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Facile Preparation of Nanostructural Controlled Ag_3PO_4 Photo-Anodes for Enhanced Photo electrochemical Water Splitting under Visible-Light

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Abstract— Cubic Ag_3PO_4 sub micro-crystals have been fabricated in high-yield by directly reacting commercial Ag foils with H_2O_2 and NaH_2PO_4 in aqueous solution at room temperature. These cubic Ag_3PO_4 photo anode exhibited much higher photoelectrocatalytic activities for the water splitting reaction than irregular Ag_3PO_4 photo anode under visible light irradiation. The cubic Ag_3PO_4 photo anode presented a photocurrent density of about 1.63 mA/cm^2 , which is nearly 1.5 times higher than that of the irregular Ag_3PO_4 photo anode (1.12 mA/cm^2) at 1.0 V vs Ag/AgCl. Furthermore, superior stability of the Ag_3PO_4 photo anode was also revealed by a 40 min successive photo electrochemical water splitting experiment. This work may provide insights into rational design and construction of a nanostructural controlled photo electrodes for efficient photo-to-chemical conversion and other photo electrochemical applications.

Index Terms— Cubic Ag_3PO_4 photo anode, nanostructural controlled, photo catalyst, visible light, water splitting.

I. INTRODUCTION

Photo electrochemical water splitting represents a promising strategy for low-cost and environmentally friendly production of clean and renewable hydrogen energy from solar light and water [1]. A key issue in this area is to fabricate nanostructured photo electrodes with desirable properties such as wide band absorption, high carrier mobility, long carrier lifetime, good structural stability, and environmental benignity [2]. The water splitting process involves two half-cell reactions, the hydrogen evolution reaction on photocathodes and oxygen evolution reaction on photo anodes. The latter is usually more complex and sluggish because it requires the removal of four electrons and two protons from two H_2O molecules, which is twice that required for hydrogen evolution reaction.

Silver orthophosphate (Ag_3PO_4) is an *n*-type semiconductor with a direct bandgap of 2.43 eV and an indirect bandgap of 2.36 eV, which ensures that Ag_3PO_4 absorbs solar energy with a wavelength shorter than about 530 nm [3]. The valence band edge of Ag_3PO_4 is located at *ca.* 2.85 V vs. NHE, which is much higher than the potential of the $\text{O}_2/\text{H}_2\text{O}$ redox couple (1.23 V vs. NHE), ensuring that the photo generated holes in the valence band of Ag_3PO_4 have sufficient energy to oxidize water [3,4]. In principle, Ag_3PO_4 can be used as a photo anode material to catalyze many oxidation reactions, such as oxygen evolution reaction and oxidation of organic pollutants. It has been reported that Ag_3PO_4 can be used as a catalyst for oxidative photo degradation of organic dyes [5-7]. Recently, Ye and co-workers demonstrated that Ag_3PO_4 also acted as a promising photo catalyst for oxygen evolution reaction [3]. They showed that, with AgNO_3 as a sacrificial reagent for photo generated electrons, Ag_3PO_4 exhibited even much higher photo activity toward oxygen evolution reaction than WO_3 and BiVO_4 , and the latter two have been well-recognized as two efficient oxygen evolution reaction photo catalysts [8-10]. However, not much work has been reported on using Ag_3PO_4 as a photo anode material for photo electrochemical water splitting [4,5], mainly because of their shortcomings such as relatively high electron-hole recombination rate and poor structural stability [11,12].

Herein, we demonstrate a facile and efficient process for the large-scale synthesis of Ag_3PO_4 with cubic structures by direct oxidation of commercial Ag foils with H_2O_2 at room temperature. It was found that the increase in PVP concentration at the Ag_3PO_4 films preparation significantly affected the photocurrent for water oxidation reaction. Enhanced water oxidation activity and stability were demonstrated by the Ag_3PO_4 with cubic structure, suggesting great potential of these cubic Ag_3PO_4 photo anodes to support efficient solar-to-fuel energy conversion and photo electrochemical applications.



