



# Efficient photoelectrochemical water splitting over $\text{Co}_3\text{O}_4$ and $\text{Co}_3\text{O}_4/\text{Ag}$ composite structure



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## ABSTRACT

In this paper,  $\text{Co}_3\text{O}_4$  with different morphologies of nanowires (NWs) and nanolayers (NLs) and Ag modified  $\text{Co}_3\text{O}_4$  are prepared on ITO substrate via a facile and low-cost hydrothermal successfully.  $\text{Co}_3\text{O}_4/\text{Ag}$  composite structure served as photocathode applied in photoelectrochemical (PEC) water splitting presents efficient PEC activity for the first time. The enhanced optical and photoelectrochemical performance are characterized, the role of Ag nanoparticles is discussed. The photocurrent densities of  $\text{Co}_3\text{O}_4/\text{Ag}$  NWs and  $\text{Co}_3\text{O}_4/\text{Ag}$  NLs are up to  $-4.73 \text{ mA cm}^{-2}$  and  $-4.26 \text{ mA cm}^{-2}$ , respectively. The improved PEC performance is attributed to a high light-harvesting efficiency, an expanded photoresponse range, accelerated holes mobility and increased interfacial photoelectrons transport of Ag nanoparticles.

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## 1. Introduction

Efficient utilization of solar energy can relieve lots of energy and environmental concerns, as the solar energy radiating the earth is exceeding the global human energy consumption far surpasses [1,2]. Over water splitting using sunlight illumination has received extensive attention for the production of hydrogen from water [3–5]. Since the first discovery of photo-assisted electrochemical water oxidation using  $\text{TiO}_2$  single-crystal photoelectrode by Honda-Fujishima in the early 1970s [6], photoelectrochemical (PEC) water splitting based on semiconductor materials has been investigated extensively [7,8]. Nowadays, solar hydrogen plays a key role in the sustainable energy societies due to its properties of storable and transportable, as well as it can be directly converted into electricity. To date, metal oxide semiconductor materials have been applied in the PEC water splitting for hydrogen evolution. Among the metal oxide semiconductors, n-type metal oxides, such as  $\text{ZnO}$ ,  $\text{TiO}_2$  and  $\text{WO}_3$  have occupied a large proportion of the literature in the area because these materials are naturally abundant, thermally and chemically stable as well as easy to process [9–13]. However, these n-type metal oxide semiconductors served as photoanodes were used to drive water oxidation for oxygen gen-

eration in the PEC process while hydrogen evolution took place at the counter electrode. Hence, the exploitation of p-type oxide semiconductors photocathodes for direct hydrogen evolution becomes a significant challenge [14].

Cobaltic oxide ( $\text{Co}_3\text{O}_4$ ) is a typical and environmentally friendly p-type metal oxide, which has been extensively used in lithium batteries, super capacitors catalysts and photoelectrochemical devices because of its excellent physical-chemical properties [15–19].  $\text{Co}_3\text{O}_4$  with an appropriate optical band gap of 2.07 eV that could harvest visible light has been used as a photocathode in the PEC procedure to produce hydrogen. Nevertheless, the main limitation of pure  $\text{Co}_3\text{O}_4$  in PEC process is the slow separation of photo-induced electron-hole pairs [20]. And now the catalytic performance of metal oxide semiconductors can be improved largely by increasing the surface area through controlling the morphology of nanolayers and nanowires, which facilitate the separation of photo-induced electron-hole pairs within the material [21]. Furthermore, loading of appropriate noble metallic nanoparticles as an electron trap is in favor of improving the PEC performance dramatically [22–25]. Among lots of different noble metals, Ag is unique in its stability that does not undergo corrosion in the photoreaction process, and it also acted as reduction active sites, which capture the photogenerated electrons from the surface of semiconductor effectively [26]. Therefore, the incorporation of conductive Ag species can obtain the higher performance over pure  $\text{Co}_3\text{O}_4$  cathode.

