Appl. Surf. Sci.*, **2013**, 271, 171–181.
- [10] J. S. Wang, H. Li, H. Y. Li, S. Yin, T. Sato, *Solid State Sci.*, **2009**, 11, 988–993.
- [11] P. Romero-Gómez, S. Hamad, J. C. González, A. Barranco, J. P. Espinós, J. Cotrino, A. R. González-Elipe, *J. Phys. Chem. C*, **2010**, 114, 22546–22557.
- [12] Y. J. Hwang, A. Boukai, P. D. Yang, *Nano Lett.*, **2009**, 9, 410–415.
- [13] G. Q. Song, Z. Q. Wang, L. Wang, G. R. Li, M. J. Huang, F. X. Yin, *Chin. J. Catal.*, **2014**, 35, 185–195.
- [14] G. Férey, *Chem. Soc. Rev.*, **2008**, 37, 191–214.
- [15] H. L. Li, M. Eddaoudi, M. O’Keeffe, M. Yaghi, *Nature*, **1999**, 402, 276–279.
- [16] Y. S. Li, W. S. Yang, *Chin. J. Catal.*, **2015**, 36, 692–697.
- [17] S. Kitagawa, R. Kitaura, S. I. Noro, *Angew. Chem. Int. Ed.*, **2004**, 43, 2334–2375.
- [18] S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa, K. Mochizuki, Y. Kinoshita, S. Kitagawa, *J. Am. Chem. Soc.*, **2007**, 129, 2607–2614.
- [19] N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O’Keeffe, O. M. Yaghi, *Science*, **2003**, 300, 1127–1129.
- [20] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O’Keeffe, O. M.

Fig. 11. Photocatalytic mechanism of the composite.

Graphical Abstract

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Synergistic effects in N-K₂Ti₄O₉/UiO-66-NH₂ composites and their photocatalysis degradation of cationic dyes

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N-K₂Ti₄O₉/UiO-66-NH₂ composites exhibit a hierarchical core-shell structure. The composites show synergistically enhanced visible-light photocatalytic activity. The composites can photodegrade cationic dyes more effectively than anionic dyes.