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II. EXPERIMENTAL

A. Preparation of Ag_3PO_4 Photo anode

In a typical Ag_3PO_4 photo anode synthesis, the silver foils (2×1 cm) was placed in aqueous solution containing the PVP (0.8 M) and NaH_2PO_4 (0.2 M). Then, 1 mL of H_2O_2 aqueous solution (30% V/V) was added with drop by drop to the above solution and kept for 3 h. The obtained Ag_3PO_4 samples for morphology and structure analysis were washed with water to remove the NaH_2PO_4 and PVP and dried under atmosphere.

B. Characterization

The powder X-ray diffractometer (XRD, RIGAKU Ultima IV, sample horizontal type) was used in order to record the diffraction patterns of photo catalysts employing $\text{Cu K}\alpha$ radiation. The fourier transform infrared spectra (FTIR) of the samples were recorded using a SPECTRUM 100 FTIR spectrometer (Perkin Elmer) equipped with an ATR assembly. X-ray photoelectron spectroscopy (XPS) measurements were carried out with a PHI Quantera SXM photoelectron spectrometer using $\text{Al K}\alpha$ radiation. A Hitachi S-4000 scanning electron microscope (SEM) was employed to observe the morphologies of the samples. The UV-visible diffuse reflectance spectra (DRS) of the photo catalysts were recorded using a Shimadzu UV-2450 spectrophotometer equipped with an integral sphere assembly.

C. Photoelectrocatalytic Measurements

For evaluation of photoelectrocatalytic performance, all measurements were carried out in a three-electrode cell. The obtained Ag_3PO_4 photo anodes, a Pt wire, an Ag/AgCl electrode, and the aqueous solution of Na_2HPO_4 (0.4 M) were utilized as the working electrode, counter electrode, reference electrode and electrolyte, respectively. Potential of working electrode was controlled with a VersaSTAT 3 potentiostat (Princeton Applied Research). Before each measurement, the electrolyte solution was stirred and purged with nitrogen gas for 30 min. During measurements, the Ag_3PO_4 photo anodes were irradiated with a 300 W xenon lamp (MAX-303, Asahi Spectra) equipped with a UV cutoff filter (>420 nm, L-42, HOYA). The scan rate was 10 mV/s for collecting each current density-potential (J-E) curve from negative to positive bias. The concentration of H_2 production during the photo electrochemical reaction was analyzed by gas chromatography (GL Sciences, GC-3200) with thermal conductivity detector (TCD). The stainless column (4 m length, 2.17 mm i.d.) packed with Molecular Sieve 5A was used for the separation. The carrier gas was high purity Ar gas. The temperature conditions of GC were 50 °C for injection, column and detector.

III. RESULTS AND DISCUSSION

Figure 1A shows the SEM image of the as-synthesized Ag_3PO_4 films, indicating that cubic structures formed uniformly on the surface of Ag foils. The cross-sectional image of the product (Fig. 1B) suggests that the thickness of as-synthesized cubic Ag_3PO_4 layers was about 1.5 μm . Figure 1C shows the distribution of the length of cubic Ag_3PO_4 . This results were obtained by measuring the lengths of 100 cubic Ag_3PO_4 , which were in the range of 40 – 75 nm. Fig. 1D shows the X-ray diffraction (XRD) pattern of $\text{Ag}/\text{Ag}_3\text{PO}_4$ product. It can be clearly seen that the main diffraction peaks could be primarily indexed to the body-centered cubic structure of Ag_3PO_4 (JCPDS no. 06-0505), and some small diffraction peaks of metallic Ag ascribed to the Ag foils have also been observed.

Fig. 2A shows the UV-visible DRS of the Ag_3PO_4 films and Ag foils. Before the oxidation reactions, the Ag foils exhibit a sharp absorption peak at 320 nm. However, when the oxidation growth process between Ag foils and H_2O_2 was initiated, the absorption peaks of metallic Ag markedly reduced, and the absorption peaks of Ag_3PO_4 crystals appeared. The as-synthesized Ag_3PO_4 products have a broader absorption in the visible light region with an absorption edge at about 530 nm. According to the plot of $(ah\nu)^{1/2}$ vs. $h\nu$, the band gap (E_g) of Ag_3PO_4 was estimated to be 2.20 eV (inset of Fig. 2A). FTIR spectra of Ag_3PO_4 films are shown in Fig. 2B. The two peaks at 972 cm^{-1} and 554 cm^{-1} are assigned to the P—O stretching vibration modes of PO_4 [13, 14].

