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Enhancing photocatalytic activity of Bi_2MoO_6 via surface co-doping with Ni^{2+} and Ti^{4+} ions

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Abstract

Photocatalytic redox reactions occur on the surface of the catalyst, and therefore the surface properties of the photocatalyst are vital for efficient catalytic reactions. Bi₂MoO₆ surface co-doped with Ni²⁺ and Ti⁴⁺ ions was fabricated through an incipient-wetness impregnation technology and calcination method. The influence of Ni²⁺ and Ti⁴⁺ co-doping with different concentrations on the crystal structure, morphology, and optical properties of Bi2MoO6 were investigated by different instrumental methods, and the characterization results confirm that the surface of Bi₂MoO₆ was doped with Ni²⁺ and Ti⁴⁺ ions. Under visible-light irradiation, the effects of Ni²⁺ and Ti⁴⁺ surface co-doping on the photocatalytic activity of Bi₂MoO₆ were evaluated by the degradation of rhodamine B, with the results suggesting Ni^{2+} and Ti^{4+} co-doping increases visible-light absorption by Bi₂MoO₆ and promotes the separation of photogenerated charge carriers. With optimum Ni²⁺ and Ti⁴⁺ co-doping, Bi₂MoO₆ surface co-doped with 0.18% Ni²⁺ and 0.192% Ti⁴⁺ exhibits the greatest photocatalytic activity and stability in the degradation of rhodamine B.

Keywords

co-doping, surface, Bi₂MoO₆, photocatalyst

Introduction

 Bi_2MoO_6 , which possesses alternate perovskite MoO_4^{2+} slabs and $[Bi_2O_2]^{2+}$ layers, has been reported as a promising solar-energy-conversion material for water splitting and organic pollutant degradation under visible-light irradiation [1-3], which is attributed to its suitable band gap (2.5–2.8 eV) [4-6] and distinctive structure, which facilitate the separation of charges because of electrostatic interaction between layers.

The photocatalytic activities of Bi₂MoO₆ materials are closely related to their morphology, crystal microstructure, and composition. For example, Bi₂MoO₆ crystals with different morphologies [1], including nanosheets [7], inverse opals, hollow microspheres [8], yolk-shell microspheres [9], nanofibers, microtubes [10], ordered arrays, elm branch-like hierarchical structures [11], and thin films [12], have been successfully fabricated by different preparation methods, such as hydrothermal, solvothermal, molten salt, electrospinning, microwave, and thermal evaporation deposition methods. The unique yolk-shell structure is beneficial for charge separation and light absorption, and Bi₂MoO₆ with a yolk-shell structure exhibits excellent photocatalytic performance and recyclability [9]. At the same time, heterostructures of Bi₂MoO₆, such as Bi₂MoO₆/Ag [13], Bi₂MoO₆/Bi [14], Bi₂MoO₆/Bi₂S₃ [15], Bi₂MoO₆/BiOBr [16], Bi₂MoO₆/TiO₂ [17, 18], Bi₂MoO₆/NiTiO₃ [19], and Bi₂MoO₆/Ag/CdS [20], have been developed to enhance the photocatalytic activity and stability of Bi₂MoO₆ because the formation of well-defined heterojunctions effectively promotes the separation and suppresses the recombination of photogenerated charge carriers. Moreover, to improve the photocatalytic performance of Bi₂MoO₆ as a catalyst, doping with ions, including B, Cl, W, and lanthanide ions [21, 22], was applied to influence the composition of Bi_2MoO_6 by changing and controlling the concentration of surface and internal defects [23]. However, it remains a challenge to realize practical applications of Bi₂MoO₆ as a catalyst because of the fast electron-hole recombination, slow carrier migration, and poor surface chemical states. Hence it is necessary to explore

ways to address these issues.

It is common knowledge that the three primary processes influencing the photocatalytic performances of semiconductor photocatalysts are the generation, separation, and surface diffusion of electron-hole pairs. Since the photocatalytic redox reactions occur on the surface of the catalyst, and the surface properties of the photocatalyst will greatly affect the three aforementioned processes, it can be concluded that the surface properties are vital for efficient photocatalytic reactions. So far, metal ion (M^{n+}) doping on the surface of Bi₂MoO₆ by the incipient-wetness impregnation method has not been reported. We believe that an M^{n+} -doped layer is induced near the surface of Bi₂MoO₆ by M^{n+} diffusion after annealing, which can change the generation, separation, and surface diffusion of the charge carriers. Hence the surface tuning of the photocatalyst to increase the activity of the photocatalyst and the utilization of solar energy should be investigated.

