

**Efficient and stable $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell nanospheres for
electrochemical water oxidation under neutral condition**

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Equipments and Apparatus

Materials: All reagents are of analytical grade and used without purification. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, CH_3COONa , $\text{HOCH}_2\text{CH}_2\text{OH}$, $\text{CH}_3\text{CH}_2\text{OH}$, HCl , NH_4OH and TEOS were purchased from Sinopharm Chemical Reagent limited corporation. The deionized water used throughout all experiments was purified through a Millipore system.

Fe_3O_4 synthesis: Fe_3O_4 nanoparticles were synthesized according to the literature [1-3]. 2.7 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 7.20 g of CH_3COONa were dissolved in a 100 ml of $\text{HOCH}_2\text{CH}_2\text{OH}$ with magnetic stirring for 5 min at room temperature. The obtained homogeneous yellow solution was transferred to a Teflon-lined stainless-steel autoclave and sealed to heat at 200°C . After reaction for 8 h, the autoclave was cooled to room temperature. The desired russet product was collected by centrifugation and washed with $\text{CH}_3\text{CH}_2\text{OH}$ several times, then dried in vacuum at 60°C for 12 h.

$\text{Fe}_3\text{O}_4@\text{SiO}_2$ synthesis: $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles were synthesized according to reference [2-4]. 0.1 g Fe_3O_4 powder were dissolved in a 50 ml of HCl aqueous (0.1 mol/L) with ultrasonication at room temperature. After the treatment for 10 min, the magnetite particles were separated and washed with water, and then homogeneously dispersed in the mixture of ethanol (80 mL), water (20 mL) and concentrated ammonia aqueous solution (1.0 mL, 28%), followed 0.8 mL of TEOS was added dropwise into the above solution under mechanical stirring. After stirring at room temperature for 6 h, the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ microspheres were separated with a magnet and washed with ethanol and water, then finally dried in vacuum at 60°C for 12 h.

Characterizations: Powder X-ray diffraction (PXRD) results were obtained with a PANalytical X'Pert Pro Diffractometer handled at 40 kV and 40 mA with $\text{Cu K}\alpha$ radiation in the 2θ range of 10° - 90° . X-Ray photoelectron spectra (XPS) were measured by ESCALAB250xi with X-ray monochromatisation. Infrared spectra (2–4 wt% sample in KBr pellets) were recorded using a Bruker VERTEX 70v FT-IR spectrometer. Transmission electron microscopy (TEM) and high-resolution TEM

(HRTEM) images were carried out on JEOL-2100F apparatus at an accelerating voltage of 200 kV. Elemental mapping and energy dispersive X-ray spectroscopy (EDS) were performed with JSM-5160LV-Vantage typed energy spectrometer. Electrochemical tests were recorded on a CHI760D electrochemical analyser with glassy carbon, Ag/AgCl, and Pt wire electrodes as the working, reference, and auxiliary electrode, respectively, in buffer solutions at room temperature with a scanning rate of 100 mV s⁻¹.

Electrocatalytic water oxidation

Electrocatalytic activities of the catalysts (0.35 mg cm⁻²) were tested in 0.2 M Tris-HCl buffer with the standard threeelectrode electrochemical glass flask using a CHI660D electrochemical analyzer at room temperature with glassy carbon (or FTO), Ag/AgCl, and Pt wire electrodes as the working, reference, and auxiliary electrode, respectively; scan rate 100 mV/s. In a typical procedure, 5 mg of the catalysts were dispersed in 1 mL of 3:1 v/v water/Nafion by sonication to form a homogeneous ink. Typically, 5 μ L well-dispersed catalysts were covered on the glassy carbon electrode and then dried in an ambient environment for measurements. The electrocatalyst was prepared with a catalyst loading of 0.35 mg cm⁻². Linear sweep voltammetry with a scan rate of 100 mV s⁻¹ was conducted in solution using Ag/AgCl (saturated KCl) as the reference electrode, Pt wire as the counter electrode, and the glassy carbon electrode with various catalysts as the working electrode. The working electrodes were activated for several times until the signals were stabilized. The potentials reported in this work were referenced to the reversible hydrogen electrode (RHE) through RHE calibration: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 \text{ V} + 0.059 \text{ pH}$, overpotential $\eta = E_{\text{vs.RHE}} - 1.23 \text{ V}$. Tafel slopes can be obtained by plotting overpotential η against logarithm of current $\log(J)$ from LSV curves. Electrochemical impedance spectroscopy (EIS) measurements of the various catalysts were carried out using above three electrode systems 1.81 V vs. RHE. The frequency range was 100 000 Hz to 0.1 Hz, and the amplitude of the applied voltage was 5 mV [5-6].

