



A two-step approach towards solar-driven water splitting

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ABSTRACT

The search for an energy efficient means of utilizing sunlight to carry out solar-driven water splitting continues to be a subject of intense investigation. In a recent publication (Z. G. Yi et al., *Nature Mater.* 9 (2010), 559–564), a simple Ag_3PO_4 semiconductor material was shown to possess strong photo-oxidative properties under visible-light irradiation. Here we report a novel two-step approach that enables energy-efficient, solar-driven water splitting at room temperature in the presence of powdered silver orthophosphate. The approach proposed avoids the use of a low-efficiency, thin-film photo-electrode and turns the instability of the silver orthophosphate semiconductor material into an advantage.

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1. Introduction

The efficient and economic conversion of solar energy into the energy stored in gaseous hydrogen via water splitting is an essential step towards the hydrogen economy and the finding of a viable solution to the building fossil fuel crisis [1–3]. Direct solar thermal approaches to water splitting are energy-intensive, while the high temperatures required impose severe constraints on the materials and equipment used [4,5]. The photoelectrochemical, or artificial photosynthesis, approach is much more viable but has long been thought to require the use of stable, sunlight-harvesting semiconductor materials [6–9]. Here we propose a novel two-step approach that enables solar-driven water splitting at room temperature using a photovoltaic cell in the presence of powdered silver orthophosphate. The approach proposed regenerates the initial raw materials continuously. The instability of the silver orthophosphate semiconductor material thus becomes an advantage and hydrogen generation can be carried out in an electrically energy-efficient manner.

In a recent publication [10], we reported that the semiconductor Ag_3PO_4 efficiently oxidizes water while simultaneously being reduced under visible-light irradiation ($\lambda < 530$ nm). The relevant reaction involved is as follows:



Based on this result and the fact that well-crystallized Ag_3PO_4 can form at room temperature in an aqueous solution containing silver

cations and phosphate anions, a photoelectrochemical cell was designed in which a thin film of silver orthophosphate deposited onto an inert conducting substrate was used as the photoanode to oxidize water, to delay photo-corrosion as well as to regenerate the Ag_3PO_4 itself when needed [10]. Unfortunately, however, the energy utilization efficiency of this Ag_3PO_4 -coated thin film electrode is much lower than that of Ag_3PO_4 powder.

2. Cell design

We have now carefully reconsidered this original cell design and think it best to abandon the conventional viewpoint that good photoelectrode materials must be able to survive photo-corrosion.

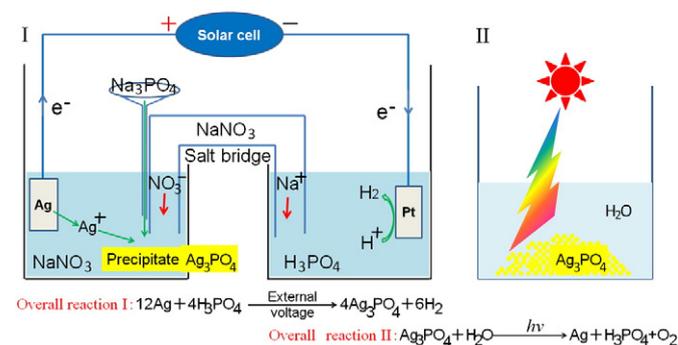


Fig. 1. Schematic diagrams illustrating the solution of solar water splitting. Left, cell configuration for H_2 and Ag_3PO_4 generation. Right, photo-oxidation of water for the generation of O_2 , Ag , and H_3PO_4 .

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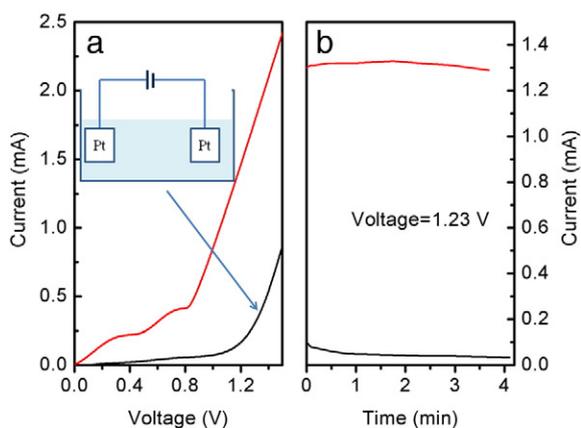


Fig. 2. Electrolytic reactions test using the two electrodes (electrode area: 1 cm^2) method. Red line: our solution using an Ag anode and a Pt cathode (see text). Black line: conventional water electrolysis using two Pt electrodes and $1 \text{ M Na}_3\text{PO}_4$ electrolyte (see inset in a).

