

MATERIALS SCIENCE

Paving the road toward the use of β -Fe₂O₃ in solar water splitting: Raman identification, phase transformation and strategies for phase stabilizationNingsi Zhang¹, Xin Wang¹, Jianyong Feng¹, Huiting Huang¹, Yongsheng Guo¹, Zhaosheng Li^{1,2,*} and Zhigang Zou^{1,2}

ABSTRACT

Although β -Fe₂O₃ has a high theoretical solar-to-hydrogen efficiency because of its narrow band gap, the study of β -Fe₂O₃ photoanodes for water splitting is elusive as a result of their metastable nature. Raman identification of β -Fe₂O₃ is theoretically and experimentally investigated in this study for the first time, thus clarifying the debate about its Raman spectrum in the literature. Phase transformation of β -Fe₂O₃ to α -Fe₂O₃ was found to potentially take place under laser and electron irradiation as well as annealing. Herein, phase transformation of β -Fe₂O₃ to α -Fe₂O₃ was inhibited by introduction of Zr doping, and β -Fe₂O₃ was found to withstand a higher annealing temperature without any phase transformation. The solar water splitting photocurrent of the Zr-doped β -Fe₂O₃ photoanode was increased by 500% compared to that of the pure β -Fe₂O₃ photoanode. Additionally, Zr-doped β -Fe₂O₃ exhibited very good stability during the process of solar water splitting. These results indicate that by improving its thermal stability, metastable β -Fe₂O₃ film is a promising photoanode for solar water splitting.

Keywords: solar energy conversion, metastable phase, phase transformation, iron oxide, photoelectrochemical water splitting

INTRODUCTION

Since the concept of a hydrogen economy was introduced, solar hydrogen production using photoelectrochemical (PEC) or photocatalytic water splitting has occupied a very important position in the artificial utilization of inexhaustible solar energy [1–6]. Solar water splitting for hydrogen production has thereby attracted intensive and ever-increasing interest from many researchers [7–15]. The solar-to-hydrogen efficiency of PEC water splitting reached over 19% using III-V multi-junction semiconductors (including In and Ga) prepared by molecular beam epitaxial growth [16]. Unfortunately, there is a lack of low-cost, environmentally friendly, efficient and stable photoelectrodes for PEC water splitting [17–22], thus hindering application of PEC cells for hydrogen production.

In recent decades, iron-based semiconductors with narrow band gaps (e.g. α -Fe₂O₃) have been considered as promising photoanode materials with

respect to nontoxicity, cost, stability and theoretical solar-to-hydrogen efficiency [23–34]. Recently, a β -Fe₂O₃ semiconductor with a direct band gap of 1.9 eV was reported by the present authors as a water splitting photoanode under Air Mass 1.5 Global spectrum (AM 1.5 G, 100 mW cm⁻²) illumination [35]. Theoretically, a β -Fe₂O₃ photoanode for solar water splitting may exhibit a solar-to-hydrogen efficiency of 20.9% because of its narrow band gap of 1.9 eV, whereas its solar photocurrent density is still very low [35]. The phase transformation of metastable β -Fe₂O₃ to mature α -Fe₂O₃ may occur initially at the surface or interface during fabrication of photoanode films because metastable β -Fe₂O₃ cannot withstand the high temperature of annealing.

Phase identification of β -Fe₂O₃ is very important to avoid the effects of impurities (e.g. α -Fe₂O₃) during the process of solar water splitting. Phase characterization of inorganic materials is frequently achieved with such methods as X-ray

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diffraction (XRD), neutron diffraction, electron diffraction, Raman scattering spectroscopy and infrared absorption spectroscopy. Among these methods, Raman spectroscopy is fast and highly sensitive toward material surface structural information. However, Raman spectra of β -Fe₂O₃ (including Raman peak position and shape) reported in the literature are often contradictory [36,37]. Thus, this study aims to clarify the debates surrounding the Raman spectra of β -Fe₂O₃.

The wavelength and power of the excitation laser should be chosen carefully during the process of Raman detection. An appropriate wavelength of laser should be selected to enhance the Raman sensitivity and minimize the fluorescence emission of the samples. It is equally important that the power of the laser be examined cautiously to avoid the influences of thermal effects caused by the laser, especially for those materials with poor thermal stability. For example, phase transformation of ε -Fe₂O₃ and γ -Fe₂O₃ may take place under laser irradiation [38,39], and β -Fe₂O₃ may be converted into α -Fe₂O₃ upon heat treatment [35,40]. Therefore, low-power laser irradiation is required to avoid phase transformation of the β -Fe₂O₃ samples.

In this study, the influence of laser wavelength and irradiation power on phase transformation of β -Fe₂O₃ to α -Fe₂O₃ was investigated, and the Raman vibrational spectrum of β -Fe₂O₃ was clarified. After being doped with Zr, the particle-assembled β -Fe₂O₃ photoanodes can withstand higher annealing temperatures during the post-treatment process. Therefore, the solar water splitting photocurrent density for the particle-assembled Zr-doped β -Fe₂O₃ photoanodes was improved significantly to 1.2 mA cm⁻², which is five times greater than that of pure β -Fe₂O₃ photoanodes. Thus, this study suggests metastable β -Fe₂O₃ films as promising photoanode materials for solar water splitting.

