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# W/Mo co-doped $BiVO_4$ for photocatalytic treatment of polymer-containing wastewater in oilfield

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ABSTRACT

Polymer flooding is an effective way to enhance oil recovery (EOR). However, the treatment of the oily wastewater becomes an urgent issue. Photocatalysis is a promising approach for this purpose. In this report, W/Mo co-doped $BiVO_4$ particles are synthesized by hydrothermal method. W/Mo co-doping could promote an effective separation of photogenerated carriers reflecting from the 6 times higher photocurrent density compared to pure $BiVO_4$. The photodegradation of partially hydrolyzed polyacrylamide (HPAM) over 0.5 at.% W and 1.5 at.% Mo co-doped $BiVO_4$ is 43% under UV–vis light irradiation for 3 h, which is much higher than that of pure $BiVO_4$ (18%).



## 1. Introduction

China's thirst for energy has driven to seek feasible technologies to enhance oil recovery (EOR) [1]. Currently, polymer flooding technology as a typical EOR process has been widely and successfully used in the later period of the Chinese oilfield [2–4]. In general, partially hydrolyzed polyacrylamide

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(HPAM) is the most widely used polymer in the flooding process. HPAM has high molecular weight and is water-soluble which can provide a significant improvement of EOR as high as 46% in field experience due to the decreasing of the gap between oil and water viscosity [5]. On the other hand, the residual HPAM in water can increase the viscosity of oily wastewater, reduce velocity rising tendency and make oil into the emulsified oil [6]. Therefore, the produced water from polymer flooding is much more difficult to be treated than that from water flooding. Moreover, as the polymer-containing wastewater can lead to the death of aquatic life and make resource toxic [7], it is highly demand to remove the polymer from the wastewater.

Photocatalysis as an advanced oxidation process has recently been applied to degrade the HPAM [8,9]. For example, Li et al. found that HPAM (100 mg/L) can be degraded by $Eu^{3+}$ doped $TiO_2$ under UV light irradiation [8]. Nevertheless, most of these work focused on the intensive studied $TiO_2$ [8,9]. Thus, this leaves room for search for other photocatalysts which have potential applications in the treatment of polymer containing wastewater. Among the investigated photocatalysts, monoclinic $BiVO_4$ with a band gap of 2.4 eV has been recently demonstrated as a promising material for photocatalytic oxidation reaction and photoelectrochemical cell [10–14]. However, more than 60% of the photoinduced electron–hole pairs could recombine before reaching the respective interfaces [15]. Therefore, poor charge carrier separation and low charge carrier mobility appear to be the major limitations of $BiVO_4$ in photocatalytic applications [16–18]. In order to overcome these problem, different strategies have been proposed including morphology control [19–21], fabrication of heterojunctions [13,22] and doping [23,24].

In this study, we report a hydrothermal method to synthesize W/Mo co-doped $BiVO_4$ particles. The influences of W and Mo doping on the photocatalytic activity of $BiVO_4$ were evaluated with respect to rhodamine B (RhB) degradation as well as photoelectrochemical (PEC) measurements. In addition, the photocatalytic degradation of HPAM over W/ Mo co-doped $BiVO_4$ and $BiVO_4$ were compared.

## 2. Experimental

### 2.1. Synthesis

In a typical procedure, 1 mmol $Bi(NO_3)_3{\cdot}5H_2O$ was dissolved into 2 mL $HNO_3$ solution (4 M), whereas 1 mmol $NH_4VO_3$ was added to 2 mL NaOH solution (2 M). Then, 0.05 g of sodium dodecyl benzene sulfonate (SDBS) was added to both of the above solutions, respectively. After that, the two solutions were mixed and stirred for 30 min with adjusting the pH to 7 using NaOH solution (2 M). The solution was then transferred to a Teflon-lined stainless steel autoclave with a capacity of 10 mL and heated at 200 °C for specific required time. For the synthesis of W or/and Mo doping samples, the $NH_4VO_3$ was partially replaced by $Na_2WO_4$ or/and $Na_2MoO_4$ with different molar ratios, if required, while keeping other reaction conditions unchanged. After being cooled down to room temperature naturally, the precipitate was collected after washed with ethanol and distilled water, and dried at 100 °C for 4 h.

### 2.2. Characterizations

The structures of the prepared samples were measured by X-ray diffraction (XRD) with a PANalytical X'Pert diffractometer operated at 40 kv and 40 mA using Kα radiation. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were performed on a Zeiss SUPRA 50VP microscopy. Diffuse reflectance spectra (DRS) data were recorded on a Shimadzu UV-2600 spectrophotometer equipped with an integrating sphere using $BaSO_4$ as the reflectance standard sample. The total organic carbon (TOC) of HPAM was measured by Shimadzu TOC-VCPH analyzer.

### 2.3. Photoelectrochemical and photocatalytic activity measurements

A three-electrode cell with an electrochemical work station (CH660D) was used to measure the PEC properties in (0.5 M) $Na_2SO_4$ solutions. A saturated calomel electrode (SCE) was used as the reference electrode, and the Pt wire was the counter electrode. The prepared samples were used as working