Procedure on recovery catalyst

FTO is regarded as a working electrode to replace the glassy carbon electrode. The $\text{Fe}_3\text{O}_4@\text{SiO}_2$ powder was grinded and deposited on FTO electrode via a drop-casting method. After 8 h water electrolysis at an applied voltage of 1.2 V vs RHE electrode in 0.2 M Tris-HCl buffer (pH=7.1), the recovered sample was carefully scraped off from the FTO and washed with anhydrous ethanol for three times, collected and then dried at room temperature.

Calculation method

Details concerning the calculation of mass activity, specific activity, and turnover frequency (TOF) are shown below.

The values of mass activity (A g^{-1}) were calculated from the catalyst loading m (0.35 mg cm^{-2}) and the measured current density j (mA cm^{-2}) at $\eta = 0.35 \text{ V}$:

$$\text{Mass activity} = j/m$$

The values of specific activity (mA cm^{-2}) were calculated from the BET surface area S_{BET} ($\text{m}^2 \text{ g}^{-1}$), catalyst loading m (0.352 mg cm^{-2}):

$$\text{Specific activity} = j/(10 \cdot S_{\text{BET}} \cdot m)$$

The values of TOF were calculated by assuming that every metal atom is involved in the catalysis: $\text{TOF} = j \cdot A / 4 \cdot n \cdot F$

Here, j (mA cm^{-2}) is the measured current density at $\eta = 0.35 \text{ V}$, A (0.071 cm^2) is the surface area of glassy carbon disk, the number 4 means 4 electrons per mole of O_2 , F is Faraday's constant ($96485.3 \text{ C mol}^{-1}$), and n is the moles of the metal atom on the electrode calculated from the molecular weight of the coated catalysts.

Calculation of electrochemically active surface area (ECSA)

The calculation of ECSA is based on the measured double layer capacitance of the catalysts on glassy carbon electrode in 1 M KOH according to a previous published report 2. Briefly, a potential range where no apparent Faradaic process happened was determined firstly using the static CV. The charging current i_c was measured from the

CVs at different scan rates, as shown in Fig. 3. The relation between i_c , the scan rate (v) and the double layer capacitance (C_{dl}) was given.

$$i_c = vC_{dl}$$

Therefore, the slope of i_c as a function of v will give a straight line with the slope equal to C_{dl} (Fig. 7a). For the estimation of ECSA, a specific capacitance (C_s) value $C_s = 0.040 \text{ mF cm}^{-2}$ in 1 M KOH is adopted from previous reports [7].

$$\text{ECSA} = C_{dl}/C_s$$

Table 1 Surface content of Fe and Si in Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{SiO}_2$ evaluated by XPS.

Nanoparticles	Surface atomic content (%)	
	Fe 2p _{3/2}	Si 2p
Fe_3O_4	22.59	0
$\text{Fe}_3\text{O}_4@\text{SiO}_2$	4.07	19.88