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Despite the  $\text{Co}_3\text{O}_4$  with p-type behavior has been mostly served as catalyst and co-catalyst that applied in the oxygen evolution reaction, but there are only few researches on cobaltic oxide for photoelectrochemical hydrogen evolution reaction [27,28]. In this article, we have firstly synthesized a series of  $\text{Co}_3\text{O}_4$  metal oxides with different morphologies of nanolayers and nanowires on ITO substrate through the hydrothermal and annealing process. Additionally, metal Ag nanoparticles were decorated on  $\text{Co}_3\text{O}_4$  to form a  $\text{Co}_3\text{O}_4/\text{Ag}$  composite structure. The  $\text{Co}_3\text{O}_4$  and  $\text{Co}_3\text{O}_4/\text{Ag}$  were utilized as the photocathodes in the PEC system, respectively. The  $\text{Co}_3\text{O}_4/\text{Ag}$  exhibits enhanced PEC performance compared to the pure  $\text{Co}_3\text{O}_4$ , in particular, the  $\text{Co}_3\text{O}_4/\text{Ag}$  composite structure with  $\text{Co}_3\text{O}_4$  nanowire morphology presents the most excellent PEC activity, exhibiting a high photocurrent and the value was up to  $4.73 \text{ mA cm}^{-2}$ . The higher photocatalytic property in PEC water splitting was obtained due to the following factors: low-dimension  $\text{Co}_3\text{O}_4$  structure has a high specific surface area, which provides a direct pathway for facile electron transfer, providing an excellent substrate for Ag NPs loading and PEC hydrogen generation. The nanostructures can efficient capture the incident light by internal multiscattering. Moreover, the existence of Ag nanoparticles can accelerate interfacial electrons transport, which enhances the charge separation efficiently and suppress the recombination of photo generated electron-hole pairs.

## 2. Experiment

### 2.1. The preparation of $\text{Co}_3\text{O}_4$

The  $\text{Co}_3\text{O}_4$  was synthesized on the indium tin oxide (ITO) substrates combing hydrothermal with heat treatment process. Firstly, the ITO glass was ultrasonically rinsed in acetone, isopropyl alcohol and ethanol for 0.5 h, respectively. Then the substrates were transformed into teflon-lined stainless steel autoclave containing 0.05 M cobalt nitrate and urea with equal concentration. The autoclave was sealed and maintained at  $100^\circ\text{C}$  for various time and then cooled down to room temperature. Finally,  $\text{Co}_3\text{O}_4$  was obtained after heat treatment of as-prepared samples in muffle at  $430^\circ\text{C}$  for 3 h.

### 2.2. The preparation of $\text{Co}_3\text{O}_4/\text{Ag}$

The ITO substrate coated with  $\text{Co}_3\text{O}_4$  sample was immersed in a mixture solution containing 1 mM silver nitrate and 0.7 mM sodium citrate at  $100^\circ\text{C}$  for 2 h. Afterwards, the  $\text{Co}_3\text{O}_4/\text{Ag}$  was rinsed with deionized water and dried in air.

### 2.3. Characterization

Morphology of the products was examined by HITACHI S-4800I field emission scanning electron microscope (FE-SEM) and HITACHI H-7650 transmission electron microscopy (TEM) operated at an accelerating voltage of 100 kV. Optical absorbance of the electrodes was tested by DU-8B UV-vis double-beam spectrophotometer. The photoelectrochemical measurement of the samples was conducted in a three-electrode configuration, which consist of the obtained samples as working electrode, a platinum as counter electrode and a saturated  $\text{Ag}/\text{AgCl}$  as reference electrode. The electrolyte was prepared by 1 M KOH aqueous solution for water splitting experiment. Electrochemical impedance spectroscopy (EIS) of the products was characterized using an electrochemical workstation. The photocurrent density was measured under AM 1.5 ( $100 \text{ mW cm}^{-2}$ ) illumination.

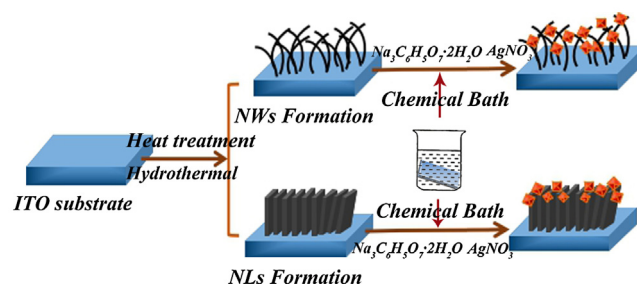


Fig. 1. Synthetic procedure of  $\text{Co}_3\text{O}_4/\text{Ag}$  composite structure.