- Yaghi, *Science*, **2002**, 295, 469–472.
- [21] M. Latroche, S. Surblé, C. Serre, C. Mellot-Draznieks, P. L. Llewellyn, J. H. Lee, J. S. Chang, S. H. Jhung, G. Férey, *Angew. Chem. Int. Ed.*, **2006**, 45, 8227–8231.
- [22] P. Horcajada, C. Serre, M. Vallet-Regí, M. Sebban, F. Taulelle, G. Férey, *Angew. Chem. Int. Ed.*, **2006**, 45, 5974–5978.
- [23] C. G. Silva, I. Luz, F. X. Llabrés i Xamena, A. Corma, H. García, *Chem.-Eur. J.*, **2010**, 16, 11133–11138.
- [24] L. J. Shen, W. M. Wu, R. W. Liang, R. Lin, L. Wu, *Nanoscale*, **2013**, 19, 9374–9382.
- [25] Q. H. Zhang, W. G. Fan, L. Gao, *Appl. Catal. B*, **2007**, 76, 168–173.
- [26] M. A. Aramendía, V. Borau, J. C. Colmenares, A. Marinas, J. M. Marin, J. A. Navío, F. J. Urbano, *Appl. Catal. B*, **2008**, 80, 88–97.
- [27] M. H. Zhou, J. G. Yu, S. W. Liu, P. C. Zhai, L. Jiang, *J. Hazard. Mater.*, **2008**, 154, 1141–1148.
- [28] M. R. Allen, A. Thibert, E. M. Sabio, N. D. Browning, D. S. Larsen, F. E. Osterloh, *Chem. Mater.*, **2010**, 22, 1220–1228.
- [29] D. Mitoraj, H. Kisch, *Angew. Chem. Int. Ed.*, **2008**, 47, 9975–9978.
- [30] C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder, G. E. Muilenberg, *Hand Book of X-Ray Photoelectron Spectroscopy*, Perkin-Elmer, Eden Prairie, MN, **1979**.
- [31] R. L. Arechederra, K. Artyushkova, P. Atanassov, S. D. Minter, *ACS Appl. Mater. Interfaces*, **2010**, 2, 3295–3302.
- [32] Y. Mosqueda, E. Pérez-Capote, J. Arana, E. Longo, A. Ries, M. Cilense, P. A. P. Nascentec, P. Arandad, E. Ruiz-Hitzky, *J. Solid State Chem.*, **2006**, 179, 308–314.
- [33] Q. Chen, Q. Q. He, M. M. Lv, Y. L. Xu, H. B. Yang, X. T. Liu, F. Y. Wei, *Appl. Surf. Sci.*, **2015**, 327, 77–85.
- [34] V. K. Gupta, A. Mittal, L. Krishnan, V. Gajbe, *Sep. Purif. Technol.*, **2004**, 40, 87–96.
- [35] X. G. Zhao, J. G. Huang, B. Wang, Q. Bi, L. L. Dong, X. J. Liu, *Appl. Surf. Sci.*, **2014**, 292, 576–582.
- [36] Y. S. Ho, G. McKay, *Process Biochem.*, **1999**, 34, 451–465.
- [37] D. Kavitha, C. Namasivayam, *Bioresource Technol.*, **2007**, 98, 14–21.
- [38] P. Xiong, Q. Chen, M. Y. He, X. Q. Sun, X. Wang, *J. Mater. Chem.*, **2012**, 22, 17485–17493.
- [39] P. Xiong, L. J. Wang, X. Q. Sun, B. H. Xu, X. Wang, *Ind. Eng. Chem. Res.*, **2013**, 52, 10105–10113.
- [40] Q. Chen, Q. Q. He, M. M. Lv, X. T. Liu, J. Wang, J. P. Lv, *Appl. Surf. Sci.*, **2014**, 311, 230–238.
- [41] X. B. Chen, L. Liu, P. Y. Yu, S. S. Mao, *Science*, **2011**, 331, 746–750.
- [42] A. J. Bard, R. Parsons, J. Jordan, *Standard Potentials in Aqueous Solution*, Marcel Dekker, New York, **1985**.
- [43] Z. G. Xiong, X. S. Zhao, *J. Am. Chem. Soc.*, **2012**, 134, 5754–5757.
- [44] M. A. Butler, *J. Appl. Phys.*, **1977**, 48, 1914–1920.
- [45] A. J. Bard, L. R. Faulkner, *Electrochemical Methods Fundamentals and Applications*, John Wiley & Sons, New York, **1980**.
- [46] T. X. Wu, G. M. Liu, J. C. Zhao, H. Hidaka, N. Serpone, *J. Phys. Chem. B*, **1998**, 102, 5845–5851.
- [47] L. Mohapatra, K. Parida, M. Satpathy, *J. Phys. Chem. C*, **2012**, 116, 13063–13070.
- [48] B. Yuan, J. X. Wei, T. J. Hu, H. B. Yao, Z. H. Jiang, Z. W. Fang, Z. Y. Chu, *Chin. J. Catal.*, **2015**, 36, 1009–1016.

N-K₂Ti₄O₉/UiO-66-NH₂ 复合材料的协同效应及其光催化降解阳离子型染料

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摘要: 半导体光催化剂作为一种可再生和可持续降解有机污染物的材料被广泛研究。K₂Ti₄O₉ 由于无毒、低成本、稳定的物理化学性质和独特的光电性能被应用于光催化反应。但是, K₂Ti₄O₉ 只能被紫外光所激发 (因为其带隙能为 3.2–3.4 eV),

所以大量工作致力于研究如何降低其带隙能,从而使其可以被太阳光中的可见光激发,扩大其应用范围.其中N元素掺杂 $\text{K}_2\text{Ti}_4\text{O}_9$ ($\text{N-K}_2\text{Ti}_4\text{O}_9$)是最常见的方法之一.单纯的 $\text{N-K}_2\text{Ti}_4\text{O}_9$ 虽然具有光催化能力,但其吸附容量太小,不能有效地将溶液中的有机物吸附至其表面,因而催化降解有机物效果不显著.

