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# Photoelectrochemical Study and Hydrothermal Synthesis of Bismuth Phosphate Nanorods

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Bismuth phosphate nanorods with the diameter about 30 nm and length about 1-2 μm were synthesized by a simple hydrothermal process. The morphology and crystal structure were characterized by SEM, HRTEM and XRD. The results show that the $BiPO_4$ nanorods that have single-crystalline nature with a preferential growth oriented along the [100] direction. Photoelectrochemical measurements show they may be more efficient in photocatalytic degradation of organic pollutants and decomposition of water.

**Key Words: Bismuth phosphates, Nanorods, Photoelectrochemical.**

## INTRODUCTION

Among the different emergent technologies to solve global energy and environmental issues, the heterogeneous photocatalysis has been utilized as a promissory alternative. The use of solar energy and semiconductor catalysts for photocatalytic degradation of organic pollutants in water and the water splitting to produce hydrogen has attracted a special attention[1-8]. Various semiconductor materials such as tungstates, molybdates, niobates, tantalates and titanates have been studied for the degradation of toxic substrates[2,5,6] and the decomposition of pure water[4,7,8].

Bismuth and its compounds have been widely studied recently because of their unique qualities. Among them, bismuth phosphates ($BiPO_4$) were reported to have special application in catalysis[9], ion sensing[10] and separating radioactive elements[11]. $BiPO_4$ is also considerably important for improving the electrical properties of phosphate glasses[12] and application in high-performance luminescence devices[13]. Recently, it was also reported that $BiPO_4$ exhibited high photocatalytic activity in degradation of dye[14]. To the best of our knowledge, there is no report on the preparation of $BiPO_4$ nanorods by the surfactant assistant hydrothermal method and the investigation of its photocatalysis. In this paper, we describe a controlled solvothermal synthesis of monoclinic phase $BiPO_4$ nanorods by through SDS method. The morphology can be adjusted by the SDS in the hydrothemal process. The as prepared $BiPO_4$ nanorods exhibits higher photocurrent than that of P25 during irradiation.

## EXPERIMENTAL

**Synthesis of $BiPO_4$ nanorods:** All chemicals were analytical grade and were used as received without further purification. In a typical synthesis, 50 mL of 0.1 M $NaH_2PO_4{\cdot}2H_2O$ solution was prepared by dissolving 5 mmol $NaH_2PO_4{\cdot}2H_2O$ into 50 mL ionic water. Mean while, 5 mmol $Bi(NO_3){\cdot}5H_2O$ was dissolved in 50 mL of $HNO_3$ (1 M), which was added 5 mmol SDS in advance. Then $NaH_2PO_4{\cdot}2H_2O$ solution was slightly added into $Bi(NO_3){\cdot}5H_2O$ solution under magnetic stirring. The precursor solution was poured into a Teflon-lined stainless steel autoclave until 80 % of the volume of the autoclave was occupied. The autoclave was heated at 180 ºC for 24 h at autogenous pressure. After the autoclave was cooled to room temperature, the precipitate was separated by filtration, washed with distilled water and absolute alcohol several times and then dried at 80 ºC for 4 h.

The powder X-ray diffraction patterns of as-synthesized samples were measured on a X-ray diffractometer (Bruker $D_8$ ADVANCE) using monochromatized $CuK_\alpha$ ($\lambda = 0.15418$ nm) radiation under 40 kV and 100 mA. The morphologies and microstructures of as-prepared samples were examined with scanning electron microscopy (SEM, JSM-6700F). Transmission electron microscopy (TEM) observations were carried out on a JEOL JEM-2100 instrument with accelerating voltage 200 kV in bright-field. The specimens used for TEM studies were dispersed in absolute ethanol by ultrasonic treatment. The sample was then dropped onto a copper grid coated with a holey carbon film and dried in air. Raman spectra

were analyzed using a German Bruker RFS 100/S Raman spectrometer.

**Photoelectrochemical measurement:** The photoelectrochemical measurements were carried out in 0.5 M $Na_2SO_4$ electrolyte by an computer-controlled CHI 650 D electrochemical workstation with the electrochemical cell equipped with quartz windows. The photocurrents were measured in a standard three-electrode configuration with $BiPO_4$ nanorods as working electrode, Ag/AgCl in saturated KCl as reference electrode and platinum wire as counter electrode, respectively. A xenon lamp was used during the photoelectrochemical measurements.