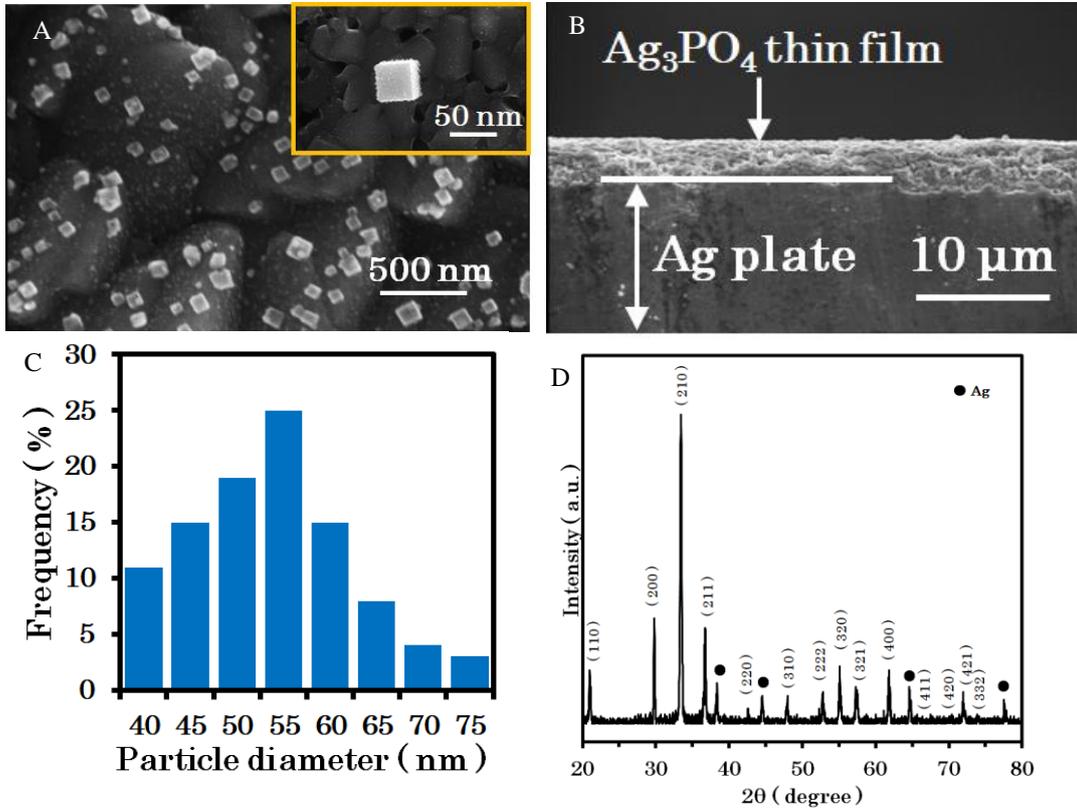


Fig. 1. SEM images of (A) top view and (B) cross section of Ag_3PO_4 films, (C) size distribution of Ag_3PO_4 crystals, (D) XRD pattern of Ag_3PO_4 films.