RESULTS AND DISCUSSION

β -Fe₂O₃ belongs to the space group Ia $\bar{3}$, T_h⁷. Irreducible representations of the Γ -point phonon modes for β -Fe₂O₃ are shown in Supplementary Table S1. Factor group analysis of β -Fe₂O₃ predicts 49 phonon modes, 22 and 17 of which are Raman active modes and infrared active modes (Supplementary Table S2), respectively. Some Raman vibrational modes of β -Fe₂O₃ were observed in previous studies, whereas Rahman and coworkers reported different Raman spectra for β -Fe₂O₃ [36,37]. To clarify the Raman vibrational modes of β -Fe₂O₃, the Raman scatter spectrum of β -Fe₂O₃ was verified, as shown in Supplementary Fig. S1. Twelve clear vibrational peaks of β -Fe₂O₃ were observed at 158,

169, 234, 258, 274, 314, 328, 368, 386, 397, 522 and 635 cm⁻¹ using the 785 nm laser of 0.4 W. These peaks can clearly be distinguished from the Raman vibration peaks of α -Fe₂O₃ (227, 246, 293, 300, 411, 499, and 613 cm⁻¹). Compared to previous results from Liang and van de Krol [36], four new vibrational peaks at 258, 397, 522 and 635 cm⁻¹ were observed, whereas the vibrational peak at 208 cm⁻¹ was not observed.

The theoretical calculations and experimental values of Raman vibrational peaks are listed in Supplementary Table S3. Among the 22 vibrational modes predicted by the theoretical calculations, only 12 significant peaks were observed in the experiments. Three weak vibrational modes are marked with asterisks. The M10 (383 cm⁻¹) and M11 (389 cm⁻¹) modes merge into one peak (386 cm⁻¹) in the experimental spectrum. As given in Supplementary Fig. S1, typical peaks corresponding to vibrational modes 158 cm⁻¹ (T_g), 274 cm⁻¹ (T_g), 368 cm⁻¹ (T_g) and 386 cm⁻¹ (E_g+T_g) can be used as a characteristic spectrum for identifying the phase of β -Fe₂O₃. In addition, the theoretically calculated infrared vibrational peaks and the experimental infrared absorption spectrum are also given in Supplementary Table S4 and Supplementary Fig. S2, respectively.

The metastable β -Fe₂O₃ phase may be converted to the mature α -Fe₂O₃ phase upon laser irradiation of different wavelengths and power. Figure 1 shows the effects of laser wavelength on the Raman spectrum of β -Fe₂O₃. The Raman peaks at 227, 293, 411, 499 and 613 cm⁻¹ belonging to α -Fe₂O₃ appeared after irradiation of the β -Fe₂O₃ samples with a 532 nm or 633 nm laser. In the case of 785 nm laser irradiation, the experimental and theoretical Raman peaks for β -Fe₂O₃ match in shape but exhibit a slight shift. These results suggest that a 785 nm laser is ideal for detecting the Raman spectra of metastable β -Fe₂O₃.

Raman spectra mapping images shown in Fig. 2 also indicate phase transformation of the particle-assembled β -Fe₂O₃ films without any necking treatment, in which the α -Fe₂O₃ phase appears when the β -Fe₂O₃ film samples are irradiated with a 10 mW laser of 532 and 633 nm. Scanning electron microscope (SEM) images also suggest this phase transformation. Even when β -Fe₂O₃ was irradiated with a laser of 785 nm with 10 mW power, slight damage of the β -Fe₂O₃ films was observed.

Additionally, the effects of laser power on the Raman spectrum of β -Fe₂O₃ were investigated. When the power of the 785 nm laser is increased, a phase change of β -Fe₂O₃ to α -Fe₂O₃ possibly occurs (Fig. 3). After β -Fe₂O₃ is irradiated by 0.4 mW 785 nm laser for an extended period of 500 s, there