## RESULTS AND DISCUSSION

The morphologies of the monoclinic $BiPO_4$ nanorods prepared by hydrothermal procedures were revealed by SEM and TEM (Fig. 1). The SEM image (Fig. 1a) clearly demonstrates that the as-prepared products are almost entirely rods-like crystals with diameter of about 30 nm and length of 1-2 μm. As shown in Fig. 1b, the TEM image also shows that the $BiPO_4$ nanorods have uniform diameters about 30 nm, which is consistent with the SEM measurements.

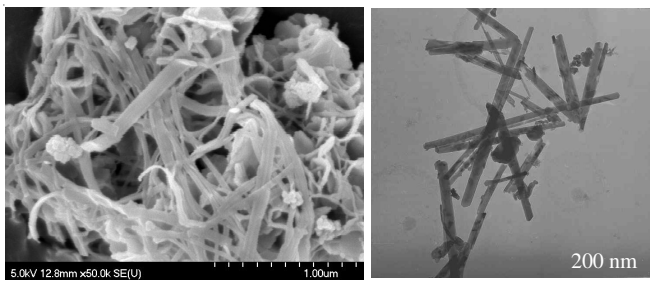


Fig. 1. SEM and TEM images of $BiPO_4$ nanorods

The phase and composition of the as prepared products were investigated using XRD measurement (Fig. 2). In Fig. 2 all diffraction peaks can be assigned to the monoclinic structure of $BiPO_4$ (JCPDS No. 01-080-0209) with space group P21/n and no other peaks for impurities were detected. The results show that the monoclinic $BiPO_4$ nanorods could be successfully synthesized by this simple hydrothermal method. The energy dispersive spectrometry analysis was employed to determine the composition of the $BiPO_4$ nanorods. The energy dispersive spectrometry pattern of the $BiPO_4$ nanorods is shown in Fig. 3. It can be seen that the main elements in the samples are O, Bi and P, which confirms that the obtained products are $BiPO_4$ nanorods. The elements of Cu and C are generated from the supporting carbon-coated copper meshes.

Fig. 4 shows a HRTEM image and a SAED pattern of the $BiPO_4$ nanorods. The HRTEM image shows that the sample is structurally uniform with an interplanar spacing of about 0.287 nm, which corresponds to the (012) lattice spacing of hexagonal $BiPO_4$. The SAED pattern recorded on an individual $BiPO_4$ nanorod reveals the single-crystalline nature of the sample with a preferential growth oriented along the (100) crystalline plane. Combined with HRTEM observations, it can be estimated that these $BiPO_4$ nanorods preferentially grow along the [100] direction.