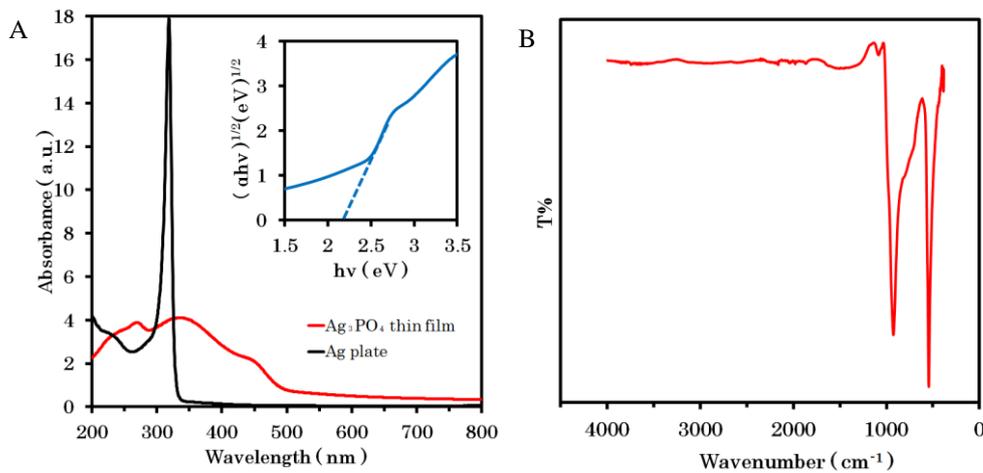


Fig. 2. (A) DRS of Ag_3PO_4 films and Ag foils (Inset: Tauc plot of Ag_3PO_4 films), (B) FT/IR of Ag_3PO_4 films.

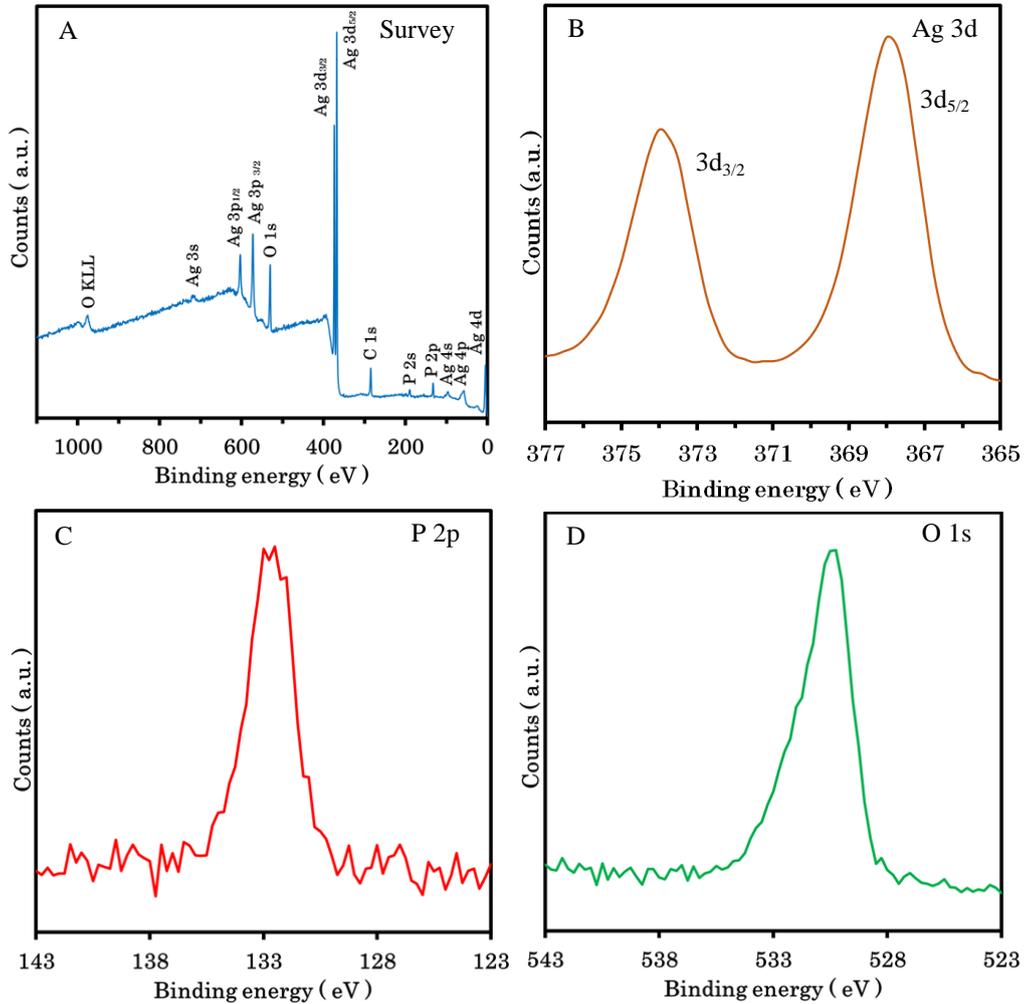


Fig. 3. XPS spectra of Ag_3PO_4 films. (A) Survey (B) Ag 3d (C) P 2p (D) O 1s narrow spectra.