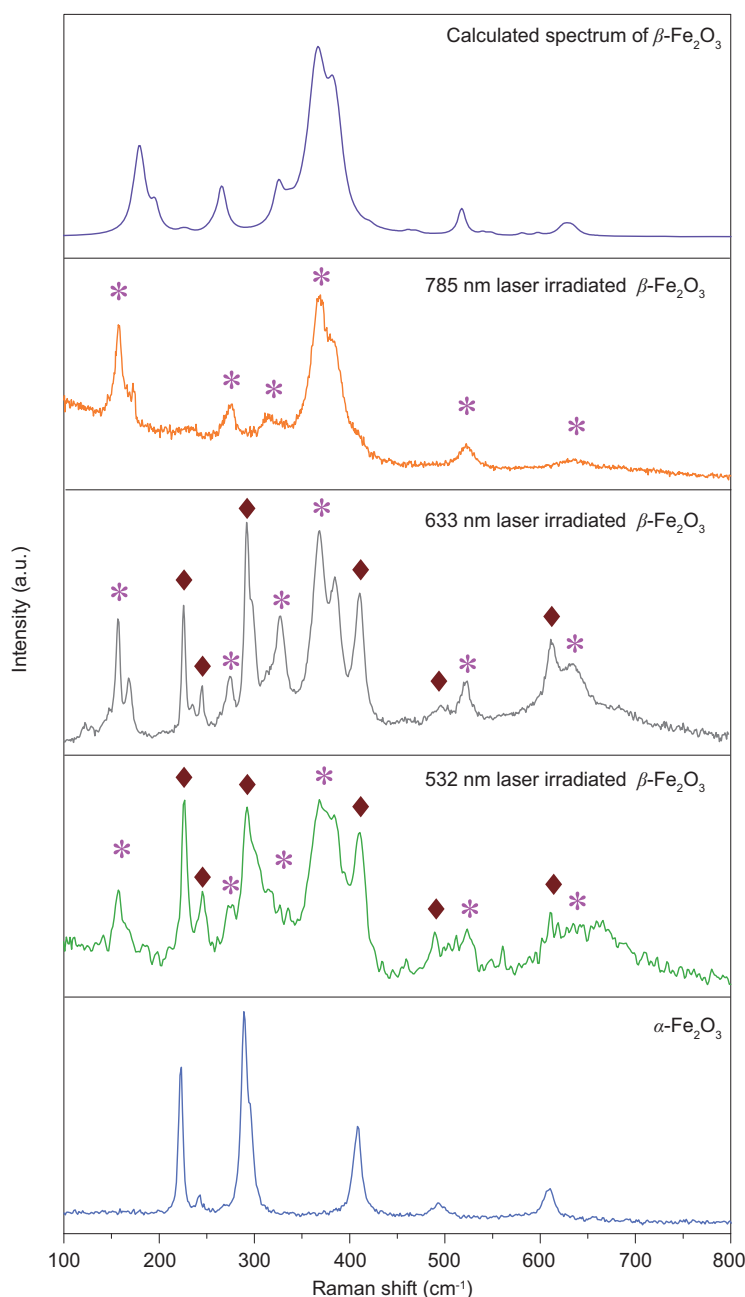


Figure 1. Theoretical calculation and experimental measurement of Raman spectra of β - Fe_2O_3 samples excited by a 0.4 mW laser at 785, 633 and 532 nm. The Raman spectrum of α - Fe_2O_3 is listed as a reference.

is no signal corresponding to α - Fe_2O_3 . A significant phase transformation occurs with as little as 2 s irradiation with a 4 mW 785 nm laser. As the laser power increases and the exposure time is prolonged, all the β - Fe_2O_3 gradually converts to α - Fe_2O_3 .

Figure 4 shows Raman spectra mapping and SEM images of the particle-assembled β - Fe_2O_3 films without any necking treatment after laser illumination of 785 nm. When the β - Fe_2O_3 films were irradiated with 785 nm laser at 0.4 W power, no α - Fe_2O_3 signal appeared. With the increasing power of the

785 nm laser, the signals of α - Fe_2O_3 were enhanced, suggesting laser-induced phase transformation of β - Fe_2O_3 to α - Fe_2O_3 . The SEM images of Fig. 4 also corroborate this result. The phase transformation of β - Fe_2O_3 to α - Fe_2O_3 is initiated by laser irradiation, likely as a result of the thermal effects of the laser. Therefore, low-power laser irradiation is required to avoid the phase transformation of metastable materials during Raman characterization to minimize its thermal effects. Thus, a 0.4 mW 785 nm laser is ideal for measuring the Raman spectra of β - Fe_2O_3 .

Figure 5 shows transmission electron microscope (TEM) and selected area electron diffraction (SAED) images of the β - Fe_2O_3 samples. A simulated SAED image of α - Fe_2O_3 is shown in Fig. 5 for comparison. The measured SAED image of β - Fe_2O_3 samples (Fig. 5a) is in good agreement with the simulated SAED image of α - Fe_2O_3 (Fig. 5d) rather than the simulated SAED image of β - Fe_2O_3 samples (Fig. 5c), suggesting that the phase transformation of β - Fe_2O_3 to α - Fe_2O_3 induced by electron irradiation was also observed in this study. Note that the use of SAED to detect β - Fe_2O_3 should be done with caution. The phase transformation of β - Fe_2O_3 to α - Fe_2O_3 may be driven by laser irradiation, electron irradiation and heating (Supplementary Figs S3 and S4).