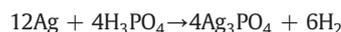
Based on this new realization, in conjunction with the fact that Ag_3PO_4 powder is the most photochemically active form, we have thus redesigned the electrolytic cell as shown in Fig. 1. Platinum and silver electrodes are now used as the cathode and anode, respectively, while (ortho)phosphoric acid and sodium nitrate solution are used as the electrolytes in the cathode and anode cells. Sodium nitrate is used as the salt bridge and a photovoltaic cell provided to induce the electrolysis reaction.

The thus configured cell can now be used to oxidize silver to generate silver cations ($\text{Ag} - \text{e}^- \rightarrow \text{Ag}^+$) at the anode and, at the same time, reduce H^+ to generate H_2 ($\text{H}^+ + \text{e}^- \rightarrow 1/2 \text{H}_2$) at the cathode. If the reaction is carried out at 25°C and 1 atm and $[\text{H}^+]$ is kept at 1 mol/l , the cell potential can be written as

$$E_{\text{cell}} = -0.799 - 0.059 \log [\text{Ag}^+] = -0.54 \text{ V} (\text{Ag}_3\text{PO}_4 : K_{\text{sp}} = 1 \times 10^{-16}).$$

The silver ion concentration then determines the required cell potential. By constantly adding sodium orthophosphate to generate the photoactive Ag_3PO_4 powder, the required cell potential can formally be kept as low as -0.54 V . Thus, only 0.54 V should be necessary to induce the desired redox reactions. This saves electricity by comparison with the 1.23 V formally needed for water electrolysis. The generated Ag_3PO_4 is used to photooxidize water to release oxygen and to balance the consumed silver and phosphoric acid. The sodium orthophosphate consumed can be continuously replenished as it is a byproduct in the cathode cell. The water-splitting reaction can thus be achieved using the two-stage reaction cycles shown below:

- (I) An electrolysis reaction to generate H_2 (external voltage required $> 0.54 \text{ V}$)



- (II) A photooxidation reaction to generate O_2 ($\lambda < 530 \text{ nm}$)

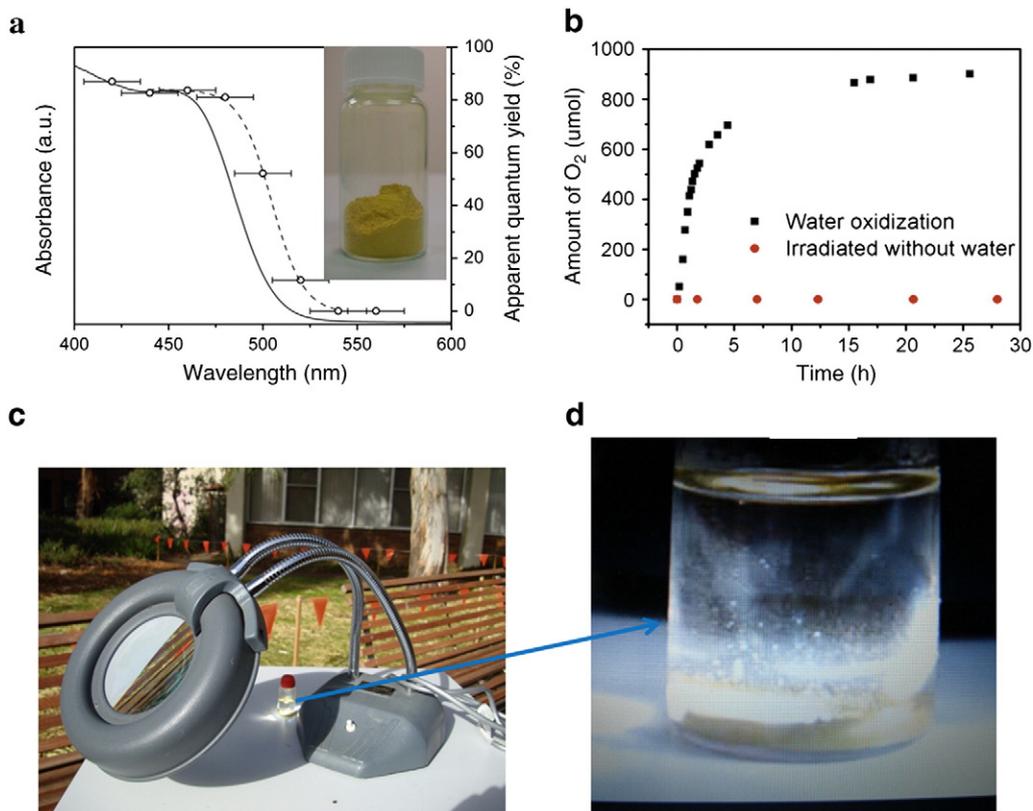
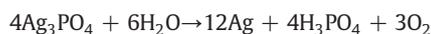