Figure 3A shows the XPS survey spectrum of the Ag_3PO_4 films, which mainly exhibited the peaks of Ag, P and O. No other impurities were presented in the sample. The XPS narrow spectra of Ag 3d, P 2p and O 1s regions are shown in Figs. 3B–D. In Fig. 3B, the Ag $3d_{3/2}$ and Ag $3d_{5/2}$ peaks could be observed at 374.0 and 368.0 eV of binding energy, respectively, suggesting the presence of Ag^+ in the as-synthesized cubic Ag_3PO_4 films. A broad peak in the range of 131 to 135 eV of the P 2p spectrum is observed for the Ag_3PO_4 sample, which is corresponding to the phosphorus came from PO_4^{3-} (Fig. 3C). O1s peak centered at 530.6 eV is associated with the O^{2-} in Ag_3PO_4 films (Fig. 3D). These above-discussed results showed clearly be synthesized the pure Ag_3PO_4 crystals on the Ag foils.

Figure 4A displays the applied bias-dependent photocurrent densities of all fabricated Ag_3PO_4 photo anodes together with the dark current densities. It is clear that as the PVP concentration at the anode preparation increased from 0 to 1.2 M, the photocurrent densities of the Ag_3PO_4 photo anodes increased up to 0.8 M, and then decreased. The 0.8-M Ag_3PO_4 photo anode showed a photocurrent density of about 1.63 mA/cm^2 at 1 V vs Ag/AgCl, which is almost 1.5 times higher than that of the 0-M Ag_3PO_4 photo anode (1.12 mA/cm^2). It could be observed from Fig. 4A that the dark current densities of Ag_3PO_4 photo anodes also increased gradually together with the photocurrent

