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# Facile formation of $Ag_2WO_4/AgX$ (X = Cl, Br, I) hybrid nanorods with enhanced visible-light-driven photoelectrochemical properties

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ABSTRACT

In this work, we demonstrated a general strategy for the preparation of a series of uniform $Ag_2WO_4/AgX$ (X = Cl, Br, I) hybrid nanorods by a facile *in-situ* anion exchange reaction occurring at room temperature between pregrown $Ag_2WO_4$ nanorods and different $X^-$ ions in water. Compared with $Ag_2WO_4$ nanorods, further investigation has revealed that the as-prepared hybrid nanorods possess significantly enhanced photocurrent response and photocatalytic activity in degrading methyl orange (MO) under visible-light irradiation. In particular, the $Ag_2WO_4/AgBr$ hybrid nanorods exhibit the highest photocatalytic activity among the three kinds of samples. The active species tests indicate that superoxide anion radicals and photogenerated holes are responsible for the enhanced photocatalytic performance.

## 1. Introduction

Semiconductor photocatalysts have attracted considerable attentions due to their great potential applications in solving current environmental problems [1–3]. As an excellent photocatalyst for water and air purification, one-dimensional (1D) semiconductor nanostrucutures, including nanowires, nanorods, nanotubes, and nanobelts, *etc*., have demonstrated significantly enhanced catalytic efficiency because of their high aspect ratio, enhanced light scattering, and absorption, rapid transport of free electron along the long axis, and efficient utilization of electron–hole pair [4–9]. Distinct from their single component counterparts, semiconductor hybrid nanostructures with a staggered alignment of band edges at the hetero-interface can improve spatial charge separation of the electron and hole in different parts of the heterostructure for photocatalytic and photovoltaic applications [10–16]. To take advantage of both materials, the fabrication of 1D semiconductor hetero-nanostructures with controllable shape and size is extremely important from the viewpoints of both fundamental research and technical applications.

Recently, various Ag-based photocatalysts including compounds and nanocomposites, such as AgX (X = Cl, Br, I) [17–19], $Ag_2CO_3$ [20], $Ag_2CrO_4$ [21], $Ag_3PO_4$ [22–24], Ag/AgX-CNTs [25], and $AgX/Ag_3PO_4$ [26],*etc*., have attracted much attention and proved to be a new family of highly efficient visible-light-driven photocatalytic materials. Our group has synthesized various kinds of metal sulfide/Ag and $Ag_nX$ (X = S, Cl, $PO_4$, $C_2O_4$) nanotubes, which exhibit enhanced photocatalytic activity under visible-light illumination [27,28]. As one of the most important metal tungstates, silver tungstate ($Ag_2WO_4$) has three different crystallographic forms: α-, β-, and γ-$Ag_2WO_4$, among which α-$Ag_2WO_4$ is the thermodynamically stable phase that has been investigated [29,30]. To date, various synthetic routes, including controlled precipitation [31,32], hydrothermal [33–35], microwave-assisted [36], and injection method [37] were reported in the literature to obtain different $Ag_2WO_4$ nanostructures. However, the preparation of metastable β-$Ag_2WO_4$ has been scarcely reported [38]. On the other hand, it is well known that AgX is easily decomposed to generate metallic Ag after light irradiation, and Ag/AgX hybrids has been used as highly efficient plasmonic photocatalysts due to the surface plasmon resonance (SPR) effect of noble metal [39–44].

In this work, we demonstrate a facile precipitation process to obtain $Ag_2WO_4$ nanorods with high yield at room temperature. Subsequently, a series of AgX nanocrystals are facilely deposited on the surface of $Ag_2WO_4$ nanorods to form $Ag_2WO_4/AgX$ hybrid nanorods by a facile *in-situ* anion exchange reaction between pregrown $Ag_2WO_4$ nanorods and different $X^-$ ions in water at room temperature. The straightforward synthesis strategy for the 1D $Ag_2WO_4/AgX$ hybrid nanorods is schematically depicted in

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Scheme 1. When $X^-$ ions are localized to a close environment surrounding the $Ag_2WO_4$ nanorods, the anion exchange reaction will occur between $WO_4^{2-}$ and $X^-$ ions: $Ag_2WO_4 + 2X^- = 2AgX + WO_4^{2-}$, leading to the deposition of AgX nanocrystals on the surface of $Ag_2WO_4$ nanorods. Ion exchange procedure has been used not only as an attractive approach for chemical transformation of inorganic nanostructured materials, but also as a very effective strategy to preserve the starting material structures [45–50]. As expected, further investigation has revealed that the as-prepared hybrid nanorods possess significantly enhanced photocurrent response and photocatalytic activity in the degradation of methyl orange (MO) under visible-light irradiation. Especially, $Ag_2WO_4$/AgBr hybrid nanorods exhibit the highest photocatalytic activity among the three kinds of samples. Furthermore, the active species tests indicate that the superoxide anion radical and photogenerated hole are responsible for the enhanced photocatalytic performance of the as-prepared $Ag_2WO_4$/AgBr hybrid nanorods.

## 2. Experimental

All reagents were analytical grade, purchased from the Shanghai Chemical Reagent Factory, and used as received without further purification.