Fig. 3. Properties test for the Ag_3PO_4 powder. (a) Ultraviolet–visible diffuse reflectance spectrum and apparent quantum yield [8]. Inset shows a photograph of the sample. (b) Oxygen evolution from the Ag_3PO_4 semiconductor powder (0.5 g) under visible-light irradiation (400 W Xe lamp , $\lambda > 400 \text{ nm}$), with 270 ml water and without water. (c) Photograph of the experimental setup for the concentration of winter sunlight on the ANU campus. (d) Photograph of oxygen bubbles evolving in experiment c.

3. Experimental verification

Following the above prescription, we firstly performed the two-electrode electrolytic reaction at ambient temperature and pressure to test the practical effect. In the experiment, 1 M orthophosphoric acid and sodium nitrate solution were used as the electrolytes in the cathode and anode cells, respectively, and a high-concentration sodium nitrate salt bridge was used to bridge the electrolytes. The electrochemical behavior of this cell was then investigated with a potentiostat. Both the obtained current–voltage curves (Fig. 2a) and current–time curves (Fig. 2b) indicate that the solution we have proposed for H₂ generation indeed works in an electrically energy-efficient manner. Keeping the voltage at 1.23 V for 4 h, the total quantity of electric charge passed through the electrodes was 18.72 C while ~0.027 g of Ag₃PO₄ and 0.09 mmol H₂ were collected. The current efficiency is therefore above 92%, both for silver oxidation and for hydrogen reduction. The origin of the two small bumps in the red curve shown in Fig. 2a presumably arises from energy losses due to kinetic and/or transport effects at the voltage used. Further investigation (beyond the scope of the current contribution), however, would be required to confirm whether or not this is the case.

The water oxidation activity of a synthesized Ag₃PO₄ powder sample was also tested under concentrated winter sunlight on the ANU campus. The O₂ generation activity under conventional laboratory Xe lamp illumination was monitored by *in situ* gas chromatography and is shown in Fig. 3a and b. Both the high apparent quantum yield (89% at 420 nm) and the ratio of O₂ generated to the amount of Ag₃PO₄ raw powder (Fig. 3b) are consistent with a photo-induced chemical reaction. The rapid evolution of oxygen bubbles under concentrated sunlight (see Fig. 3c and d) indicates further the validity of our approach for O₂ generation.

4. Conclusions

The benefits of this design include (I) the necessity to prepare a thin film Ag₃PO₄ electrode is avoided; (II) Ag₃PO₄ powder with a much higher water oxidization efficiency can be used directly; (III) problems associated with the stability of the Ag₃PO₄ semiconductor are not a

problem anymore (photo-corrosion of the Ag₃PO₄ semiconductor becomes an advantage); (IV) the raw materials required are continuously regenerated.

It is acknowledged, however, that there may be weaknesses associated with our proposed design that need to be addressed such as (I) the extra energy required to collect the nanoscale silver powder formed during the water oxidation process and to press it into an electrode for electrolysis and (II) the control of the [Ag⁺] and [H⁺] to reduce energy loss during electrolysis. Further study including the involvement of an industrial partner will be required in order to assess the economic feasibility of scaling up the proposed process.

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