In our previous work, phase transformation of β - Fe_2O_3 to α - Fe_2O_3 occurred after annealing at 650°C [29]. Phase transformation of β - Fe_2O_3 was also proven by the appearance of the Raman peaks of α - Fe_2O_3 (Supplementary Fig. S3). In this study, Zr was introduced into the metastable β - Fe_2O_3 to inhibit phase transformation of β - Fe_2O_3 to α - Fe_2O_3 . The formation energy of $\text{Zr}_{0.03}\text{Fe}_{1.97}\text{O}_3$ (Zr-doped β - Fe_2O_3) was calculated as -0.16 eV relative to pure β - Fe_2O_3 , suggesting that Zr can be doped into the lattice of β - Fe_2O_3 to form a more stable structure. The density of states (DOS) for $\text{Zr}_{0.03}\text{Fe}_{1.97}\text{O}_3$ indicates that the band gap of β - Fe_2O_3 does not change obviously by doping Zr (Supplementary Fig. S5).

The XRD pattern of Zr-doped β - Fe_2O_3 (Supplementary Fig. S6) is in good agreement with β - Fe_2O_3 (JCPDS#39-0238), suggesting that there is no impurity phase after doping with Zr. The X-ray photoelectron spectroscopy in Supplementary Fig. S7 shows that Zr was doped into the sample. The absorption spectra of pure β - Fe_2O_3 and Zr-doped β - Fe_2O_3 are shown in Supplementary Fig. S8. After annealing, the band gap of pure β - Fe_2O_3 changed, whereas the band gap of Zr-doped β - Fe_2O_3 did not. In previous work, we have reported that the absorption spectrum of β - Fe_2O_3 varies after different calcining processes [35]. The change in band gap indicates that a phase transformation may

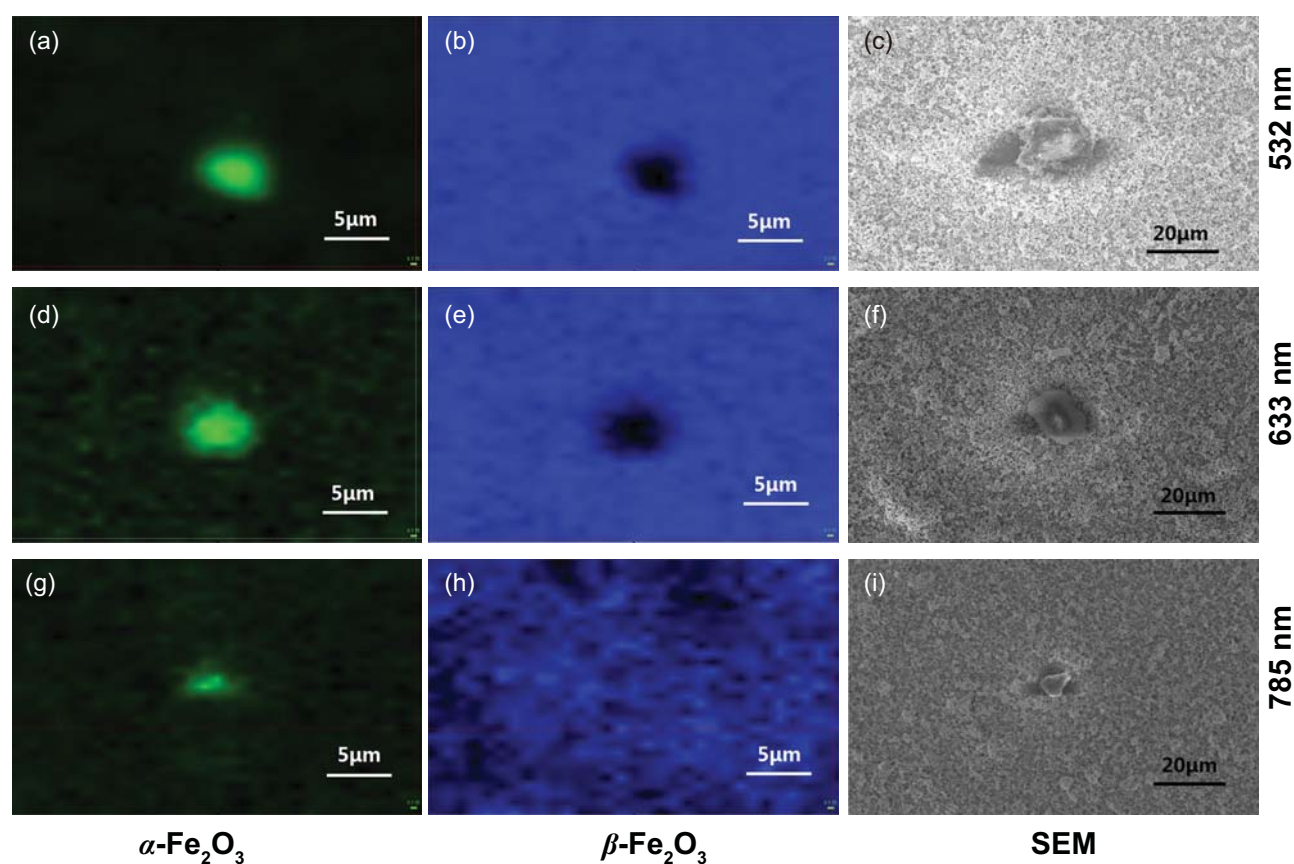


Figure 2. Raman mapping and SEM images of particle-assembled β - Fe_2O_3 films excited by a 0.4 mW laser at 785 nm after irradiation by a 10 mW laser with various wavelengths: (a-c) 532 nm, (d-f) 633 nm and (g-i) 785 nm. (a, d, g) α - Fe_2O_3 ; (b, e, h) β - Fe_2O_3 .