In this article, Bi_2MoO_6 photocatalysts with the surface co-doped with Ni^{2+} and Ti^{4+} ions were fabricated through an incipient-wetness impregnation technology and calcination method. The photocatalytic activity of the Ti^{4+}/Ni^{2+} co-doped Bi_2MoO_6 surface was investigated through the degradation of rhodamine B (RhB) under visible-light irradiation. The effect of different doping amounts of Ni^{2+} and Ti^{4+} was also studied. Bi_2MoO_6 surface co-doped with 0.18% Ni^{2+} and 0.192% Ti^{4+} (Ni/Ti/BMO-3) showed excellent visible-light-driven photocatalytic performance.

2. Experimental

2.1. Preparation of pure Bi_2MoO_6

All reagents were analytically pure and used without further purification. In a typical solvothermal synthesis, first, 2 mmol of $Bi(NO_3)_3 \cdot 5H_2O$ (0.97 g) was added to 30 mL of ethylene glycol and the resulting mixture was magnetically stirred for 30 min. Then 1 mmol of $Na_2MoO_4 \cdot 2H_2O$ (0.242 g) was dissolved in Bi^{3+} solution and the resulting mixture was stirred for 20 min. Second, 10 mL of

ethylene glycol was added to the aforementioned solution and the resulting mixture was stirred for 120 min at room temperature. Third, the solution was transferred into a 50 mL Teflon-lined stainless steel autoclave and heated at 160 \square for 20 h. After the reaction, the autoclave was cooled to room temperature in air. The sample was collected by centrifugation, washed with ethanol and deionized water several times, and then dried at 70 \square for 10 h. Pure Bi₂MoO₆ was obtained.

2.2. Preparation of Bi_2MoO_6 with the surface co-doped with Ni^{2+} and Ti^{4+}

The catalysts with Ni²⁺ and Ti⁴⁺ doping on the surface of Bi₂MoO₆ were prepared by incipient-wetness impregnation using as-obtained Bi₂MoO₆ as a catalyst support. The Ni²⁺ (or Ti⁴⁺) monosupported catalysts were prepared through impregnation of the aforementioned catalyst supports with Ni(NO₃)₂ (or tetrabutyl titanate) aqueous solution, kept static at room temperature for 6 h and then dried at 80 ° C overnight, and finally calcined at 400 °C for 2 h in air. Ni²⁺ and Ti⁴⁺ co-supported catalysts were synthesized by the same impregnation of the catalyst supports with the corresponding Ni(NO₃)₂ or tetrabutyl titanate aqueous solution.

The catalysts obtained were denoted as Ni/BMO (where BMO refers to Bi_2MoO_6 , and the percentage of Ni^{2+} is 0.06%), Ti/BMO (the percentage of Ti^{4+} is 0.064%), and Ni/Ti/BMO-*x* (where x = 1, 2, 3, 4, and 5, corresponding to Ni^{2+}/Ti^{4+} loading percentages of 0.06%/0.064%, 0.12%/0.128%, 0.18%/0.192%, 0.24%/0.256%, and 0.30%/0.32%, respectively). The final content of Ni^{2+} and Ti^{4+} in Bi_2MoO_6 was determined by inductively coupled plasma optical emission spectrometry (Varian 715-ES, Varian, Australia). The results indicate that the Ni^{2+} and Ti^{4+} contents in Ni/Ti/BMO-3 were 0.176% and 0.181%, respectively.

2.3. Characterization

The X-ray diffraction (XRD) data were obtained with a powder X-ray

diffractometer (Rigaku D/max-2550 PC). X-ray photoelectron spectroscopy (ESCALab MKII spectrometer with an excitation source of Mg Kα radiation) was used to determine the chemical binding states of the constituent elements. Scanning electron microscopy (SEM; JEOL S-4800), transmission electron microscopy (TEM; JEOL JEM-2100F) and high-resolution TEM (JEM-2100F) images were obtained to investigate the morphology of the products. UV-vis diffuse reflectance spectroscopy (DRS) was performed with a UV3600 spectrophotometer (SHIMADZU).

