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# $Bi_2WO_6$ photocatalytic films fabricated by layer-by-layer technique from $Bi_2WO_6$ nanoplates and its spectral selectivity

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**Abstract**

$Bi_2WO_6$ multilayer films have been fabricated successfully by a layer-by-layer (LbL) technique from $Bi_2WO_6$ nanoplates, which show higher visible-light photoactivity ($\lambda > 420$ nm) than that of $Bi_2WO_6$ nanoplate powders and P25 $TiO_2$ films. The films were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), and UV–visible absorption spectroscopy. Photocatalytic activities of the films were evaluated by the rhodamine B (RhB) decomposition under UV and visible-light irradiation. Thickness and photoactivity of the film can be modified easily by changing the deposition cycles. $Bi_2WO_6$ films have the spectral selectivity of the photocatalytic degradation of RhB. Under the wavelength greater than 300 nm, the RhB molecules tend to be transformed to rhodamine over $Bi_2WO_6$ films selectively. However, in the case of shorter wavelength ($\lambda = 254$ nm) light irradiation, the RhB molecules can be photodegraded completely.

*Keywords:* $Bi_2WO_6$; Nanoplates; Layer-by-layer; Photocatalysis; Rhodamine B; Spectral selectivity

## 1. Introduction

Semiconductor photocatalysts have attracted great interests for their application in the environmental remediation, water splitting, the fixation of $CO_2$ and $N_2$, and the photosynthesis of organic compounds [1–3]. $TiO_2$ has by far the most popular one for its higher photocatalytic activity, good photostability, non-toxicity, and low price. But the large bandgap of $TiO_2$ (3.2 eV) makes it necessary for excitation only by UV light with wavelengths below 387 nm, which limits the usage efficiency of solar energy (max. 5%) and hinders the commercialization of this technology. Therefore, in order to eliminate the drawback, exploitation of new visible-light-driven photocatalysts has received considerable attention.

In recent years, $Bi_2WO_6$ has been demonstrated to be a good visible-light-driven photocatalysts. Kudo and Hijii [4] first demonstrated the photocatalytic $O_2$ evolution over $Bi_2WO_6$ from $AgNO_3$ solution. Subsequently, Tang et al. [5] reported that $Bi_2WO_6$ was also active for photocatalytic mineralizing both $CHCl_3$ and $CH_3CHO$. More recently, we successfully enhanced its photocatalytic activity by synthesizing nanostructured $Bi_2WO_6$, i.e. the nanoplates by hydrothermal process [6–8], and the nanoparticles by calcining amorphous complex precursor [9]. Yu et al. [10] also prepared the $Bi_2WO_6$ nanoparticles by hydrothermal method. Especially, $Bi_2WO_6$ nanoplates show higher activity, and have the potential use in environmental remediation induced by solar energy. Unfortunately, $Bi_2WO_6$ has a bigger molecular weight than that of $TiO_2$, and is more difficult to be dispersed in aqueous solution, which is a drawback for heterogeneous photocatalysis by photocatalysts dispersion [8]. For the photocatalytic reaction is a surface reaction, in order to eliminate the previous drawback, it is essential to expose the surface of $Bi_2WO_6$ nanoplates to the contaminants and the light. The $Bi_2WO_6$ films should be one of the best choices.

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Hamada et al. [11] epitaxially deposited $Bi_2WO_6$ films on Nb-doped $SrTiO_3$ substrate by pulsed laser deposition, and investigated the dielectric properties. Ishikawa et al. [12] deposited $Bi_2WO_6$ films by metalorganic chemical vapor deposition, and investigated the ferroelectricity. Recently, we have fabricated the $Bi_2WO_6$ films from amorphous complex precursor, and investigated the photoelectric properties [13]. However, to the best of our knowledge, there are still no reports about photocatalytic activity of $Bi_2WO_6$ films.

Layer-by-layer (LbL) technique by sequential adsorption of oppositely charged materials (ranged from polyelectrolytes to inorganic materials) is one of the most promising ways of fabricating multilayer thin films with precisely controlled composition, thickness, and architecture on a nanometer scale [14–23]. Recently, some researchers reported the photocatalytic films fabricated by LbL technique [24–28]. But few reports are about the fabrication of multilayer films of complex oxide visible-light-driven photocatalysts.