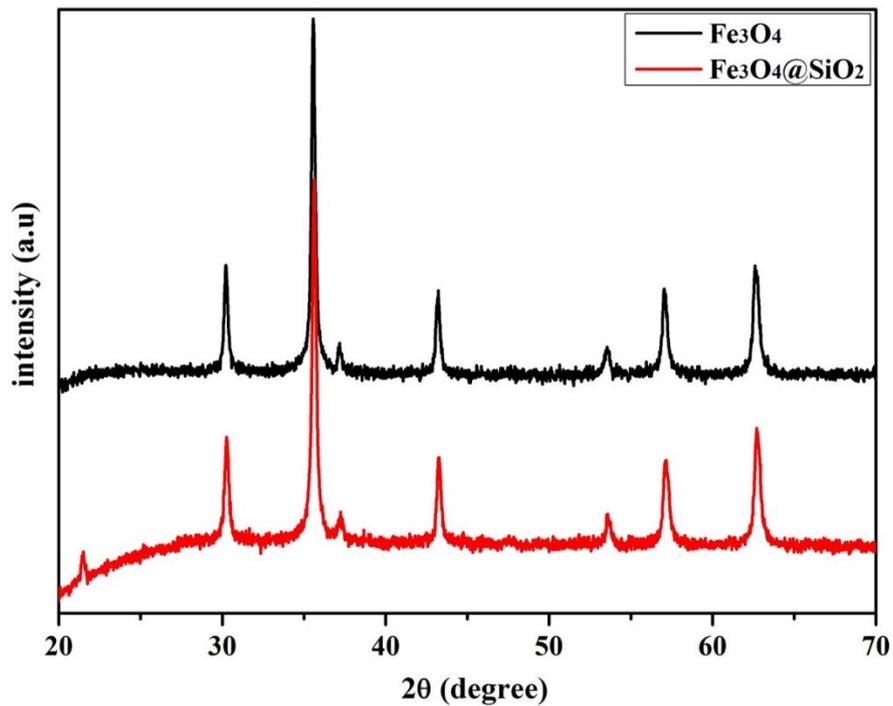


Fig. 1 XRD patterns of (black) Fe_3O_4 and (red) $\text{Fe}_3\text{O}_4@\text{SiO}_2$.

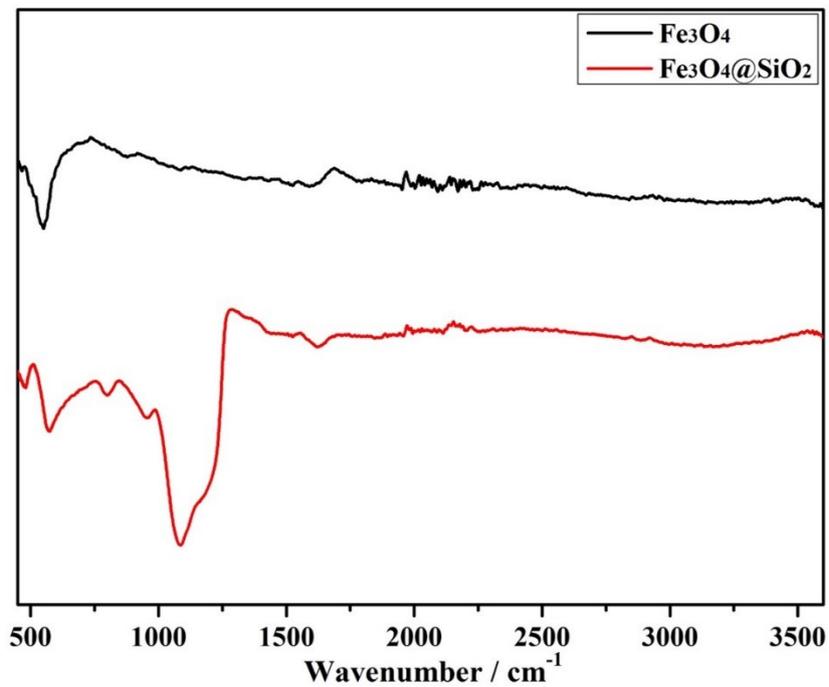


Fig. 2 FT-IR spectra of (black) Fe_3O_4 and (red) $\text{Fe}_3\text{O}_4@\text{SiO}_2$.

