



# Efficient photoelectrochemical water splitting using three dimensional urchin-like hematite nanostructure modified with reduced graphene oxide



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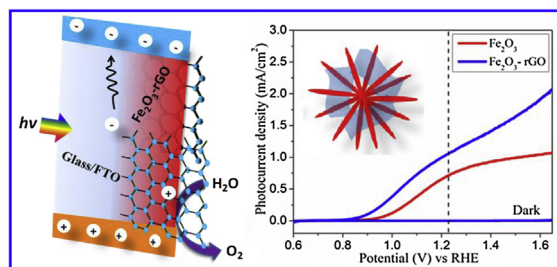
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## HIGHLIGHTS

- rGO modified 3D  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is synthesized using hydrothermal and spin coating methods.
- The rGO sheet act as both conductive scaffold and surface passivation layer.
- $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> modified with optimum amount of rGO show superior photocatalytic activity.
- rGO modified  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> exhibits higher charge separation and charge injection efficiency.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Herein, we present a highly photoactive photoanode for solar water oxidation using three dimensional (3D) urchin-like hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) nanostructures modified with ultra-thin reduced graphene oxide (rGO). rGO acts as both electron conducting scaffold and surface passivation layer. By virtue of these combined effects, the composite photoanode exhibits 1.47 times higher photocurrent density (1.06 mA cm<sup>-2</sup>, at 1.23 V vs. reversible hydrogen electrode (RHE)) and two-fold enhancement in the photoconversion efficiency than that of pristine  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The dual effect of rGO as both electron conducting scaffold and surface passivation layer is further evidenced from the 1.82 and 1.67 fold enhancements in charge separation and charge injection efficiencies at 1.23 and 1 V vs. RHE respectively. To get further evidence about the origin of the improved photoactivity of the rGO modified photoanode, a series of electrochemical, photoelectrochemical and impedance spectroscopy measurements were carried out. Our results demonstrate the benefits of a noble metal free highly promising photoanode for photoelectrochemical water oxidation.

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## 1. Introduction

The efficient conversion of solar energy to hydrogen through photoelectrochemical (PEC) water splitting, using semiconductor

electrodes, is a long-standing challenge that offers the hope of converting solar energy into synthetic fuels [1]. The selection of semiconductor electrodes for PEC water splitting must satisfy a number of requirements. Of paramount importance is the ability to perform reactions at high efficiencies. Among various water splitting semiconductor electrodes, hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) (“ $\alpha$ -” is omitted henceforth) is one of few materials that favorably combines several promising properties such as; stability in aqueous solutions, visible-light absorption, non-toxicity, abundance and low cost [2]. With an energy band gap of 2.1 eV, hematite can theoretically reach water oxidation current density as high as  $12.6\text{ mA cm}^{-2}$  under air mass 1.5 global (AM 1.5G) solar irradiation; thereby potentially enabling a maximum solar-to-hydrogen conversion efficiency of 15.5% [3]. However, the PEC activity of hematite is limited by several factors such as relatively poor absorption coefficient, very short excited-state lifetime ( $\sim 10^{-12}\text{ s}$ ), poor oxygen evolution reaction kinetics, and a short hole diffusion length (2–4 nm) [4].

To alleviate these limitations and improve the solar conversion efficiency, enormous efforts have been made. Some of these strategies include tailoring of hematite nanostructures, e.g. nanorod arrays, nanowires, nanocorals, cauliflower structures, worm-like structures etc [4–8]. Nanostructures with a very large interfacial area between the electrolyte and the semiconductor would facilitate charge collection by reducing the diffusion length of photo-excited holes. Doping is another strategy to improve the conductivity of hematite, where the enhanced electrical conductivity can extend the lifetime of the charge carriers by reducing the recombination of photogenerated electron–hole pairs. So far hematite has been doped with Ge, Mn, Si, Sn, Ti, Zr as n-type [4,6,9,10] and Co, Cu, Mg as p-type dopants [11–13]. N-type doping can boost the conductivity of hematite by introducing additional majority carriers [14]. On the other hand p-type doping enhances the utilization of solar energy by altering band-edge energies [12]. To minimize the large applied potential required, various catalysts have been added to the hematite surface including  $\text{IrO}_2$ , Co–Pi, Ni–Bi,  $\text{Ni(OH)}_2$ , NiOOH etc [15–19]. Surface modification by catalysts improves the PEC oxygen evolution kinetics, either by lowering potential-dependent rate constants for surface-mediated charge recombination, or by increasing the rate constant for hole transfer from the photo-electrode to the molecular reactant [20]. Another efficient approach to enhance the PEC performance of hematite is to incorporate electron conducting scaffolds in to the hematite nanostructure so as to improve the charge separation efficiency. Among the most known conducting scaffolds, graphene is widely recognized as an excellent electron collector and transporter that can efficiently hinder the recombination of photogenerated electron–hole pairs [21,22]. For thermodynamically feasible electron transport from a semiconductor to graphene, the conduction band of the semiconductor should be smaller than the work function of graphene. Typically, the work function of graphene is  $\sim 4.5\text{ eV}$  [23] and the conduction band edge of hematite is  $\sim -4\text{ eV}$  vs. vacuum at pH 14 [24]. Such an energy level configuration is beneficial for transporting photogenerated electrons from the hematite surface to the graphene sheet. On this premise, several hematite-graphene composite photoanodes have been demonstrated recently for PEC water splitting. For example, Meng et al. reported that incorporating hematite nanoparticles to reduced graphene oxide (rGO) nanosheet can suppress charge recombination and enhances charge separation [25]. Similarly, He et al. reported N-doped graphene– $\text{Fe}_2\text{O}_3$  nanocomposite for photoelectrochemical water oxidation and for photocatalytic colorless pollutant degradation [26]. However, many of these reports are suffering from too low PEC performance. Moreover, no direct experimental evidence has yet been provided to prove the charge separation and charge injection

