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Short communication

Study on the energy band structure and photoelectrochemical performances of spinel $Li_4Ti_5O_{12}$

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ABSTRACT

Energy band structure, photoelectrochemical performances and photocatalysis activity of spinel $Li_4Ti_5O_{12}$ are investigated for the first time in this paper. $Li_4Ti_5O_{12}$ possesses more positive valence band potential and wider band gap than TiO_2 due to its valence band consisting of Li_{1s} and Ti_{3d} orbitals mixed with O_{2p}. $Li_4Ti_5O_{12}$ shows typical photocatalysis material characteristics and excellent photocatlytic activity under UV irradiation.

1. Introduction

Since the discoveries that water can be spilt to H_2 and O_2 on *n*-TiO_2 electrode under UV irradiation in 1971 and organic compounds can be degraded to CO_2 and H_2O on TiO_2 powder under UV light in 1976, a great deal of effort has been devoted to develop novel photocatalysts and highly photoactive electrodes [1–3]. The use of semiconductor oxide particles as photocatalysts is well established and has shown great utility in environmental applications [4,5]. Particularly, anatase and rutile TiO_2 are highly studied photocatalysts from both fundamental and applied aspects [6,7].

Spinel $Li_4Ti_5O_{12}$ has attracted much attention as a superior anode insertion material for energy storage cells due to its high thermodynamic stability, excellent cycle life and safety [8–12]. Although spinel $Li_4Ti_5O_{12}$ is a kind of titanate possessing the same element content with TiO_2 except for containing Li, no investigation is reported on its energy band structure and photoelectrochemical characteristics.

In this study, UV–vis diffuse reflectance spectra (DRS), Mott–Schottky experiments (MS), cyclic voltammograms (CV) tests, electrochemical impedance spectroscopy (EIS) and decomposition experiments were employed to study the energy band structure and photoelectrochemical performances of spinel $Li_4Ti_5O_{12}$. Experiment results reveal that spinel $Li_4Ti_5O_{12}$ with a wide band gap is a tipical photocatalysis material and displays improved photocatalysis performance comparing with anatase TiO_2 due to its positive valence band potential. We anticipate that this preliminary study offers a potential competitor to anatase TiO_2 and opens new perspectives in investigation of other lithium-based compounds for new photocatalyst.

2. Experiment

2.1. Preparation of the $Li_4Ti_5O_{12}$

The $Li_4Ti_5O_{12}$ was prepared as our previous studies via solid-state method [13,14]. Appropriate amount of Li_2CO_3 and rutile TiO_2 were used as starting materials and mixed with methanol as medium by planetary ball milling. The resulting mixture was dried at 100 °C and calcined in a muffle furnace at 800 °C for 12 h in air. The sample was reground, palletized and heated for another 12 h at 800 °C in air. In the preparation, the dosage of Li_2CO_3 was 3 wt.%

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excess of its stoichiometry for compensating of lithium volatilization during the high temperature heating.

2.2. Measurements

The UV–vis diffuse reflectance spectra (DRS) were recorded on a Varian Cary 500 Scan UV–vis-NIR spectrometer with $BaSO_4$ as the background between 200 and 800 nm.

Electrochemical measurements were carried out in a three electrode cell that comprised of a dye-coated film working electrode, a platinum plate as counter electrode, and a saturated Ag/AgCl (3 M KCl) electrode as reference electrode. The working electrode was fabricated by dropping a total of 5 mg of synthesized samples on the ITO glass and the resulting films (1.0 cm× 1.0 cm) were heated in air at 400 °C for 1 h to improve adhesion. The electrolyte was a 0.2 M Na_2SO_4 aqueous solution without additive and was purged with nitrogen gas for 2 h prior to the measurements. CV measurements were conducted with a BAS Epsilon workstation. The light was generated using a Xe xenon lamp (CHF-XM500). EIS experiments were taken on a Precision PARC workstation. For Mott–Schottky test, the potential ranged from −0.5 to −1.0 V (vs. NHE), and the perturbation signal were 10 mV with the frequency at 1 KHz. For impedance plots measurements, the perturbation signal were also 10 mV but the frequency ranged from 100 KHz to 10 mHz.

