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Electronic Supplementary Information

Ir-Phosphate Cocatalyst for Photoelectrochemical Water Oxidation using α-Fe₂O₃

Ahamed Irshad and Nookala Munichandraiah*

Department of Inorganic and Physical Chemistry

Indian Institute of Science, Bangalore - 560012, India

*Corresponding author; e-mail: muni@ipc.iisc.ernet.in; Tel: +91-80-2293 3183

S1: XRD of Ir-Pi on FTO

It was intended to examine the crystallinity of the Ir-Pi catalyst. For this, very thick layer of the Ir-Pi was deposited onto FTO glass plates at 1.10 V vs. SCE for 3 h from 2 mM Ir³⁺ in 0.1 M phosphate solution (pH 7). The deposit was rinsed well with double distilled water and dried in air prior to the analysis. XRD was recorded for both bare FTO substrate and FTO coated with Ir-Pi catalyst. As it is seen from Fig. S1(i), sharp diffraction peaks are obtained for the FTO substrate. However, only these peaks are observed even after depositing thick Ir-Pi layer, indicating the amorphous nature of the Ir-Pi catalyst.



Fig. S1. XRD patters of (i) FTO and (ii) Ir-Pi coated FTO.

S2: TEM Images

The morphology of the Ir-Pi loaded Fe_2O_3 was examined by transmission electron microscopy (TEM). For this, the deposit was scrapped off from the electrode surface using a razar blade and the material so obtained was dispersed in acetone. TEM image of Ir-Pi-Fe₂O₃ in Fig. S2a shows big lumps of Fe₂O₃ formed by the fusion of several particles. These Fe₂O₃ bumps are further wrapped with thick sheets of Ir-Pi catalyst. The sharp interface between crystalline Fe₂O₃ and amorphous Ir-Pi layer is evident from the HRTEM image (Fig. S2b). The lattice fringes are from the crystalline planes of Fe₂O₃. For instances, (104) planes of Fe₂O₃ with a d spacing value of 0.27 nm is marked in the image.



Fig S2: (a). TEM and (b). HRTEM images of Ir-Pi-Fe₂O₃.

S3: Efficiency

The applied bias photon to current efficiency (ABPE) was calculated for both Fe_2O_3 and Ir-Pi loaded Fe_2O_3 electrodes at different voltage bias. Assuming 100 % Faradaic efficiency, the ABPE can be calculated using the equation,^{R1}

$$ABPE = \frac{j_{ph} (1.23 - V_b)}{P_{light}}$$

where j_{ph} is the photocurrent density (mA cm⁻²) obtained under an applied bias, V_b and P_{light} is the power density of incident light (100 mW cm⁻²). A maximum efficiency of 0.027 % was obtained for Ir-Pi-Fe₂O₃ at 0.90 V whereas it is almost 10 times less (around 0.0027 %) for bare Fe₂O₃ at 1.10 V. The high photoconversion efficiency in the presence of Ir-Pi catalyst is due to the suppression of charge carrier recombination at the electrode/electrolyte interface and fast kinetics of water oxidation reaction.



Fig S3: ABPE as a function of applied potential (obtained using three electrode system) for (i) Fe_2O_3 and (ii) Ir-Pi-Fe_2O_3 electrodes in 0.1 M phosphate buffer electrolyte (pH 7.0).

S4: Detection of evolved oxygen using Pt electrode

The evolved O_2 was detected by electrochemical oxygen reduction reaction (ORR) on a Pt electrode. An air-tight electrochemical cell equipped with a cleaned Pt foil and Ir-Pi-Fe₂O₃ electrode as the working electrodes for ORR and OER, respectively, was used. The cell was filled with neutral phosphate solution and purged with high purity Ar-gas. Then, the Pt electrode was subjected to linear sweep voltammetry (LSV) from 0.0 to -0.35 V vs. SCE at 50 mV s⁻¹. Small current flows due to the reduction of trace amount of dissolved O₂ present in the solution even after purging with Ar gas and ORR current peak appears at -0.27 V (Fig. S4(i)). Then, the photoelectrolysis was initiated at Ir-Pi-Fe₂O₃ electrode under illumination at 1.10 V vs. RHE. After 30 min, photoelectrolysis was terminated and Pt electrode was subjected to LSV again. The current peak at -0.27 V due to ORR is significantly enhanced (Fig. S4(ii)). This indicates that the photoelectrochemical reaction on Ir-Pi-Fe₂O₃ electrode had generated O₂ gas which subsequently underwent reduction at Pt foil.



Fig S4: Linear sweep voltammograms of O_2 reduction reaction (ORR) on a Pt electrode in a 0.1 M phosphate electrolyte (pH 7.0) under (i) Ar-purged condition, and (ii) after 30 min of O_2 production by photoelectrolysis at 1.10 V vs. RHE using Ir-Pi-Fe₂O₃. Scan rate: 50 mV s⁻¹.

S5: IPCE Spectra

Incident photon-to-current efficiency (IPCE) was measured at 1.50 V vs. RHE for both Fe_2O_3 and Ir-Pi-Fe₂O₃. IPCE was calculated according to the equation,^{R2}

IPCE (
$$\lambda$$
) = $\frac{1240 \cdot J_{ph}}{P_{\lambda} \cdot \lambda}$

where J_{ph} is the measured photocurrent density (mA cm⁻²), P_{λ} is power density at the specific wavelength (mW cm⁻²) and λ is the wavelength (nm). As evident from Fig. S5(i), Fe₂O₃ exhibits increasing IPCE by decreasing wavelength from about 550 nm in agreement with its bandgap. However, efficiency increases slowly till 450 nm and rises rather quickly at lower wavelengths. The maximum efficiency of around 5 % is obtained at 380 nm. Similar trend is observed for Ir-Pi-Fe₂O₃ (Fig. S5(ii)), indicating that the primary phoresponse is from the underlying Fe₂O₃ only. However, Ir-Pi-Fe₂O₃ electrode shows higher IPCE values compared with bare Fe₂O₃ in the range 550 - 360 nm. A maximum IPCE of 7.3 % is obtained at 380 nm. High efficiency in the presence of Ir-Pi can be attributed to a fast interfacial charge transfer. This again confirms the role of Ir-Pi as an efficient cocatalyst for water oxidation reaction.



Fig S5: IPCE spectra of (i) Fe₂O₃ and (ii) Ir-Pi-Fe₂O₃ at 1.50 V vs. RHE.

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