2.4. Photocatalytic activity experiments

The catalytic activities of the samples were evaluated by our measuring the degradation of RhB (maximum absorption peak at 554 nm) under visible light at room temperature (25 °C) according to our previously reported method [24]. The experimental procedure was as follows: The photocatalyst sample (20 mg) was suspended in 50 mL of RhB solution (5.0 mg L^{-1}) to form a suspension. Afterward, the suspension was stirred in the dark for 60 min to ensure an adsorption-desorption equilibrium. Then the suspension under magnetic stirring was placed approximately 10 cm below a xenon lamp (500 W, model PLS-SXE300, Beijing PerfectLight) and an optical filter glass was used to cut out light of wavelength below 400 nm. About 3.5 mL of suspension was sampled every 20 min and centrifuged. The solution of the clear upper layer was measured with a UV-1901 spectrophotometer (Shanghai Aucy) to obtain the absorption spectrum of RhB solution. After testing, the solution was returned from the reactor top. Radical-trapping experiments were performed by our adding 1 mM benzoquinone, 1 mM ammonium oxalate, 6 mM AgNO₃, and 1 mM tert-butanol to the RhB (50 mL, 5 mg L⁻¹) solution before the photocatalysis tests.

3. Results and discussionThe crystalline structures of all as-obtained samples were analyzed by powder XRD measurements. Fig. 1a shows the XRD patterns

of the eight synthesized samples. In the XRD pattern of pure Bi_2MoO_6 , all diffraction peaks match well with the standard orthorhombic Bi_2MoO_6 structure (JCPDS card no. 21-0102). No obvious peaks of other impurities were detected, indicating that high-quality orthorhombic phase Bi_2MoO_6 was obtained. In the XRD pattern of Bi_2MoO_6 samples loaded with Ni^{2+} and Ti^{4+} , no new peak was observed in the samples with different loadings. This is attributed to the extremely low loading of Ni^{2+} and Ti^{4+} and high dispersion of Ni^{2+} and Ti^{4+} on the Bi_2MoO_6 surface. Careful observation of these XRD patterns (Fig. 1b) indicates that the doping with Ni^{2+} and Ti^{4+} caused a decrease in the intensity of the peak at 28.3° in M^{n+} -doped Bi_2MoO_6 compared with pure Bi_2MoO_6 , which suggests that Ni^{2+} and Ti^{4+} ions were successfully incorporated in the Bi_2MoO_6 was doped with Ni^{2+} and Ti^{4+} ions by a simple incipient-wetness impregnation technology and calcination method.

X-ray photoelectron spectroscopy spectra of pure Bi_2MoO_6 and Ni/Ti/BMO-3 are shown in Fig. 2 and were used to determine the elemental composition and chemical state. There are peaks at 159.2 and 164.5 eV for pure Bi_2MoO_6 and at 159.1 and 164.4 eV for Ni/Ti/BMO-3, corresponding to Bi $4f_{7/2}$ and Bi $4f_{5/2}$. In Fig. 2c, the binding energy peaks at 232.5 and 235.6 eV for pure Bi_2MoO_6 and at 232.4 and 235.6 eV for Ni/Ti/BMO-3 are assigned to Mo $3d_{5/2}$ and Mo $3d_{3/2}$ of Mo⁶⁺ [26, 27]. The binding energy of O 1s is 530.1 eV for pure Bi_2MoO_6 and 530.0 eV for Ni/Ti/BMO-3. The binding energies of Ni 2p in Ni/Ti/BMO-3 are 873.6 and 855.6 eV for Ni/Ti/BMO-3 [28, 29]. The binding energy of Ti was observed to be 465.9 eV [30] in accordance with Ti $2p_{1/2}$ in Ni/Ti/BMO-3. This confirmed that the surface of Bi_2MoO_6 was successfully doped with Ni²⁺ and Ti⁴⁺ ions.

The morphologies of pure Bi_2MoO_6 , Ti/BMO, Ni/BMO, and Ni/Ti/BMO-*x* samples were analyzed by SEM. The images obtained are shown in Fig. 3. From these images, we can see that the samples are all composed of flowerlike microspheres with diameters of 1–3 µm. These microspheres are built from

two-dimensional nanosheets. With increase of Ni^{2+} and Ti^{4+} doping/co-doping on the surface of Bi_2MoO_6 , the M^{n+} -doped Bi_2MoO_6 microspheres display a flowerlike shape similar to that of pure Bi_2MoO_6 .