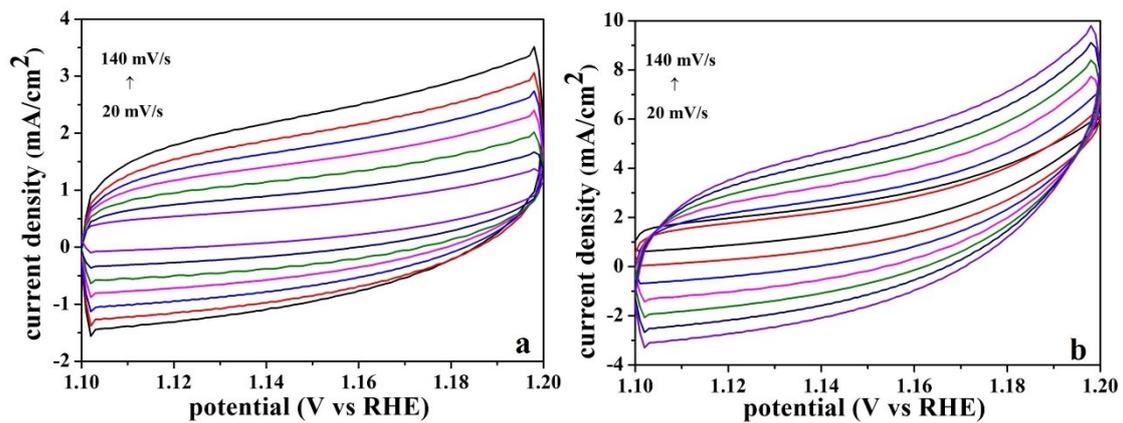


Fig. 3 CV curves measured within the range of 1.1 to 1.2 V vs. RHE with scan rate from 20 to 140 mV s^{-1} of Fe_3O_4 (a) and $\text{Fe}_3\text{O}_4@\text{SiO}_2$ (b).

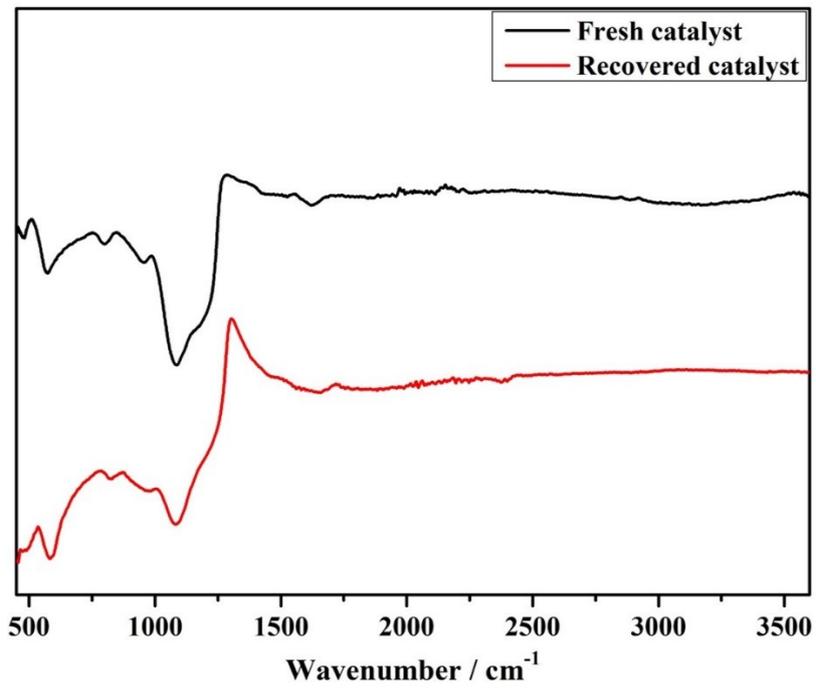


Fig. 4 FT-IR of Fe₃O₄@SiO₂ before and after water electrolysis.