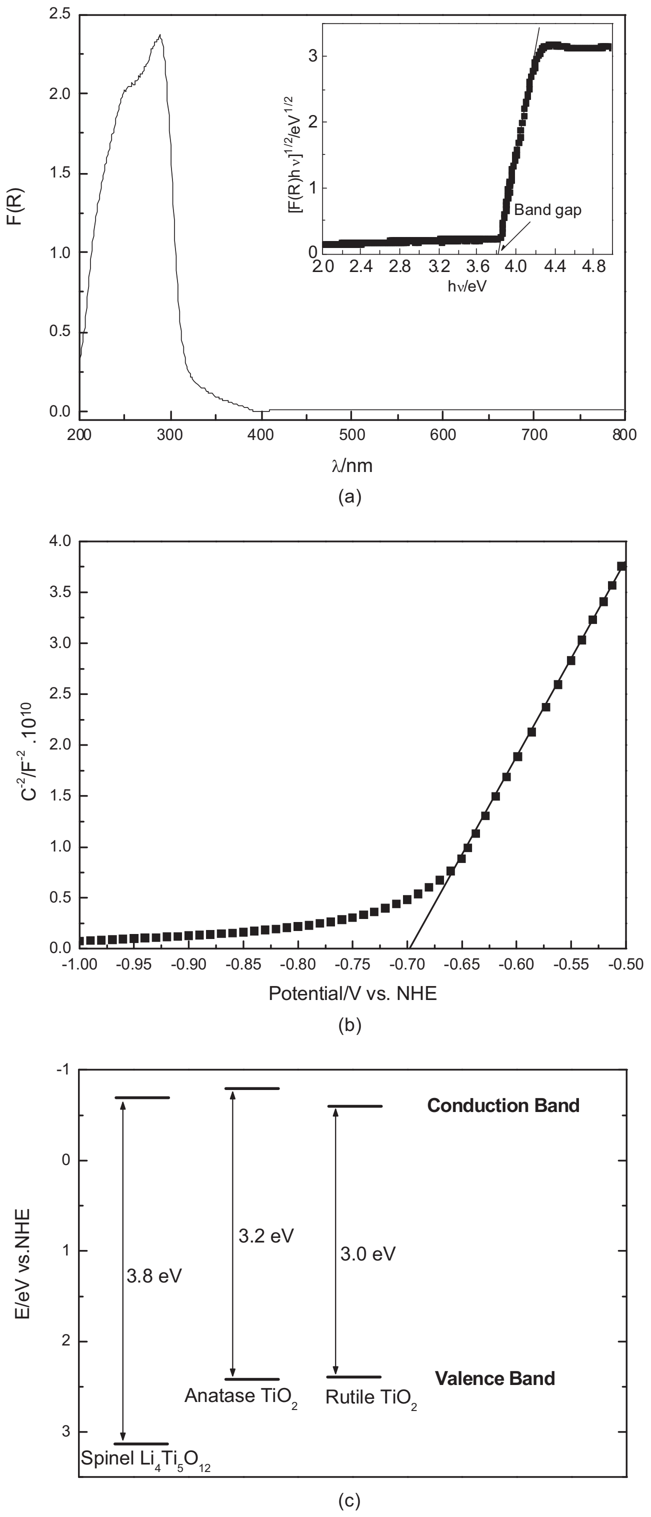
In order to estimate the photocatalytic activity of the $Li_4Ti_5O_{12}$, the photocatalytic decomposition of methyl orange was performed with and without UV irradiation. A total of 0.1 g of each photocatalyst was suspended in aqueous solution of 10 ppm methyl orange (100 ml) under vigorous stirring. The resulting solution was analyzed on a Varian UV–vis-NIR spectrophotometer (model: Cary-500). The percentage of degradation was reported as C/C_0. C was the absorption of methyl orange at each irradiated time interval of the main peak of the absorption spectrum at wavelength 465 nm. C_0 was the absorption of the starting concentration when adsorption/desorption equilibrium was achieved.

3. Result and discussion

3.1. Energy band structure

Fig. 1(a) shows the UV–vis diffuse reflectance spectra of spinel $Li_4Ti_5O_{12}$. The $Li_4Ti_5O_{12}$ exhibits UV absorption (<400 nm). Its wavelength at the absorption edge is 320 nm (the intercept on the wavelength axis for a tangent line drawn on absorption spectra), corresponding to a wide band gap [15]. In order to determine band gap energy of $Li_4Ti_5O_{12}$ from the absorption spectra, a plot of $[F(R)\,h\nu]^{1/2}$ vs. $h\nu$ is introduced [16]. As shown in the inset of Fig. 1(a), the band gap energy of spinel $Li_4Ti_5O_{12}$ estimated by extrapolating the linear part of $[F(R)\,h\nu]^{1/2}$ plot to the energy axis is 3.8 eV, wider than that of anatase TiO_2 (3.2 eV) and rutile TiO_2 (3.0 eV) [6]. Fig. 1(b) exhibits the Mott–Schottky plot of spinel $Li_4Ti_5O_{12}$. Similarly to TiO_2, $Li_4Ti_5O_{12}$ displays typical n-type semiconductor characteristic due to the positive slope of the linear plot [17]. The flat-band potential of spinel $Li_4Ti_5O_{12}$, x intercepts of the linear region obtained from the Mott–Schottky plot [18], is roughly −0.7 V vs. NHE.

Therefore, according to the experiment results derived from Fig. 1(a) and (b), the energy band structure of spinel $Li_4Ti_5O_{12}$ is demonstrated in Fig. 1(c). And the energy band structure of anatase and rutile TiO_2 [6] are also given in Fig. 1(c) for discussion. The energy band structure of anatase TiO_2 is similar with that of rutile TiO_2, indicating that the consisted elements but not crystal structure plays a determined role on the formation of energy band structure. In principle, the conduction bands of stable oxide semiconductor photocatalysts consisting of metal cations with a d_0 and d_{10} configuration consists of empty orbitals (LUMO) of the metal cations. On the other hand, the valence bands are formed via the full orbitals of metal cations mixing with O_{2p} [6,19].



(a)

(b)

(c)

Fig. 1. (a) UV–vis diffuse-reflectance spectra and plot of $[F(R)\,h\nu]^{1/2}$ vs. $h\nu$ (inset) of spinel $Li_4Ti_5O_{12}$. (b) Mott–Schottky plot of spinel $Li_4Ti_5O_{12}$. (c) Energy band structure of spinel $Li_4Ti_5O_{12}$, anatase and rutile TiO_2.

As shown in Fig. 1(c), the conduction band potential of spinel $Li_4Ti_5O_{12}$ is near to that of anatase and rutile TiO_2, which suggested that the $Li^+(2s^0)$ in the spinel $Li_4Ti_5O_{12}$ played little influence on the formation of conduction band. Different from other lithium-based