The TEM images in Fig. 4 further verify that the flowerlike microspheres of Bi_2MoO_6 and Ni/Ti/BMO-3 comprise two-dimensional nanosheets with a thickness of 20–30 nm. Furthermore, the high-resolution TEM images in Fig. 4b and d clearly reveal a set of fringes with lattice spacings of 0.235 and 0.316 nm, ascribed to the (221) and (131) planes of Bi_2MoO_6 .

 N_2 adsorption-desorption measurements were performed (Fig. 5). The Brunauer-Emmett-Teller (BET) surface area of pure Bi₂MoO₆ is 21.2 m² g⁻¹. Ni/Ti/BMO-3 exhibits a slight increase of the BET surface area (28.9 m² g⁻¹). Moreover, the pore size distributions calculated on the basis of Barrett-Joyner-Halenda analysis reveal most pores are of size approximately 25 nm in both Bi₂MoO₆ and Ni/Ti/BMO-3 (inset in Fig. 5). Ni/Ti/BMO-3 with nanopores and a high BET surface area favors photocatalysis [31].

The optical absorption spectra of Bi_2MoO_6 , Ni/BMO, Ti/BMO, and Ni/Ti/BMO-*x* are shown in Fig. 6a. Bi_2MoO_6 exhibits absorption peaks in both the UV region and the visible region. The onset of the absorption edge for Bi_2MoO_6 is at approximately 470 nm (2.36 eV), which is in accordance with the literature [31, 32]. It can be see that the introduction of Ni²⁺ and Ti⁴⁺ broadens and increases the visible-light absorption intensity of Bi_2MoO_6 . In comparison with Bi_2MoO_6 , Ni/BMO, and Ti/BMO, Ni/Ti/BMO-3 clearly exhibits enhanced absorption in the visible range (~450–700 nm), corresponding to a band gap of 2.23 eV (Fig. 6b), suggesting that Ni/Ti/BMO-3 might exhibit good photocatalytic behavior under visible light.

As indicated above, UV-visible absorption results for Ni/Ti/BMO-3 predict its improved photocatalytic performance in visible light. The photocatalytic performance was tested by the degradation of RhB. RhB displays a characteristic absorption peak at a wavelength of around 554 nm and is a popular probe molecule in heterogeneous catalytic reactions. For comparison,

the photocatalytic activities of Bi₂MoO₆, Ni/BMO, Ti/BMO, and Ni/Ti/BMO-x (x = 1, 2, 4, and 5) were also evaluated under the same conditions. Fig. 7a shows the temporal evolution of the absorption spectrum of RhB solution with Ni/Ti/BMO-3 as the catalyst after exposure to visible light. It can be seen that the main absorption peak at 554 nm decreases rapidly with increase of the exposure time and completely disappears after about 60 min, confirming that the RhB solution can be efficiently photodegraded by Ni/Ti/BMO-3. The photographs of the color change of RhB solution clearly reveal that RhB was successfully degraded within 60 min, as shown in Fig. 7b. Fig. 7c shows the photodegradation curves for RhB over different catalysts. From the blank experiment, we confirm that no RhB is degraded without the catalysts after 60 min of irradiation. From the adsorption equilibrium curves (dark), it can be seen that the different catalysts show very little adsorption ability for RhB after treatment for 60 min. When P25 and pure Bi₂MoO₆ are used as the photocatalyst, only 39.1% and 64.3% of RhB is degraded, respectively. All the surface-doped catalysts, such as Ni/BMO, Ti/BMO, and Ni/Ti/BMO-x (x = 1, 2, 2) 3, 4, and 5) display higher activities than pure Bi₂MoO₆, and the degradation rate of RhB solution is 87.1%, 92.2%, 88.4%, 90.4%, 98.8%, 76.1%, and 88.7%, respectively. Among them, Ni/Ti/BMO-3 displays the highest photocatalytic activity, suggesting the optimal weight ratio of Ni2⁺, Ti4⁺, and Bi_2MoO_6 is 0.075:0.075:1. In comparison with other Bi_2MoO_6 morphologies for degradation of RhB [21, 23, 32], Ni/Ti/BMO-3 exhibited enhanced photocatalytic activity. Moreover, the photocatalytic degradation kinetics of RhB was investigated. The photocatalytic degradation data were fit to a pseudo-first-order model [33], $-\ln(C/C_0) = kt$, where k is the photocatalytic reaction rate constant and t is the light irradiation time. Fig. 7d shows the kinetic curves for RhB under visible-light irradiation. The reaction rate constant k is equal to the corresponding slope of the simulation curve. The k values for RhB with P25, Bi_2MoO_6 , Ni/BMO, Ti/BMO, and Ni/Ti/BMO-x (x = 1, 2, 3, 4, and 5) are $0.0075 \pm 0.0002 \text{ min}^{-1}$, $0.00147 \pm 0.00046 \text{ min}^{-1}$, 0.00320 ± 0.00024