Here, we reported the fabrication of $Bi_2WO_6$ films by sequential adsorption of $Bi_2WO_6$ nanosheets and polyelectrolytes, which showed higher photocatalytic activities under visible-light irradiation ($\lambda > 420$ nm). Thicknesses and photocatalytic activities of $Bi_2WO_6$ films were easily controlled by modifying the deposition layer numbers. The spectral selectivity of the rhodamine B (RhB) photodegradation on the surface of $Bi_2WO_6$ films was also discussed.

## 2. Experimental

### 2.1. Materials

Polyethylenimine (PEI), 50 wt% aqueous solutions, with molecular weight of $6 \times 10^5$, was purchased from Aldrich Co. and used without further purification. All solutions were prepared from deionized water. All other solvents and chemicals were of reagent grade. P25 $TiO_2$ (ca. 80% anatase, 20% rutile; BET area ca. $50\,m^2\,g^{-1}$) was kindly supplied by Degussa Co.

$Bi_2WO_6$ nanoplates were prepared by the hydrothermal synthesis according to the previous reports [6,7]. In a typical synthesis procedure, 5 mmol $Bi(NO_3)_2 \cdot 5H_2O$, 2.5 mmol $H_2WO_4$, and 5 mmol KOH were added to 35 mL deionized water with magnetic stirring. The mixture was sealed in a Teflon-lined stainless steel autoclave and heated at 180 °C for 24 h. After cooling, the resulting samples were collected and washed with deionized water and dried at 80 °C in air.

### 2.2. LbL assembly

Deposition of the $Bi_2WO_6$ films by LbL technique was carried by the similar procedure as reported in other related studies [20], which was described as follows.

Quartz substrates were cleaned by 3:7 (vol%) $H_2O_2$/$H_2SO_4$ (piranha solution) at 100 °C for ca. 40 min, followed by sonication in deionized water for 1 h, and then extensive rinsed with deionized water [29]. After cleaning, the substrates were negatively charged. $Bi_2WO_6$ nanoplates were dispersed in deionized water to yield a $2\,g\,L^{-1}$ suspension, and the pH of the suspension was adjusted to 10 by 1 M KOH solution to create a negatively charged surface for $Bi_2WO_6$ nanoplates.

Substrates were primed by being treated with a PEI solution ($2.5\,g\,L^{-1}$) to introduce the positive charge to the substrate surface. Primed substrates were dipped into $Bi_2WO_6$ nanoplates suspension to prepare a monolayer film by electrostatic deposition principle. Substrates and films were rinsed with water to remove the excessively adsorbed species and dried with air blow between the deposition steps. Repeating these layers produces $n$ layers on the substrates.

As comparison, $TiO_2$ films were also prepared by the similar procedure. The $TiO_2$ (P25 $TiO_2$) suspension was $1\,g\,L^{-1}$, with the pH of 10.

### 2.3. Characterizations

XRD patterns were collected using a Rigaku Rint 2000S powder diffractometer with graphite monochromatized Cu$K\alpha$ radiation ($\lambda = 0.15405$ nm). The surface morphology of LbL films was observed by field emission scanning electron microscopy (FE-SEM; JEOL, JSM-6700F). UV–-visible absorption spectra for monolayer and multilayer films fabricated on a quartz-glass substrate were recorded using a ThermoSpectronic UV500 UV–visible spectrometer.

### 2.4. Photochemical experiments

Photocatalytic activities of the films were evaluated by the RhB decomposition under UV and visible-light irradiation. UV light was obtained by a 25 W Hg lamp ($\lambda = 254$ nm) and the average light intensity was $400\,\mu W\,cm^{-2}$. A 500 W xenon lamp (Beijing TrusTech Science and Technology Co.) and different cutoff filters ($\lambda > 300$ nm, $\lambda > 350$ nm, and $\lambda > 420$ nm) were used to obtain the desired irradiation. The average light intensity was $100\,mW\,cm^{-2}$. The radiant flux was measured with a photometer (International Light Model IL1400A).

$Bi_2WO_6$ or $TiO_2$ films were dipped into the RhB solution ($1 \times 10^{-5}$ M, 50 mL) in a quartz vessel ($3 \times 3 \times 10\,cm^3$) vertically. The light was irradiated from side and perpendicular to the surface of the films. The size of the films was about $2.5 \times 2.5\,cm^2$. Air was bubbled into the reactor with a flow rate of $40\,mL\,min^{-1}$. At given time intervals, 1 mL aliquots were sampled, and analyzed by recording the variations of the absorption band maximum (554 nm) in the UV–visible spectrum of RhB using a ThermoSpectronic UV500 UV–visible spectrometer.