occur. Indeed, after being annealed at 1023 K, the characteristic Raman peaks of α - Fe_2O_3 appeared in the Raman spectrum of the β - Fe_2O_3 sample (Supplementary Fig. S9a), indicating that there was a phase transformation. The Raman spectra of Zr-doped β - Fe_2O_3 did not change after being annealed at 1023 K (Supplementary Fig. S9b), indicating that there was no phase transformation. Note that the results of differential scanning calorimetry show that the phase transition temperature of Zr-doped β - Fe_2O_3 is clearly increased, as shown in Supplementary Fig. S10. The above results show that Zr doping effectively increases the phase transition temperature of metastable iron oxide.

SEM images of the particle-assembled β - Fe_2O_3 photoanodes with and without Zr doping are shown in Supplementary Fig. S11. Figure 6a shows a comparison of the PEC performances of the particle-assembled β - Fe_2O_3 photoanodes with and without Zr doping under AM 1.5 G irradiation (100 mW cm^{-2}). The results show that the photocurrent of Zr-doped β - Fe_2O_3 photoanodes is much higher than that of pure β - Fe_2O_3 photoanodes. Zr-doped β - Fe_2O_3 photoanodes also exhibit much larger monochromatic incident

photon-to-electron conversion efficiency (IPCE) than pure β - Fe_2O_3 photoanodes (Fig. 6b). Compared to the pure β - Fe_2O_3 , the carrier density of Zr-doped β - Fe_2O_3 has been improved from 1.8×10^{20} to $4.6 \times 10^{20} \text{ cm}^{-3}$, which can be estimated from the Supplementary Fig. S12a. As shown in Supplementary Fig. S12b, the charge separation efficiency of Zr-doped β - Fe_2O_3 is improved by approximately four times at 1.6 V versus Reversible Hydrogen Electrode (RHE), compared to that of β - Fe_2O_3 . The increase in the carrier concentration may favor the charge transport and contribute to the improvement in water splitting photocurrent of the Zr-doped β - Fe_2O_3 photoanode.

Under AM 1.5 G irradiation (100 mW cm^{-2}), both Zr-doped and pure β - Fe_2O_3 photoanodes exhibit very good photochemical stability for water splitting during the PEC reaction over 10 h, as shown in Fig. 6c. In the case of particle-assembled Zr-doped β - Fe_2O_3 photoanodes, the Faradaic efficiencies for hydrogen production and oxygen production are 85% and 80%, respectively (Fig. 6d). This result suggests that the photocurrent of the particle-assembled β - Fe_2O_3 photoanodes is mainly attributed to water splitting.

