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Ultrathin hematite film for photoelectrochemical water splitting enhanced with reducing graphene oxide

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ABSTRACT

Ultrathin hematite films have been prepared on FTO using a separated two-phase hydrolysis–solvothochemical reaction. The film thickness can be controlled by the number of deposition cycles. The Photoanode based on hematite film with 7 deposition cycles generated a photocurrent of 0.61 mA cm⁻² at +1.5 V vs. RHE. The photocurrent can be improved by coating a layer of reducing graphene oxide (RGO) through spin coating. The enhanced performance is attributed to the promoting effects of RGO which acted as hole collector and transporter in the electrodes. This research demonstrates that graphene can be used as an alternative co-catalyst to enhance photoelectrochemical water splitting activity of ultrathin hematite film. The as-prepared photoanodes were notably stable under water oxidation conditions.

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Introduction

Hydrogen is regarded as a clean and renewable fuel in the future because of its high-energy capacity and environmental friendliness. Solar-induced water splitting using semiconductor photocatalysts is one of the most promising technologies for hydrogen production from abundant resources of water and sunlight [1–3]. Hematite (α -Fe₂O₃) is an attractive semiconductor material for use as a photoanode due to its

visible light absorption up to 590 nm and appropriate stability in alkalinity [4–8]. The theoretical solar-to-hydrogen efficiency for the α -Fe₂O₃ can be 15.5% and a total photocurrent as high as 12.6 mA/cm² of water splitting has been predicted under AM 1.5G solar irradiation [9]. However, several factors have greatly limited the practical performance of hematite for solar water splitting, such as poor conductivity, short hole diffusion length (2–4 nm) and poor oxygen evolution reaction kinetics [10,11]. The low electrical conductivity of the material limits the charge transport, while the short diffusion distance

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of the holes hinders the efficient transport of holes to the hematite/liquid interface [12,13]. These features of hematite result in rapid electron–hole recombination processes occurring in the bulk and at the surface of the photoanode [2,14].

In recent years, great efforts have been devoted to decrease the bulk charge recombination for photocurrent improvement. Doping elements, such as Ti, Si, Al, Ge and Sn are being reported to improve the electric properties of hematite and promote charge transfer ability by increasing its donor density [15–22]. Some strategies of nanostructured architectures including nanorods, nanowires, and nanotubes are developed for reducing bulk recombination through shortening the pathway of photoexcited electrons/holes to surface [23–28]. Synthesis of ultrathin hematite films by spray pyrolysis [29,30], atomic layer deposition (ALD) [31], and APCVD [32] is another successful approach for reducing bulk charge recombination.

Usually, surface charge recombination occurs at the substrate/hematite interface and the hematite/electrolyte interface. The former can be reduced by adding an underlayer, and the latter can be decreased by using an overlayer or a co-catalyst. As oxide underlayers, for instance, thin films Ga_2O_3 , SiO_x , Nb_2O_5 and TiO_2 thin films have been prepared by the ALD method, which significantly increased photocurrent due to the suppression of charge recombination at the interface of substrate (FTO) and hematite thin film [29,30,33]. A thin overlayer, such as Al_2O_3 , Ga_2O_3 , or In_2O_3 , has been demonstrated to effectively passivate surface states with a shift of the photocurrent onset potential for solar water oxidation [34,35]. It was reported that an ultrathin coating of the Al_2O_3 overlayer by ALD reduced the overpotential by as much as 100 mV and enhanced the photocurrent by a factor of 3.5 (from 0.24 mA cm^{-2} to 0.85 mA cm^{-2}) at +1.0 V vs. RHE (the reversible hydrogen electrode) [34]. A similar overlayer of Sn-treated hematite nanorods allowed photocurrent density to increase from 1.24 to 2.25 mA cm^{-2} at 1.23 V vs. RHE. The photocurrent improvement is mainly attributed to the formation of $\text{Fe}_x\text{Sn}_{1-x}\text{O}_4$ at the hematite nanorod surface which resulted in a reduced electron–hole recombination at the hematite/electrolyte interface [36]. Co-catalysts such as IrO_2 , NiO_x , and Co-Pi were coated on hematite films and enhanced photocurrent dramatically [32,37–39]. These co-catalysts generally facilitate hole transfer and suppress surface charge recombination which results in increased water oxidation efficiency. However, these metal-based co-catalysts often suffer from multiple competitive disadvantages, including their high cost, poor durability, and detrimental environmental effects caused by catalyst residues [40]. Therefore, it is highly desirable to develop inexpensive, metal-free, and high-performance co-catalysts for water splitting.