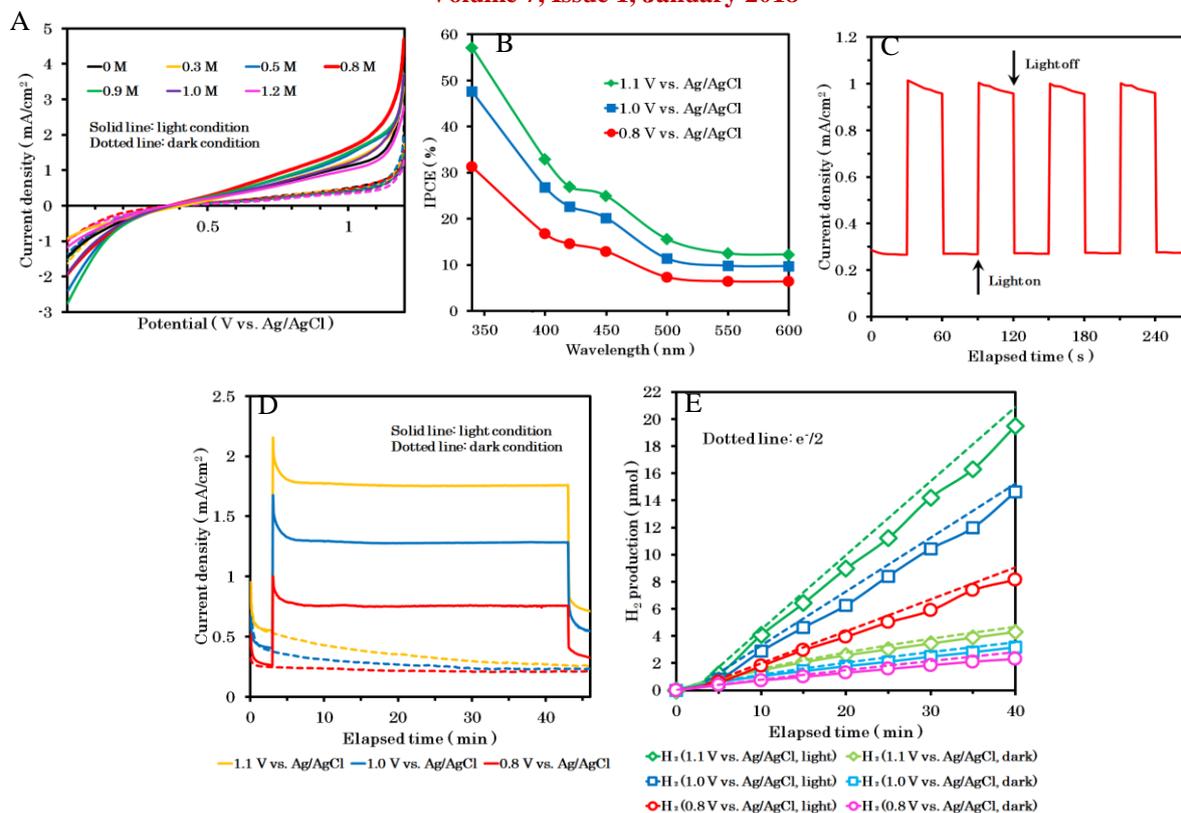


Fig. 4. (A) Linear sweep voltammograms of Ag_3PO_4 photo anodes prepared with PVP (0-1.2 M), (B) IPCEs of Ag_3PO_4 photo anode, (C) I-T responses of Ag_3PO_4 photo anode at 0.8 V vs Ag/AgCl under chopped visible light irradiation, (D) Long-term stability of Ag_3PO_4 photo anode, (E) Time courses of H_2 evolution using Ag_3PO_4 photo anode under visible light.

densities. This phenomenon here is similar to previous reports [3,11,12], suggesting that Ag_3PO_4 also have electro catalytic activity. The incident photon-to-electron conversion efficiency (IPCE) profiles of the 0.8-M Ag_3PO_4 photo anode measured at 0.8, 1.0 and 1.1 V vs Ag/AgCl are shown in Fig. 4B. The IPCEs under 420 nm photo irradiation were calculated to be 14.6, 22.7 and 27.0% for the photo electrochemical oxidation of water at 0.8, 1.0 and 1.1 V vs Ag/AgCl, respectively. Figure 4C shows the current density-time response at a bias of 0.80 V vs Ag/AgCl under chopped irradiation using the 0.8-M Ag_3PO_4 photo anode. It clearly shows that the photo anode exhibits a stable photocurrent density during four on-off cycles. The long-term stability of the 0.8-M Ag_3PO_4 photo anode was tested under visible light irradiation for 40 min. The photocurrent densities-time responses of the 0.8-M Ag_3PO_4 photo anode at 0.8, 1.0 and 1.1 V vs Ag/AgCl are shown in Fig. 4D. For all biases, the photocurrent densities were the almost constant for 40 min of irradiation time, suggesting that the photoanode was stable during the water splitting reaction. The Faradaic efficiencies of water splitting reaction for 40 min using the 0.8-M Ag_3PO_4 photo anode were calculated to be near 100% based on the H_2 evolution amount detected utilizing a gas chromatography with TCD detector (Fig. 4E), which further confirmed the stability of the Ag_3PO_4 photo anode for the photoelectrocatalytic water oxidation reaction.

IV. CONCLUSION

In summary, we have demonstrated a facile and efficient oxidation process for the large scale synthesis of cubic



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Ag₃PO₄ structures by utilizing commercial Ag foils as the precursor at room temperature. Moreover, these cubic Ag₃PO₄ photo anode (0.8-M PVP) exhibited much higher photoelectrocatalytic activities for the water splitting reaction than irregular Ag₃PO₄ one (0-M PVP) under visible light irradiation. The 0.8-M Ag₃PO₄ photo anode presented a photocurrent density of about 1.63 mA/cm², which is nearly 1.5 times higher than that of 0-M Ag₃PO₄ photo anode (1.12 mA/cm²) at 1.0 V vs Ag/AgCl. Furthermore, superior stability of the Ag₃PO₄ photo anode was also revealed by a 40 min successive photoelectrocatalytic water splitting test. This work may provide insights into rational design and construction of a nanostructural controlled photo electrodes for efficient photo-to-chemical conversion and other photoelectrocatalytic applications.

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