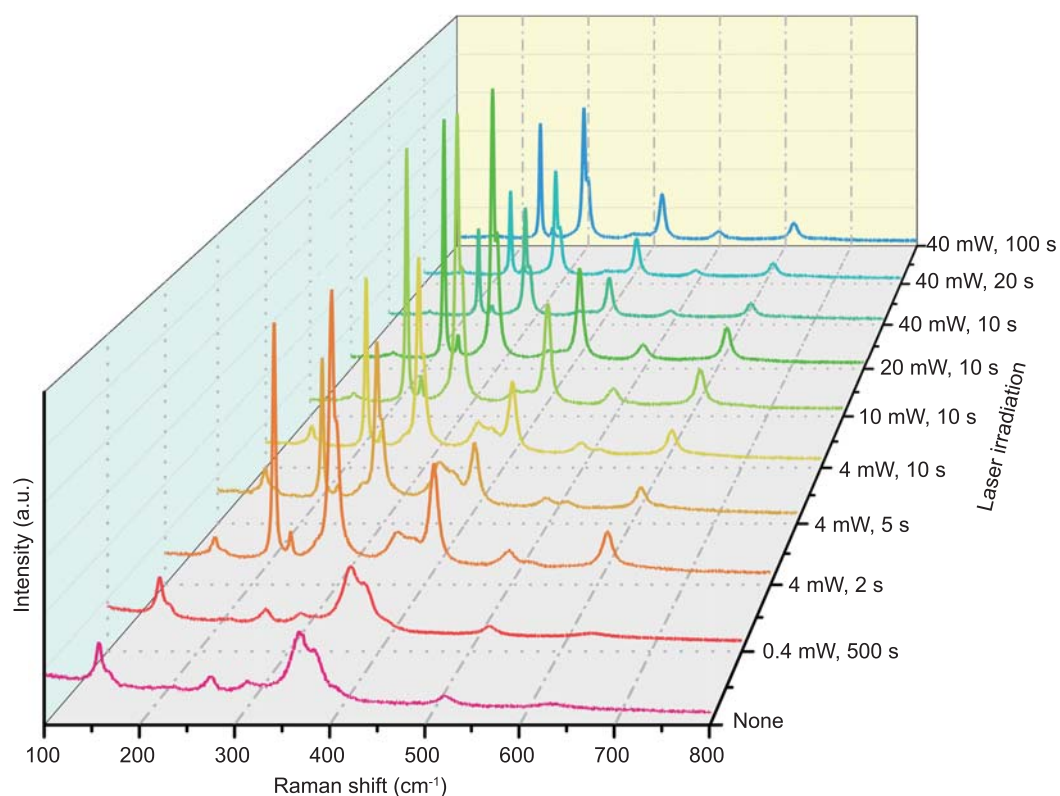


Figure 3. Raman spectra of β -Fe₂O₃ under different power laser irradiations of 785 nm.

During the process of solar water splitting, β -Fe₂O₃ as a photoanode material may be exposed to standard simulated sunlight for a long time. To assess the possibility for phase transformation of β -Fe₂O₃ to α -Fe₂O₃ under simulated sunlight, the Raman spectra of the samples were measured before and after the photochemical stability testing. As shown in Supplementary Fig. S13, the phase of the β -Fe₂O₃ photoanodes before and after the reaction of PEC water splitting remains unchanged. In a typical PEC reaction, the intensity of the light used is not sufficient to promote the phase transformation of β -Fe₂O₃ particle-assembled films. Therefore, β -Fe₂O₃ is a promising photoanode for water splitting. The PEC performance of β -Fe₂O₃ may be improved further by not only the rational design of electrocatalysts but also the optimization of preparation methods [41,42].

CONCLUSION

In conclusion, the Raman spectrum of β -Fe₂O₃ under excitation by a 785 nm laser with 0.4 W power shows 12 significant vibrational modes corresponding to β -Fe₂O₃. The phase transformation of metastable β -Fe₂O₃ to mature α -Fe₂O₃ may be observed under laser irradiation, electron irradiation

and heating. Zr doping was introduced to particle-assembled β -Fe₂O₃ films, thus not only increasing the carrier concentration but also suppressing the phase transformation of β -Fe₂O₃. The PEC performance of the Zr-doped β -Fe₂O₃ photoanode was vastly boosted, in comparison with that of the pure β -Fe₂O₃ photoanode. This study demonstrates that metastable β -Fe₂O₃ remains stable during the PEC reaction and is a promising photoanode material for decomposing water, thus paving the road toward the use of β -Fe₂O₃ in solar water splitting (Supplementary Scheme S1).

METHODS

In this study, β -Fe₂O₃ powder was synthesized by calcining the mixture of NaFe(SO₄)₂ (or 1.5% ZrSO₄ doped NaFe(SO₄)₂) and NaCl in a muffle furnace at 450°C for 1 h [43]. As-prepared β -Fe₂O₃ powder was then deposited on fluorine-doped tin oxide (FTO) glass by electrophoretic deposition to prepare the particle-assembled films. In the case of necking treatment for the particle-assembled β -Fe₂O₃ films, 0.2 μ mol of TiCl₄ in methanol solution was dropped on the particle-assembled β -Fe₂O₃ films. Afterward, the