min⁻¹, 0.0385 \pm 0.0020 min⁻¹, 0.0308 \pm 0.0035 min⁻¹, 0.0332 \pm 0.0030 min⁻¹, 0.0584 \pm 0.0011 min⁻¹, 0.0246 \pm 0.0025 min⁻¹, and 0.0316 \pm 0.0031 min⁻¹, respectively. Notably, *k* is the highest for Ni/Ti/BMO-3 among the catalysts, and is 4.0, 1.5, and 2.4 times higher than for Bi₂MoO₆, Ti/BMO, and Ni/Ti/BMO-4, respectively.

The catalyst stability is also an important factor for practical application, and a five-cycle photocatalytic experiment with Ni/Ti/BMO-3 was conducted. Fig. 8a illustrates the variation of the RhB relative concentration C/C_0 with irradiation time in the five cycles. In the first cycle the degradation rate of RhB was 98.3%, and in the second cycle was 98.4%. After the procedure had been performed five times, the degradation rate was 95.5%. Moreover, the used Ni/Ti/BMO-3 (Fig. 8b) exhibits SEM features similar to those of fresh Ni/Ti/BMO-3 (Fig. 3f). These results reveal that the photocatalytic activity of Ni/Ti/BMO-3 can remain stable and efficient during organic dye degradation.

To better understand the photocatalytic mechanism of Ni/Ti/BMO-3, the dominant active species in the photocatalytic process were investigated (Fig. 9). The scavengers benzoquinone, ammonium oxalate, AgNO₃, and tert-butanol are usually used to capture superoxide (O_2^{\bullet}) , photogenerated holes, photogenerated electrons, and hydroxyl radicals (•OH), respectively [34, 35]. As shown in Fig. 9a, RhB degradation was greatly inhibited when benzoquinone was added: the RhB degradation efficiency decreased from 98.8% to 0.031% after 60 min of reaction, and the degradation rate decreased from 0.0584 to 0.00049 min⁻¹ (Fig. 9d), indicating that superoxide (O_2^{\bullet}) is the dominant active species. The RhB degradation efficiency decreased from 98.8% to 76.6% when ammonium oxalate was used as the scavenger, indicating that photogenerated holes were the active species. However, the photocatalytic efficiency of RhB was not affected by the addition of tert-butanol (Fig. 9b) and silver nitrate (Fig. 9c), suggesting that photogenerated electrons and •OH are not the dominant active species. Therefore it can be concluded that ${\rm O_2}^{\mbox{--}}$ and photogenerated holes are the dominant active species.

On the basis of the results of the characterization and photodegradation tests, three reasons are proposed to account for the enhanced photocatalytic activity induced by Ni²⁺ and Ti⁴⁺ surface doping. The first is the increase in optical absorption. The UV-visible spectra confirmed that doping with Ni²⁺ and Ti^{4+} could enhance visible-light absorption by $\mathrm{Bi}_2\mathrm{MoO}_6$ and decrease the band gap of 2.23 eV. The second reason is that Ni/Ti/BiMO-3 exhibited an increase of surface area compared with Bi_2MoO_6 due to Ni^{2+} and Ti^{4+} surface doping. The third reason is that Ni^{2+} and Ti^{4+} on the surface of Bi_2MoO_6 can capture the photogenerated electrons, and Ni²⁺ and Ti⁴⁺ ions as electron scavenger agents react with the photogenerated electrons and restrain the recombination of the electron-hole pairs during the photocatalytic reaction [25,36]. Then the Ni²⁺ and Ti^{4+} ions transfer the electrons to O₂ adsorbed on the surface of Ni/Ti/BMO-x to form superoxide radical (O_2^{\bullet}) . At the same time, extra holes are produced. Therefore it is well recognized that O_2^{\bullet} radicals plays an important role, and holes play a secondary role in the photodegradation process. The photocatalytic mechanism is consistent with the results of the trapping experiment, which prove that O_2^{\bullet} and photogenerated holes are the dominant active species.