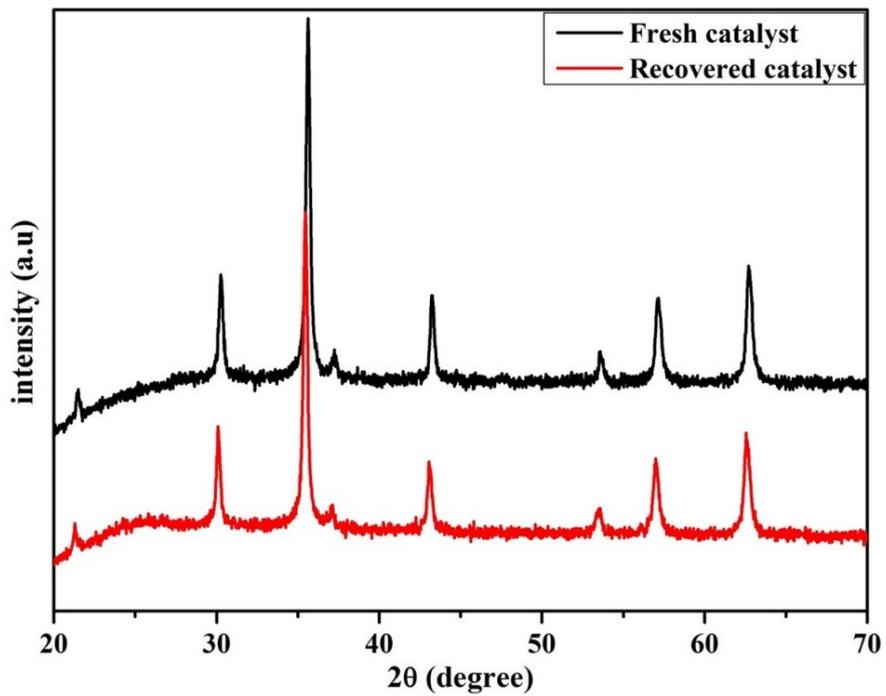


Fig. 5 XRD of Fe₃O₄@SiO₂ before and after water electrolysis.

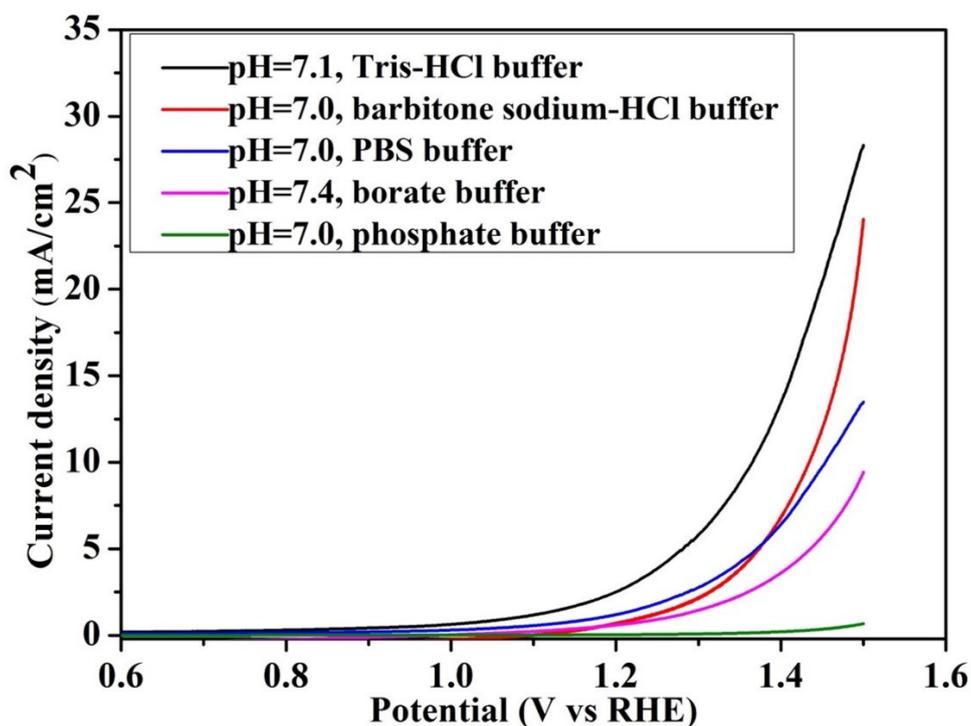


Fig. 6 LSVs of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ (0.35 mg/cm^2) use different kinds of buffers (0.2 M).

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