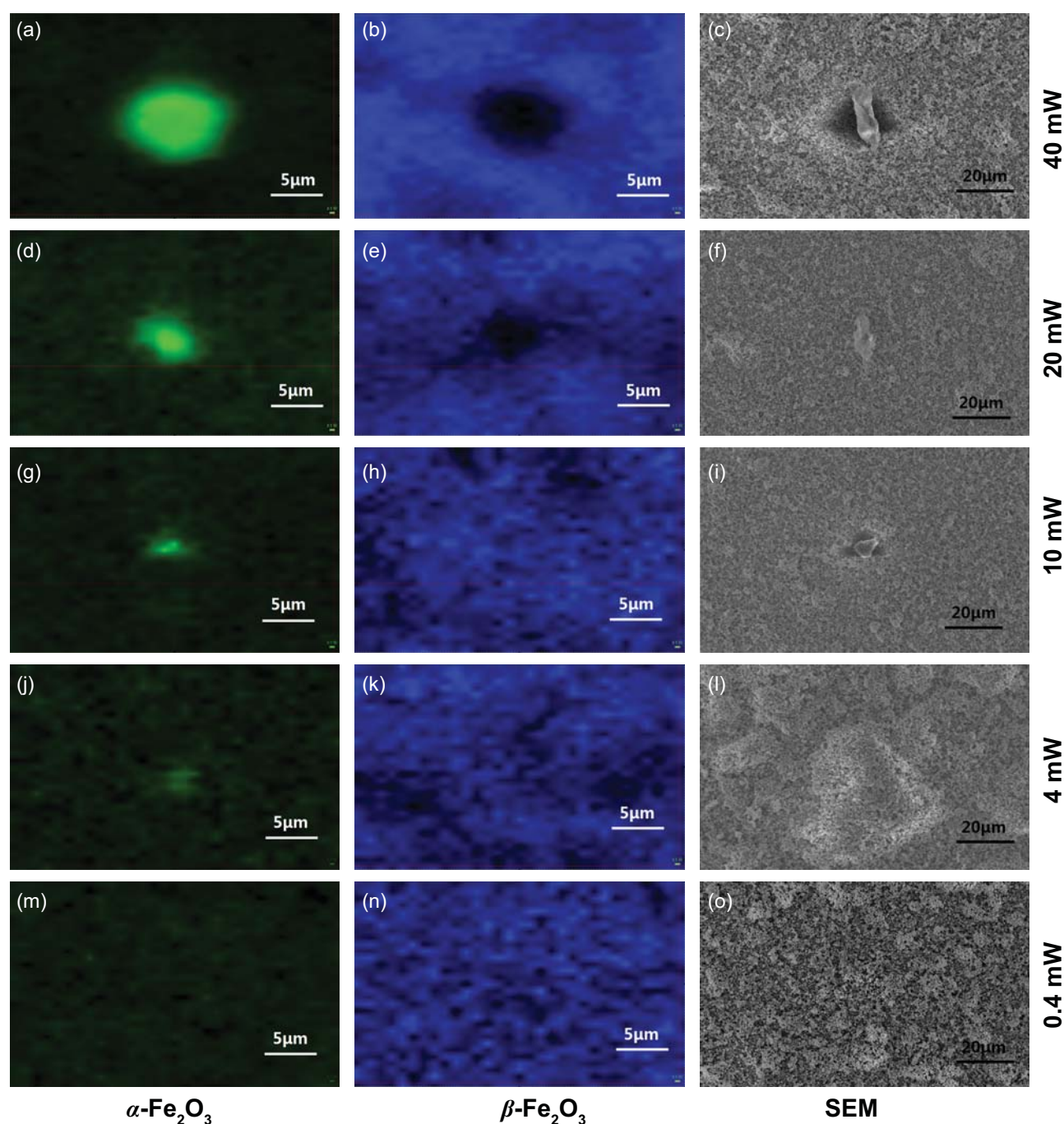


Figure 4. Raman mapping and SEM images of particle-assembled β - Fe_2O_3 films excited by a 0.4 mW laser of 785 nm after the irradiation of 785 nm laser with various power: (a-c) 40 mW, (d-f) 20 mW, (g-i) 10 mW, (j-l) 4 mW and (m-o) 0.4 mW. (a, d, g, j, m) α - Fe_2O_3 ; (b, e, h, k, n) β - Fe_2O_3 .

films were annealed in a muffle furnace at 600°C (or 650°C) for 1 h.

Raman spectra of the samples were characterized with a confocal laser Raman spectrometer (Japan, Horiba, LabRAM Aramis, calibrated with silicon). Except for Fig. 1, all of the Raman spectra data acquisition used a 785 nm laser as the excitation source. Except for Fig. 3, all of the Raman spectra data acquisition used a 0.4 mW power

laser as the excitation source. Raman imaging was obtained using a 785 nm, 0.4 mW laser. All laser-induced phase-change samples were confirmed using a 785 nm laser as the excitation source before laser irradiation to ensure that the samples contained no α - Fe_2O_3 . The phosphor spectrum calculations were calculated in Material Studio with the Local Density Approximate, using the norm-conserving situation.