Recently, carbon nanomaterials have been demonstrated to be promising metal-free alternatives for low-cost catalytic processes owing to their environmental friendliness, corrosion resistance, and unique surface properties [41]. Graphene, a unique planar structure, has excellent transparency, superior electron conductivity and large specific surface area. Also, it has been an excellent candidate for photocatalyst carriers or promoters [42–46]. Graphene-based CdS and TiO_2 afforded an enhanced photocatalytic water splitting activity due to that graphene possesses high conductivity for facilitating charge

separation and efficient controllability of particles growth for offering more active reaction centers [42,47]. In a Z-scheme photocatalysis system, reducing graphene oxide (RGO) has been demonstrated to be an effective solid electron mediator for photocatalytic water splitting [48].

The graphene-semiconductor composite photocatalysts are often used as particles dispersed in water solution. So far, few studies have focused on graphene-semiconductor film for photoelectrochemical water splitting [43,49]. Herein, we report an ultrathin hematite film coating with a layer of RGO for photoelectrochemical water splitting under visible light. The hematite film was synthesized through a separated two-phase interface hydrolysis method. The hydrolysis reaction occurs at the interface area and is suitable to prepare highly crystallized, and ultrafine nanocrystals [50]. It was found that the as prepared ultrathin hematite film on FTO substrate was very stable and showed good performance for water splitting. The photocurrent density was further enhanced by RGO nanosheets coated on the hematite film through a simple spin coating process. This research demonstrates that graphene can be used as an inexpensive co-catalyst to enhance the photoelectrochemical water splitting activity.

Experimental section

Materials preparation

(a) Preparation of ultrathin hematite films

The hematite films on conductive glass substrate were synthesized through a separated two-phase hydrolysis–solvothermal reaction of iron(III) acetylacetonate and aqueous ammonia [51]. A clean FTO (fluorine-doped SnO_2 overlayer, sheet resistance of $10 \Omega/\text{sq}$) glass was put into a 20-mL beaker containing 4 mL n-butanol and 0.12 mmol $\text{Fe}(\text{acac})_3$. To a 100-mL Teflon-lined autoclave were added 4 mL deionised water and 0.2 mL aqueous ammonia (30%) to form an aqueous solution. Next, the 20-mL beaker containing $\text{Fe}(\text{acac})_3$, n-butanol and FTO glass was carefully placed into the 100-mL Teflon-lined autoclave, keeping the water solution separate from the organic solution. The autoclave was maintained in an oven at 140°C for 6 h under autogenous pressure and then air cooled to room temperature. After washing with deionised water and absolute ethanol in turn and then sintering at 500°C for 0.5 h in air, an ultrathin hematite film on FTO was produced. The whole process is considered to be one deposition cycle of the hematite film. Hematite films with different thickness were prepared by repeating different cycles of the above process. Based on the number of repeating deposition cycles, the samples were abbreviated as (Fe_2O_3) -1, (Fe_2O_3) -2, (Fe_2O_3) -3, and so on. The as-prepared hematite film is used as a photoanode with an exposed Fe_2O_3 surface area of $1.0 \text{ cm} \times 1.0 \text{ cm}$.

(b) Preparation of ultrathin hematite films coating with reducing graphene oxide (RGO)

Graphene oxide was synthesized from graphite powder (325 mesh, Qingdao, China) using a modified Hummers'

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