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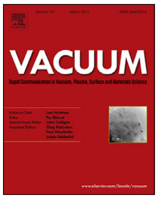

Visible-light-driven photocatalytic performance of nanohybrid incorporating nickel ions into the tetratitanate interlayer

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ABSTRACT

Ni-intercalated tetratitanate with a Ni:Ti molar ratio of 1:6.3 was prepared by electrostatically-driven self-assembly of the negatively charged exfoliated nanosheets and the positively charged nickel ions. The introduction of Ni^{2+} makes the doped titanate to possess spectral responses to visible light, contributed by the hybridization of the 3d orbits of Ni and Ti in the conduction band. The as-prepared materials exhibit mesoporous textures with expanded specific surface areas of more than 90 m^2/g and highly photocatalytic activities in the degradation of methylene blue under visible-light irradiation.

1. Introduction

The search of highly active semiconductor photocatalysts is of great importance for the social sustainable development, reflecting their widely potential applications in the conversion of solar energy into chemical energy and in the treatment of pollution [1,2]. TiO_2 and layered titanates are usually adopted as effective catalysts in photocatalytic procedures [1–4]. However, their band gaps are large and only can be excited by ultraviolet light [3]. Attempts to improve the solar energy utilization, many strategies including doping have been employed to enhance their spectral responsive ability to visible light [5–10]. Among them, transition metal doping can introduce new energy levels close to the conduction band (CB) to narrow the band gap, which are responsible for visible light absorption [5,10–13]. This modification retains the powerful oxidizability of the valence band (VB) holes unchanged, which favors the photodegradation of organic pollutants [5]. However, it is hard to uniformly dope high dopant content into a semiconductor matrix to narrow its band gap that allows it to respond to visible light. An unsuitable dopant amount always forms the combination centre of the photogenerated carriers, resulting in a decrease in photocatalytic efficiency [11].

Layered titanates have been extensively studied for photocatalytic applications [14,15]. It was reported that layered titanates can be delaminated into 2D individual nanosheets through liquid exfoliation [16]. An intercalative hybridization between 2D nanosheets and guest nanoparticles can provide a feasible route to prepare porous nanohybrids with enhanced photoactivities. Many efforts have made to prepare porous pillared nanohybrids fabricated by hybridizing exfoliated titanate nanosheets and metal oxide nanoparticles for developing high active photocatalysts [6,16–23]. Since the exfoliated nanosheets are negatively charged, it is expected to achieve porous oxides with high dopant content through assembling nanosheets and transition metal cations. Nanohybrids incorporating Co^{2+} into the titanate interlayer [24] and into the tantalotungstate interlayer [25] with good photocatalytic activities have been reported. However, it is still a challenge to develop high-performance visible-light photocatalysts through highly doping transition metal ions into a semiconductor matrix. In this work, a new intercalated tetratitanate with high nickel dopant content has been prepared by assembling the negatively charged exfoliated tetratitanate nanosheets and the positively charged Ni^{2+} ions. The as-prepared intercalate exhibits a good visible-light-driven activity in the decomposition of methylene blue (MB) under visible-light irradiation.

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2. Experimental

2.1. Preparation of catalysts

The protonic $H_2Ti_4O_9$ was prepared from $K_2Ti_4O_9$ by an ion-exchange route. The exfoliation of tetratitanate was accomplished by reacting $H_2Ti_4O_9$ with tetrabutylammonium hydroxide solution under ultrasonication at roomtemperature for 3 h, as reported previously [9]. The nickel-intercalated tetratitanate (denoted as $Ni(H_2O)_x$–Ti_4O_9), was prepared by slowly adding a 0.01 M aqueous solution of nickel acetate into the colloidal suspension of nanosheets (pH = 7) under vigorous stirring with a molar ratio of $Ti_4O_9^{2-}$:Ni^{2+} being 1:1. Flocculation occurred immediately after mixing the solutions. After stirring for 4 h, the resulted product was separated by centrifugation, washed thoroughly with distilled water and then dried under vacuum at 70 °C overnight. Finally, $Ni(H_2O)_x$–Ti_4O_9 was calcined at 200 °C for 3 h and referred as Ni–Ti_4O_9. The referred $TiO_{2-x}N_x$ was prepared according to the previous reported procedure [26].

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were measured on a Rigaku SmartLab 3 kW diffractometer using Cu Kα radiation ($\lambda = 0.15418$ nm) at ambient temperature. High-resolution transmission electron microscope (HRTEM) images were performed using a JEOL JEM-2100 with an accelerating voltage of 200 kV, combined with energy dispersive X-ray spectroscopy (EDX, Oxford 7021) for determination of metal composition. The samples were suspended in ethanol and sonicated over 10 min and a drop of the supernatant dispersion was subsequently placed onto a carbon film supported by a copper grid. X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG Escalab MK II spectrometer (Scientific Ltd.) with non-monochromatic Al K X-ray (1486.6 eV). The pressure in the chamber during the experiments was less than 10^{-6} Pa. The analyzer was operated at 20 eV pass energy with an energy step size of 0.1 eV. Nitrogen adsorption-desorption isotherms were examined on a Quantachrome Autosorb-iQ instrument at liquid-nitrogen temperature, in which the samples were degassed at 120 °C for 3 h in flowing N_2 prior to the measurements. UV-Vis diffuse reflectance spectra were recorded on a Shimadzu UV-2550 spectrophotometer with a 60-mm integrating sphere using $BaSO_4$ as the reference. Photoelectrochemical measurements were carried out in a conventional three-electrode quartz glass cell using a CHI660E potentiostat/galvanostat. The as-prepared powders of the samples were deposited on the indium-oxide (ITO)-coated glass by a coating method and served as the working electrode. The counter and reference electrodes were Pt-black wire and Ag/AgCl in KCl, respectively. An aqueous solution containing 0.1 M Na_2SO_4 was used as the supporting electrolyte and a 300 W Xe lamp with a 400 nm cutoff filter was used as the visible-light source to excite the electrode surface.