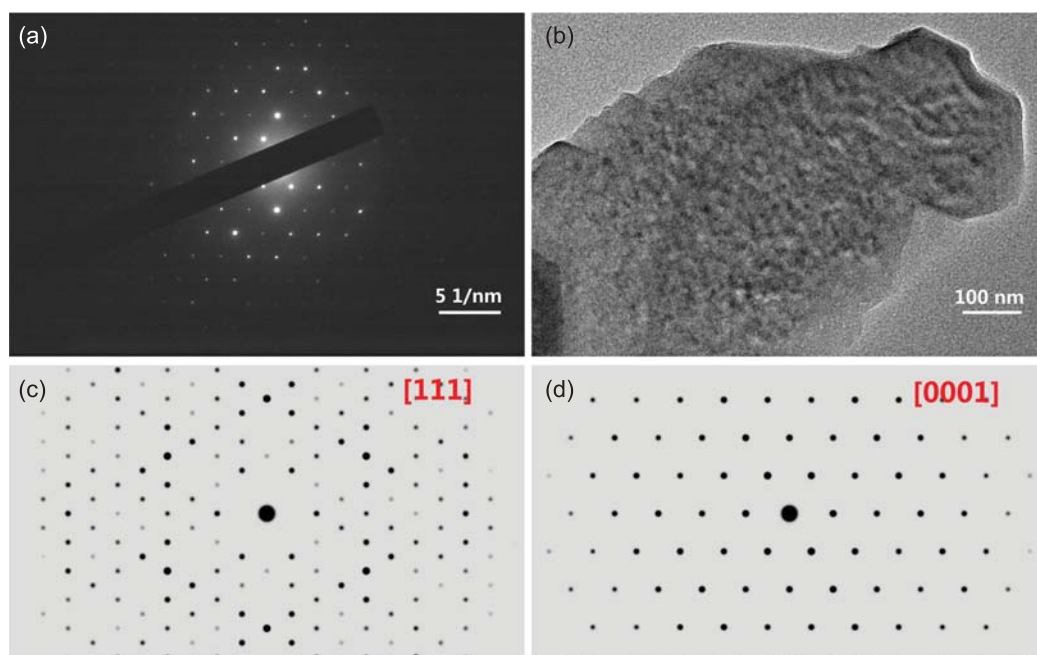


Figure 5. SAED and TEM images of the samples. (a) Measured SAED image of the β - Fe_2O_3 sample. (b) TEM image of the β - Fe_2O_3 sample. (c) Simulated SAED image of β - Fe_2O_3 . (d) Simulated SAED image of α - Fe_2O_3 .

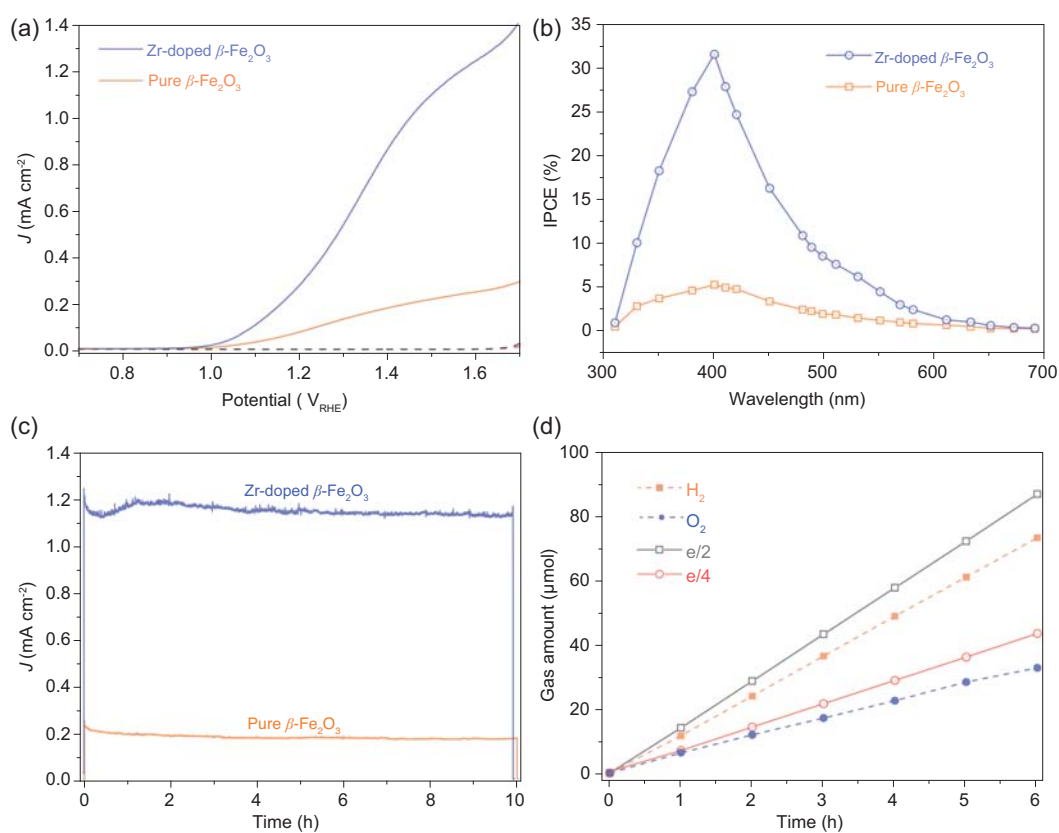


Figure 6. (a) Photocurrent density, (b) IPCE, (c) photochemical stability at 1.6 V_{RHE} and (d) Faradic efficiencies of the particle-assembled β - Fe_2O_3 films with Zr doping under illumination of standard simulated sunlight (100 mW cm^{-2}) in 1 M NaOH electrolyte ($\text{pH} = 13.6$). Reference sample: α - Fe_2O_3 .

Density functional theory calculations on Zr-doped β -Fe₂O₃ were implemented in the VASP (Vienna Ab-initio Simulation Package) with a projected-augmented-wave method in the scheme of generalized-gradient approximation, whereas the strong on-site Coulomb repulsion among the localized Fe 3d electrons was described with the generalized-gradient approximation +U approach ('U' is 'the strength of the on-site Coulomb interaction').

SEM images were obtained on an SEM (Germany, Zeiss, Ultra 55) and SAED images of the samples were obtained on a TEM (Japan, JEOL, Ltd. JEM2100).

PEC water splitting of the β -Fe₂O₃ particle-assembled films was carried out in 1 M NaOH solution (pH = 13.6) under AM 1.5 G standard simulated sunlight (American, Newport, Oriel Sol3A, 100 mW cm⁻²).

SUPPLEMENTARY DATA

Supplementary data are available at NSR online.

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Conflict of interest statement. None declared.

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