UiO-66-NH_2 是一种Zr基金属-有机骨架化合物,它对阳离子染料具有良好的吸附性能,且具有一些常规无机半导体光催化材料所没有的性质.本文将 UiO-66-NH_2 和 $\text{N-K}_2\text{Ti}_4\text{O}_9$ 经高温焙烧制备了 $\text{N-K}_2\text{Ti}_4\text{O}_9/\text{UiO-66-NH}_2$ 复合材料,发现该复合材料不仅具有 UiO-66-NH_2 优良的吸附性能,还因为复合提高了其光电性能,从而大大提高了光催化性能,当 $\text{N-K}_2\text{Ti}_4\text{O}_9/\text{ZrCl}_4$ 质量比为3:7时光催化性能最佳.

为了考察 $\text{N-K}_2\text{Ti}_4\text{O}_9/\text{UiO-66-NH}_2$ 复合材料的微观形貌、复合结构及光生电子-空穴分离效率,首先通过场发射透射电镜分析 $\text{N-K}_2\text{Ti}_4\text{O}_9$, UiO-66-NH_2 和 $\text{N-K}_2\text{Ti}_4\text{O}_9/\text{UiO-66-NH}_2$ (3:7)复合材料的形貌,然后采用能量散射谱测定复合材料的元素分布,并利用 $\text{N-K}_2\text{Ti}_4\text{O}_9$ 和 UiO-66-NH_2 中代表性元素K,Ti和Zr的分布判断复合材料的复合结构,最后运用高分辨电镜观察复合材料中 $\text{N-K}_2\text{Ti}_4\text{O}_9$ 和 UiO-66-NH_2 的异质结界面,确定了两者的通过自组装复合在一起,而不是简单的物理混合.X射线衍射结果表明,复合材料具有 $\text{N-K}_2\text{Ti}_4\text{O}_9$ 和 UiO-66-NH_2 两者的特征衍射峰,仅在强度和位置上略有变化.这可能是 $\text{N-K}_2\text{Ti}_4\text{O}_9/\text{UiO-66-NH}_2$ 异质结构所致.通过 UiO-66-NH_2 和 $\text{N-K}_2\text{Ti}_4\text{O}_9$ 的紫外-可见吸收光谱,用公式计算出它们的带隙能分别是2.645和3.195 eV,与文献结果基本一致.

由于光催化剂的光生载流子迁移速率同样影响光催化性能,因此我们在CHI-660D电化学工作站上控制光源反复开关数次,同时记录 $\text{N-K}_2\text{Ti}_4\text{O}_9$, UiO-66-NH_2 和 $\text{N-K}_2\text{Ti}_4\text{O}_9/\text{UiO-66-NH}_2$ (3:7)的光响应电流,发现 $\text{N-K}_2\text{Ti}_4\text{O}_9/\text{UiO-66-NH}_2$ (3:7)复合材料展现出最高的光响应电流强度,表明其具有最高的光生载流子迁移速率和最低的光生载流子复合速率.可见, $\text{N-K}_2\text{Ti}_4\text{O}_9$ 和 UiO-66-NH_2 复合有利于光生载流子迁移,这可能是由于 $\text{N-K}_2\text{Ti}_4\text{O}_9/\text{UiO-66-NH}_2$ 异质结界面有利于光生载流子在两种材料之间迁移所致.

测试了 $\text{N-K}_2\text{Ti}_4\text{O}_9/\text{UiO-66-NH}_2$ (3:7)复合材料对不同染料的光催化降解性能.结果发现,该材料对阳离子型染料(罗丹明B和亚甲基蓝)的光催化性能远远高于对阴离子型染料(甲基橙和刚果红).这是由于它对阳离子型染料的吸附性能远高于对阴离子型染料,因此 $\text{N-K}_2\text{Ti}_4\text{O}_9/\text{UiO-66-NH}_2$ 复合材料对阳离子型染料具有选择性光催化.

关键词: 氮掺杂的钛酸钾; UiO-66-NH_2 ; 选择性光催化; 协同效应; 复合物

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