## 3. Results and discussion

An illustrative synthetic process of  $\text{Co}_3\text{O}_4/\text{Ag}$  is summarized in Fig. 1. Firstly,  $\text{Co}_3\text{O}_4$  was fabricated on ITO substrate glass via hydrothermal procedure after annealing in air. The morphology of  $\text{Co}_3\text{O}_4$  can be controlled by adjusting the hydrothermal time. In detail,  $\text{Co}_3\text{O}_4$  nanowires (NWs) can be achieved when the hydrothermal time is 3 h. While the hydrothermal process is stretched to 6 h,  $\text{Co}_3\text{O}_4$  nanolayers (NLs) are obtained. In the reaction process, when putting the ITO substrate into the autoclave, a lot of  $\text{Co}_3\text{O}_4$  precursor nuclei appear on the surface of the substrate. After a 3 h reaction process, nanowires based on the nuclei and the effect of urea appeared, grown with high density on the conductive substrate. With the hydrothermal time increasing to 6 h, the nanowires turned into nanolayers structure. The transformation of the morphology seems to be related to the difference of surface energy. In other words, in order to reduce the surface energy of as-prepared products, the nanowire with large surface will translate into nanolayer structure with relative lower surface energy. Therefore, the formation procedure is an analogous phenomenon in the crystal growth process. Sequentially, Ag nanoparticles (NPs) were prepared by putting the ITO glass which obtained the as-prepared  $\text{Co}_3\text{O}_4$  with different morphologies in the mixed solution containing silver nitrate and sodium citrate. After chemical bath reaction at  $100^\circ\text{C}$  condition, Ag NPs were grown uniformly on the surface of  $\text{Co}_3\text{O}_4$  and  $\text{Co}_3\text{O}_4/\text{Ag}$  composite structure is prepared finally.

The morphology of as-prepared samples was characterized by the typical SEM measurement. Fig. 2(a) and (b) shows a top-view SEM image of  $\text{Co}_3\text{O}_4$  NWs and  $\text{Co}_3\text{O}_4$  NLs, respectively. It is obvious that  $\text{Co}_3\text{O}_4$  NWs and  $\text{Co}_3\text{O}_4$  NLs were uniformly and densely covered on the substrate after the hydrothermal grow process. The surface of both  $\text{Co}_3\text{O}_4$  NWs and  $\text{Co}_3\text{O}_4$  NLs are smooth, and reveal a diameter of 70 nm as well as a thickness of 60 nm. The morphologies of the  $\text{Co}_3\text{O}_4/\text{Ag}$  composite structure were investigated. As shown in Fig. 2(c) and (d), the final products inherit the original morphology of as-prepared  $\text{Co}_3\text{O}_4$  NWs and  $\text{Co}_3\text{O}_4$  NLs. It can be clearly observed that the surface of NWs and NLs appears to be coarse, and many Ag nanoparticles were loaded on the surface of the NWs and NLs core.

Detailed microstructure information of  $\text{Co}_3\text{O}_4/\text{Ag}$  NWs and  $\text{Co}_3\text{O}_4/\text{Ag}$  NLs is investigated through HRTEM measurement accompanied by selected area electron diffraction (SAED). The HRTEM image in Fig. 3(a) shows the distinct lattice fringe of  $\text{Co}_3\text{O}_4/\text{Ag}$  NWs. The fringes spacing is measured to be 0.2359 nm, which corresponded to the (111) lattice spacing of Ag. A typical TEM image of the  $\text{Co}_3\text{O}_4/\text{Ag}$  NLs was shown in Fig. 3(b), revealing that the Ag particles were loaded on the  $\text{Co}_3\text{O}_4$  NL closely. In addition, the SAED of the  $\text{Co}_3\text{O}_4/\text{Ag}$  NLs was also displayed as the inset of Fig. 3(b), implying that the  $\text{Co}_3\text{O}_4$  and Ag are well crystallized. Additionally, the specific surface area of the  $\text{Co}_3\text{O}_4/\text{Ag}$  samples with different morphologies was calculated and the data of  $\text{Co}_3\text{O}_4/\text{Ag}$  NWs and

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