4. Conclusions

 Bi_2MoO_6 photocatalysts surface co-doped with Ni^{2+} and Ti^{4+} ions were successfully fabricated through an incipient-wetness impregnation technology and calcination method. The influence of Ni^{2+} and Ti^{4+} concentration on the morphology and optical properties of Bi_2MoO_6 catalysts was investigated. The photocatalytic activity experiment on the degradation of RhB under visible-light irradiation indicated that the optimum Ni/Ti/BiMO-3 resulted in about 4.0, 1.5, and 2.4 times increase in the degradation rate with respect to pure Bi_2MoO_6 , Ti/BMO, and Ni/Ti/BMO-4, respectively. At the same time, Ni^{2+} and Ti^{4+} co-doping can obviously increase visible-light absorption by Bi_2MoO_6 and promote the separation of photogenerated electrons and holes. This study on Bi_2MoO_6 surface co-doped with Ni^{2+} and Ti^{4+} is not only scientifically interesting and technologically promising for Bi_2MoO_6 materials but is also useful for fabrication of other Bi-based materials.

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Fig. 1. X-ray diffraction patterns of different catalysts. BMO, Bi_2MoO_6 ; Ni/BMO, Bi_2MoO_6 surface doped with 0.06% Ni²⁺; Ti/BMO, Bi_2MoO_6 surface doped with 0.064% Ti⁴⁺; Ni/Ti/BMO-1, Bi_2MoO_6 surface co-doped with 0.06% Ni²⁺ and 0.064% Ti⁴⁺; Ni/Ti/BMO-2, Bi_2MoO_6 surface co-doped with 0.12% Ni²⁺ and 0.128% Ti⁴⁺; Ni/Ti/BMO-3, Bi_2MoO_6 surface co-doped with 0.18% Ni²⁺ and 0.192% Ti⁴⁺; Ni/Ti/BMO-4, Bi_2MoO_6 surface co-doped with 0.24% Ni²⁺ and 0.256% Ti⁴⁺; Ni/Ti/BMO-5, Bi_2MoO_6 surface co-doped with 0.30% Ni²⁺ and 0.32% Ti⁴⁺.

Fig. 2. (a) X-ray photoelectron spectroscopy (XPS) survey spectrum of Bi_2MoO_6 surface co-doped with 0.18% Ni²⁺ and 0.192% Ti⁴⁺ (Ni/Ti/BMO-3). XPS spectra of Bi (b), Mo (c), and O (d) in Bi_2MoO_6 and Ni/Ti/BMO-3. XPS spectra of Ni (e) and Ti (f) in Ni/Ti/BMO-3.

Fig. 3. Scanning electron microscopy images of pure Bi_2MoO_6 (a), Bi_2MoO_6 surface doped with 0.064% Ti^{4+} (b), Bi_2MoO_6 surface doped with 0.06% Ni^{2+} (c), Bi_2MoO_6 surface co-doped with 0.06% Ni^{2+} and 0.064% Ti^4 (d), Bi_2MoO_6

surface co-doped with 0.12% Ni^{2+} and 0.128% Ti^{4+} (e), Bi_2MoO_6 surface co-doped with 0.18% Ni^{2+} and 0.192% Ti^{4+} (f), Bi_2MoO_6 surface co-doped with 0.24% Ni^{2+} and 0.256% Ti^{4+} (g), and Bi_2MoO_6 surface co-doped with 0.30% Ni^{2+} and 0.32% Ti^{4+} (h).

Fig. 4. Transmission electron microscopy images of Bi_2MoO_6 (a, b) and Ni Bi_2MoO_6 surface co-doped with 0.18% Ni²⁺ and 0.192% Ti⁴⁺ (c, d).

Fig. 5. N_2 adsorption-desorption isotherms of Bi_2MoO_6 (BMO) and Bi_2MoO_6 surface co-doped with 0.18% Ni^{2+} and 0.192% Ti^{4+} (Ni/Ti/BMO-3). The inset shows the pore size distribution.