2.3. Photocatalytic test

The photocatalytic activity was tested in the photodegradation of MB aqueous solution at ambient temperature under visible-light irradiation. A 300 W Xe lamp with a 400 nm cutoff filter was used as the visible-light source with the light intensity of 57 mW/cm^2. For each case, 30 mg catalyst was dispersed in 60 ml of 20 mg L^{-1} MB aqueous solution. Before illumination, the suspension was magnetically stirred for 120 min in dark to establish an adsorption-desorption equilibrium of MB on the sample surface. A continuous magnetic stirrer was employed throughout the experiments. The concentration of MB at given intervals was detected by measuring the maximum absorbance at 664 nm using a UV-Vis spectrophotometer.

3. Results and discussion

As depicted in Fig. 1, $K_2Ti_4O_9$ and $H_2Ti_4O_9$ show well-ordered layered structures with sharp diffractions (JCPDS 32-0661 and 38-0699). The replacement of K^+ in $K_2Ti_4O_9$ by H_3O^+ resulted in that the (200) reflection of $H_2Ti_4O_9$ shifted towards a low angle. This reflection of $Ni(H_2O)_x$–Ti_4O_9 was further shifted to 8.9° with an interlayer spacing of 0.99 nm. The interlayer spacing value was determined from the Bragg equation $2d\sin\theta = \lambda$, where d, θ and λ are the neighboring planar distance, the diffraction angle and the wavelength of the employed X-ray, respectively. The gallery height of $Ni(H_2O)_x$–Ti_4O_9 was estimated to be 0.42 nm after deducting from the thickness of tetratitanate nanosheet (ca. 0.57 nm) [24]. Due to the water molecule size of 0.35 nm, the gallery height indicates that the encapsulated species should be Ni^{2+} ions with hydrated H_2O molecules. After calcination, this reflection was shifted toward 10.1° with an interlayer spacing of 0.88 nm and gallery height of 0.31 nm. This decrease is from the release of the hydrated H_2O molecules. Notably, the in-sheet diffractions (004) and (020) of titanate almost remain intact, suggesting that the 2D sheet skeleton in $Ni(H_2O)_x$–Ti_4O_9 and Ni–Ti_4O_9 was reserved. The molar ratios of Ni:Ti in $Ni(H_2O)_x$–Ti_4O_9 and Ni–Ti_4O_9 were given by EDX to be 1:6.3. The dosage of nickel is lower than the calculated value (1:4) based on the charge requirements. This reflects that there exist some H^+ cations between the sheets for the requirement of charge compensation. It is expected that the introduced nickel species and H^+ ions were randomly distributed between the titanate interlayer, which would induce partial 2D titanate sheet skeletons to form stress deformation and eventually resulted in that the (020) reflection for $Ni(H_2O)_x$–Ti_4O_9 and Ni–Ti_4O_9 appears a broad and doublet peak in their XRD patterns. The HRTEM image of Ni–Ti_4O_9 displays (Fig. 2) the titanate nanosheets in an intercalated crystallite are parallel to each other with a vertical distance

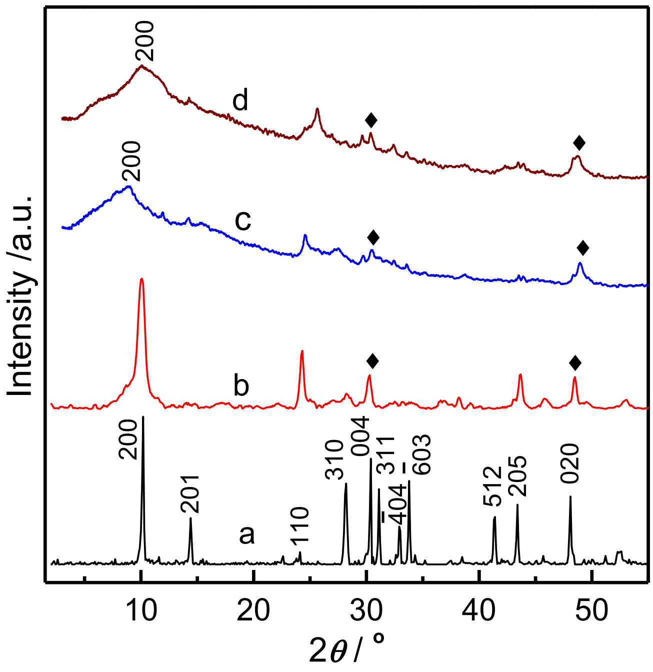

Fig. 1. Powder XRD patterns of $K_2Ti_4O_9$ (a), $H_2Ti_4O_9$ (b), $Ni(H_2O)_x$–Ti_4O_9 (c) and Ni–Ti_4O_9 (d), where ◆ for in-sheet diffractions of tetratitanate sheets.