### 2.1. Synthesis of $Ag_2WO_4$ nanorods

The $Ag_2WO_4$ nanorods were prepared by a facile precipitation process at room temperature. In a typical synthesis, 0.5 mmol of $Na_2WO_4$ was dissolved in 20 mL of deionized (DI) water to form a clear solution, followed by a dropwise addition of 20 mL of $AgNO_3$ aqueous solution (0.025 M) containing 1.0 g of polyvinylpyrrolidone (PVP, MW ~58 K). After several minutes, the solution turned white, indicating the formation of $Ag_2WO_4$ nanorods. The mixture was continuously stirred for 1 h at room temperature and collected by centrifugation. After washed with DI water and ethanol for three times each, the as-prepared $Ag_2WO_4$ nanorods were dried at 60 °C for 6 h.

### 2.2. Synthesis of $Ag_2WO_4$/AgX (X = Cl, Br, I) hybrid nanorods

In a typical procedure, 0.05 g of PVP (MW ~58 K) and 0.023 g of the as-prepared $Ag_2WO_4$ were added into 15 mL of DI water with the assistance of ultrasonication to form a mixture. Then, 15 mL of aqueous solutions containing 0.0017 M of NaCl, KBr, or KI were dropwise added into the above mixture under vigorous stirring, respectively. After continuously stirred for 2 h in the dark at room temperature, the products were collected by centrifugation, after washing with DI water and ethanol for three times, dried at 60 °C for 6 h.

### 2.3. Characterizations

Powder X-ray diffraction (XRD) measurements of the samples were performed with a Philips PW3040/60 X-ray diffractometer using Cu Kα radiation at a scanning rate of 0.06 deg $s^{-1}$. Scanning electron microscopy (SEM) was performed on a Hitachi S-4800 scanning electron micro-analyzer with an accelerating voltage of 15 kV. UV–vis diffuse reflectance spectra (UV–vis DRS) of the as-prepared samples were recorded over the range of 200–800 nm in the absorption mode using a Thermo Nicolet Evolution 500 UV–vis spectrophotometer equipped with an integrating sphere attachment. The absorption spectra were measured using a PerkinElmer Lambda 900 UV–vis spectrophotometer at room temperature. The photoluminescence spectra were recorded on an Edinburgh FLSP920 fluorescence spectrometer. The Fourier transform infrared (FT-IR) spectra of the samples were recorded using Nicolet 670 FTIR spectrometer and the FTIR absorbance spectra were obtained with 100 scans per sample over the range of 400–4000 $cm^{-1}$.

### 2.4. Photoelectrochemical test

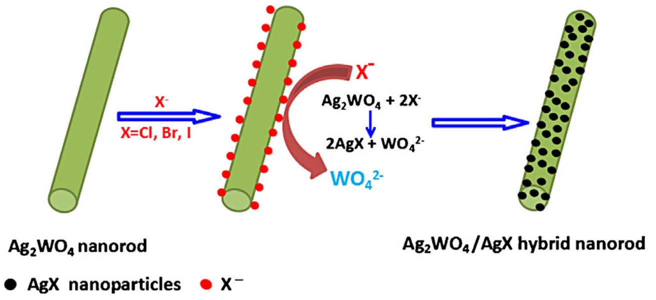
The photoelectrochemical characteristics were measured using a CHI840C electrochemical workstation with conventional three-electrode setup under visible light illumination. The as-prepared pure $Ag_2WO_4$ nanorods and $Ag_2WO_4$/AgX hybrid nanorods paste were coated onto an ITO glass with an area of $1 \times 1\ cm^2$ employed as the working electrode, respectively. A platinum wire and a saturated (Ag/AgCl) solution were used as the counter and reference electrodes, and 0.1 M of $Na_2SO_4$ aqueous solution was used as electrolyte. A 500 W Xe lamp (CEL-HXF300) equipped with a 420 nm cut-off filter was utilized as the visible light source. Potentials were given with respect to the reference electrodes. The photoresponse of the photocatalysts as light on and off was measured at 0.0 V [51].

### 2.5. Photocatalytic degradation of MO

Photocatalytic activities of the as-prepared products were evaluated by the degradation of MO under visible-light irradiation from a 500 W Xe lamp with a 420 nm cut-off filter. The reaction cell was placed in a sealed black box with the top opened and the cut-off filter was placed to provide visible-light irradiation. In a typical process, 0.06 g of the as-prepared photocatalyst was dispersed into100 mL of MO solution (10 mg/L). After being kept in an ultrasonic bath for 5 min, the mixture was stirred for 2 h in the dark to acquire adsorption equilibrium between the photocatalyst and the dye solution and then was exposed to visible-light irradiation. The samples were collected by centrifugation at given time intervals to measure the dyes degradation concentration by UV–vis spectroscopy.

## 3. Results and discussion

The phase composition and structure of the as-prepared pure $Ag_2WO_4$ nanorods and $Ag_2WO_4$/AgX hybrid nanorods were examined by XRD, as shown in Fig. 1. For $Ag_2WO_4$ nanorods, all the peaks can be well indexed to the pure hexagonal phase β-$Ag_2WO_4$ with cell constants of $a = 11.09$ Å and $c = 7.542$ Å (JCPDS card no. 33-1195). No additional peaks were detected, indicating the high purity of the resultant samples. For $Ag_2WO_4$/AgCl hybrid nanorods, in addition to the obvious $Ag_2WO_4$ diffraction peaks, other peaks can be well assigned to face-centered cubic phase AgCl (JCPDF card no. 31-1238, $a = b = c = 5.549$ Å). Because the peak of (2 2 0) crystal planes of $Ag_2WO_4$ are very adjacent to the diffraction peaks of (2 0 0) of AgCl, they are overlapped with each other.



**Scheme 1.** Schematic illustrations for the formation process of the $Ag_2WO_4$/AgX hybrid nanorods.