Fig. 6. (a) UV-visible spectra and (b) the band gaps of different catalysts. BMO, Bi₂MoO₆; Ni/BMO, Bi₂MoO₆ surface doped with 0.06% Ni²⁺; Ti/BMO, Bi₂MoO₆ surface doped with 0.064% Ti⁴⁺; Ni/Ti/BMO-1, Bi₂MoO₆ surface co-doped with 0.06% Ni²⁺ and 0.064% Ti⁴⁺; Ni/Ti/BMO-2, Bi₂MoO₆ surface co-doped with 0.12% Ni²⁺ and 0.128% Ti⁴⁺; Ni/Ti/BMO-3, Bi₂MoO₆ surface co-doped with 0.18% Ni²⁺ and 0.192% Ti⁴⁺; Ni/Ti/BMO-4, Bi₂MoO₆ surface co-doped with 0.24% Ni²⁺ and 0.256% Ti⁴⁺; Ni/Ti/BMO-5, Bi₂MoO₆ surface co-doped with 0.30% Ni²⁺ and 0.32% Ti⁴⁺.

Fig. 7. (a) UV-visible spectra of rhodamine B (RhB) solution with time. (b) Photographs of the color change of RhB solution in the presence of Bi_2MoO_6 surface co-doped with 0.18% Ni^{2+} and 0.192% Ti^{4+} (Ni/Ti/BMO-3) under visible-light irradiation. (c, d) Photodegradation curves and degradation rate constants (d, inset) for RhB over different catalysts. BMO, Bi_2MoO_6 ; Ni/BMO, Bi_2MoO_6 surface doped with 0.06% Ni^{2+} ; Ti/BMO, Bi_2MoO_6 surface doped with 0.06% Ni^{2+} ; Ti/BMO, Bi_2MoO_6 surface doped with 0.064% Ti^{4+} ; Ni/Ti/BMO-1, Bi_2MoO_6 surface co-doped with 0.06% Ni^{2+} and 0.128% Ti^{4+} ; Ni/Ti/BMO-2, Bi_2MoO_6 surface co-doped with 0.12% Ni^{2+} and 0.128% Ti^{4+} ; Ni/Ti/BMO-4, Bi_2MoO_6 surface co-doped with 0.24% Ni^{2+} and 0.256% Ti^{4+} ; Ni/Ti/BMO-5, Bi_2MoO_6 surface co-doped with 0.30% Ni^{2+} and 0.32% $Ti^{4+.}$

Fig. 8. (a) Five cycles in the photocatalytic degradation of rhodamine B by Ni/Ti/BMO-3. (b) Scanning electron microscopy image of the used Bi_2MoO_6

surface co-doped with 0.18% Ni^{2+} and 0.192% Ti^{4+} .

Fig. 9. UV-visible spectra of rhodamine (RhB) solution with time of the RhB solution over Bi_2MoO_6 surface co-doped with 0.18% Ni²⁺ and 0.192% Ti⁴⁺ (Ni/Ti/BMO-3) in the presence of (a) benzoquinone (BQ) and (b) *tert*-butanol (TBA). (c, d) Photodegradation curves and degradation rate constants (d, inset) for RhB over Ni/Ti/BMO-3 in the presence of different scavengers. AO, ammonium oxalate.

Graphical abstract

 Bi_2MoO_6 surface co-doped with Ni^{2+} and Ti^{4+} ions was fabricated through an incipient-wetness impregnation technology and calcination method. Surface co-doping of Ni^{2+} and Ti^{4+} obviously increased visible-light absorption by Bi_2MoO_6 and promoted the separation of photogenerated charge carriers. Bi_2MoO_6 surface co-doped with 0.18% Ni^{2+} and 0.192% Ti^{4+} exhibits the greatest photocatalytic activity and stability in the degradation of rhodamine B.















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Highlights

- Ni/Ti/Bi₂MoO₆ was fabricated through incipient-wetness impregnation.
- Surface co-doping with Ni^{2+} and Ti^{4+} increased the photocatalytic activity of Bi_2MoO_6 .
- The amount of Ni^{2+} and Ti^{4+} surface co-doping affects the catalytic activity of Bi_2MoO_6 .