properties of graphene composite electrodes. Herein, we combined a 3D urchin-like nanostructured  $\text{Fe}_2\text{O}_3$  with ultra-thin rGO sheet using a facile synthetic approach to use as an efficient water splitting photoanode. At optimum amount, the ultra-thin rGO sheet acts as a conducting scaffold to capture photogenerated electrons from the host  $\text{Fe}_2\text{O}_3$  photocatalyst and thereby reduce electron–hole recombination and as a surface passivation layer to improve the sluggish water oxidation reaction. To investigate the dual effect of rGO on the PEC performance of  $\text{Fe}_2\text{O}_3$ , we carried out PEC measurements in the presence of 0.5 M hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) hole scavenger, which gives direct evidence on the charge separation and injection properties.

## 2. Experimental section

### 2.1. Synthesis of 3D urchin-like $\alpha\text{-Fe}_2\text{O}_3$ photoanode

The 3D urchin-like hematite nanostructures were prepared via a simple solution-based method followed by two-step *in situ* annealing as described in literature with minor modification [27]. First, an aqueous solution containing 1 mmol of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 1 mmol of  $\text{Na}_2\text{SO}_4$  was prepared. In the meantime, a piece of fluorine doped tin oxide (FTO) coated glass was cleaned ultrasonically with EXTRAN MA 02 (neutral liquid detergent) and washed with de-ionized (DI) water and isopropyl alcohol followed by excess DI water. Then the clean FTO coated glass was put into Teflon-lined stainless steel autoclave. 20 mL precursor solution was added to the autoclave, sealed and heated at  $120\text{ }^\circ\text{C}$ . After 6 h reaction time, the autoclave was cooled down naturally. Then the FeOOH coated substrate was taken out of the Teflon, washed with absolute ethanol and DI water separately then air dried. A uniform yellow FeOOH film was coated on the glass substrate. The FeOOH film was changed to  $\text{Fe}_2\text{O}_3$  via two-step *in situ* annealing, initially at  $500\text{ }^\circ\text{C}$  for 3 h then at  $800\text{ }^\circ\text{C}$  for 20 min. The first annealing stage is responsible for converting the FeOOH phase to hematite phase while the later helps to enhance the crystallinity and diffusion of tin from the FTO to hematite bulk resulting tin doped hematite (Sn– $\text{Fe}_2\text{O}_3$ ).

### 2.2. Synthesis of graphite oxide (GO)

Graphite oxide was prepared from natural graphite precursor (purity  $>99.8\%$ , Alpha Aesar) according to a modified Hummer's method [21]. In brief, a 9:1 mixture of concentrated  $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$  (360:40 mL) was added to a mixture of graphite flakes (3.0 g, 1 wt. equiv.) and  $\text{KMnO}_4$  (18.0 g, 6 wt. equiv.), producing a slight exothermic reaction ( $35\text{--}40\text{ }^\circ\text{C}$ ). The reaction mixture was then heated to  $50\text{ }^\circ\text{C}$  and stirred for 12 h and then cooled to room temperature and poured in to ice water ( $\sim 400\text{ mL}$ ) containing 30%  $\text{H}_2\text{O}_2$  (3 mL). The dispersion was centrifuged (4000 rpm for 30 min) and the supernatant was decanted. The remaining solid material was washed in succession with 200 mL of DI water, 200 mL of 30% HCl, and 200 mL of ethanol (each two times). After successive washing, the mixture was centrifuged at 4000 rpm for 1 h and dried overnight at  $60\text{ }^\circ\text{C}$  under vacuum.

### 2.3. Synthesis of reduced graphene oxide (rGO) modified 3D urchin-like $\text{Fe}_2\text{O}_3$

First, dried GO was exfoliated in a mixture of DI water and ethanol (1:1 volume ratio) using ultrasonic treatment for 30 min to form a colloidal suspension ( $2\text{ mg mL}^{-1}$ ). Then  $50\text{ }\mu\text{L}$  of GO suspension was deposited into  $1\text{ cm}^2$   $\text{Fe}_2\text{O}_3$  film and allowed to wet the surface for 1 min. Subsequently, the substrate was allowed to spin at 800 rpm for 30 s to create uniform spreading of the solution on

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