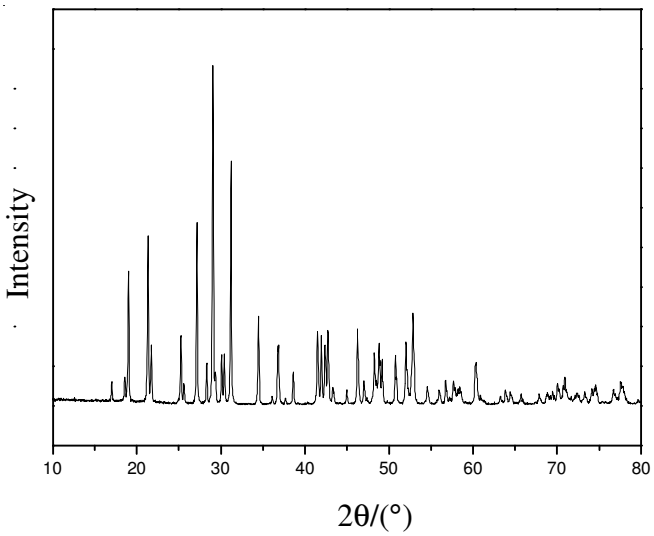


Fig. 2. XRD pattern of $BiPO_4$ nanorods

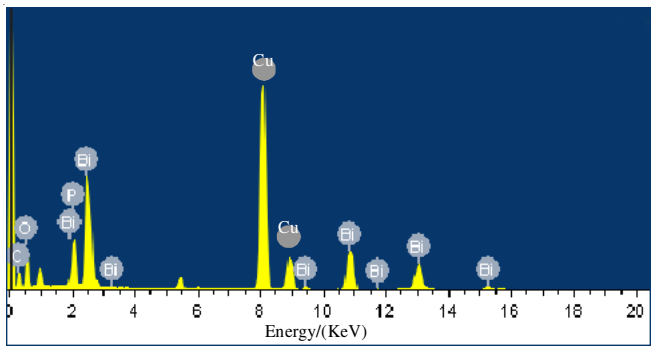


Fig. 3. EDS pattern of $BiPO_4$ nanorods

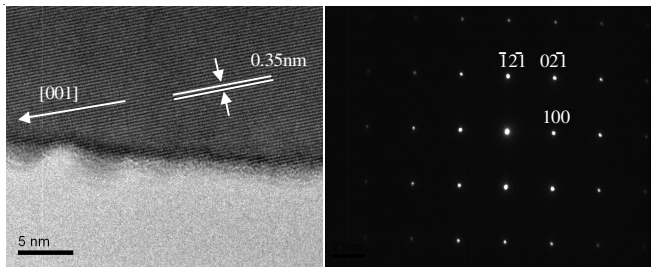


Fig. 4. HRTEM and SAED of $BiPO_4$ nanorods

Systematic photoelectrochemical measurements were carried out on the photoelectrodes prepared from $BiPO_4$ nanorods and $TiO_2$ (P25). A set of linear-sweep voltammagrams (LSV) were recorded in dark and under illumination of xenon lamp, as shown in Fig. 5. The potential was swept linearly at a scan rate of 2 mV/s between -0.5 and 1.0 V. In dark condition, both the $BiPO_4$ and $TiO_2$ photoelectrodes showed almost no photocurrent, which indicated that no electrocatalytic oxygen evolution occurred. Under illumination the current density is about $2.5 \times 10^{-5}$ A/cm$^2$ on $BiPO_4$ nanorods higher than that of $TiO_2$. The $BiPO_4$ nanorods showed higher photocurrent density throughout the potential window which suggested efficient charge separation. These results implied that the $BiPO_4$ nanorods may be more efficient in photocatalytic degradation of organic pollutants in water and the decomposition of water to produce hydrogen.

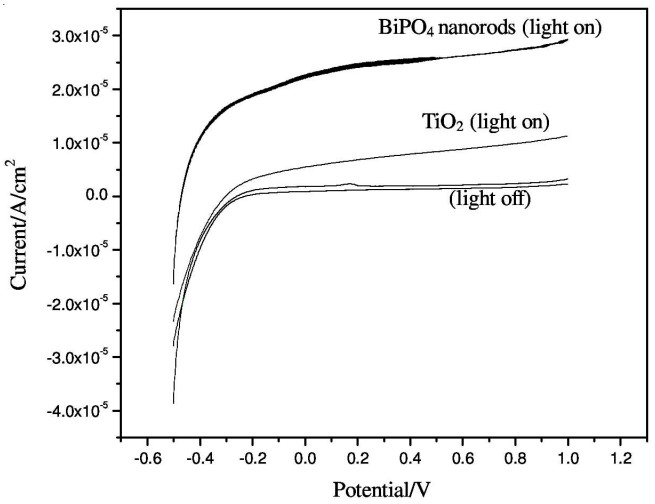


Fig. 5. Current-voltage characteristics measured on the $BiPO_4$ nanorods and $TiO_2$ electrodes under irradiation

## Conclusion

In summary, the monoclinic $BiPO_4$ nanorods have been synthesized by a facile hydrothermal process. The $BiPO_4$ nanorods with the diameter about 30 nm and length about 1-2 μm have the single-crystalline nature with a preferential growth oriented along the [001] direction. The photoelectrochemical measurements show that the $BiPO_4$ nanorods display higher photocurrent density throughout the potential window, which suggests they may be good photocatalyst in organic degradation or decomposition of water.

## ACKNOWLEDGEMENTS

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