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Light absorption modulation of novel Fe₂TiO₅ inverse opals for photoelectrochemical water splitting†

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TiO₂ and Fe₂O₃ are the most promising anode materials for the assembly of photoelectrochemical devices. However, their intrinsic poor light absorption (TiO₂) and poor electrical conductivity (Fe₂O₃) seriously limit their industrial feasibility. Thus, it is of great importance to develop novel Fe–Ti–O systems which can combine the characteristics of high charge mobility, long carrier lifetime and visible light-driven activity. In this paper, novel Fe₂TiO₅ inverse opals with modulated light absorption were prepared using polystyrene (PS) photonic crystals as templates. The maximum overlap between the stop-bands and the absorption edges was found to be beneficial for the multiple scattering of visible light. Due to the enhanced light absorption and superior charge separation, inverse opals fabricated using 250 nm PS spheres exhibited higher photocurrent density than Fe₂O₃, TiO₂ and disordered Fe₂TiO₅ film. The performance of the photoanodes could be further improved by the deposition of FeOOH as a cocatalyst. This work provides a principal method for the development of novel photoanodes with modulated microstructures for efficient photoelectrochemical applications.

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Introduction

With the concern of the global energy crisis and the desire for alternative fuel sources, photoelectrochemical (PEC) water splitting has attracted considerable attention in recent decades. By far, it is still a challenge to develop photoanodes that can fulfil the requirements for stable and efficient devices constructed from earth-abundant materials.¹ As the most industrially feasible metal oxide semiconductor, the low solar light-harvesting capability of TiO₂ limits its further application due to its large band gap (3.2 eV). Therefore, tremendous efforts have been devoted to exploring efficient photoelectrode materials with smaller bandgaps, such as Fe₂O₃, BiVO₄, WO₃ and Ta₃N₅.^{2–5} Among them, hematite has proven to be an optimal candidate due to its favourable band gap. Although the spectral response of Fe₂O₃ shifts to the visible range, its water photooxidation efficiency is still below the theoretical maximum value.⁶ This is largely determined by its intrinsic disadvantages compared to TiO₂, such as its poor electrical conductivity, slow oxygen evolution reaction kinetics and

short hole diffusion length. As a d⁵ transition metal oxide insulator, the charge transfer ability of Fe₂O₃ is orders of magnitude lower than that of TiO₂.⁷

The specific requirement for stable oxides with good conductivity and strong light absorption encourages research into Fe–Ti–O systems. In fact, both Ti doping and Fe doping have been proven to be effective for improving the photoactivities of Fe₂O₃ and TiO₂.^{8,9} Nevertheless, several existing drawbacks limit the potential of the doping strategy, such as the unfavourable role of the recombination centers. Therefore, it is of both scientific and industrial importance to develop a new material strategy for designing novel Fe–Ti–O photoanodes in order to achieve the unique characteristics of high charge mobility, long carrier lifetime and visible light-driven activity.

Fe₂TiO₅, a newly developed semiconductor with a narrow bandgap of 2.1 eV, has recently received much attention.^{10,11} Due to the simultaneous combination of visible light-driven activity and good charge mobility, it should provide a promising path for tackling the low charge transport properties of hematite and the limited absorption of TiO₂.^{12,13} The development of robust Fe₂TiO₅-based materials is looming on the horizon, but most research focuses on heterostructured photoanodes.¹⁴ For example, Liu *et al.* deposited pseudobrookite Fe₂TiO₅ ultrathin layers on TiO₂ nanotube arrays, which can result in high photon-to-current efficiencies of 40–50% under 400–600 nm irradiation and total energy conversion efficiencies of 2.7%.¹⁵ The microstructure design of Fe₂TiO₅ nanostructured photoanodes is

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seriously overlooked, although it is crucial for structural optimization.

A photonic crystal is a periodic structure that can confine and manipulate photons. Because of its strong coherent multiple scattering, it offers a unique way to improve light absorption and enhance PEC performance. By far, various kinds of metal oxide inverse opals with superior photoactivities have been explored.^{16–18} Unfortunately, to the best of our knowledge, there are still no reports focused on Fe_2TiO_5 photonic crystals. The development of Fe_2TiO_5 inverse opals might open up more opportunities in the design of efficient and low-cost photoanodes for PEC applications.

In this paper, highly ordered Fe_2TiO_5 inverse opals were prepared using a polystyrene (PS) photonic crystal as the template. Through photonic crystal modulation, face-centered cubic (fcc) structures with different pore sizes were obtained. Due to the maximum overlap between the stop-bands and the absorption edge of Fe_2TiO_5 , inverse opals fabricated using 250 nm PS spheres exhibited superior photocurrent density. The slow photon effect and multiple scattering of light in the porous structures resulted in a 3-fold enhancement compared to the disordered samples. As a proof of concept, a FeOOH electrocatalyst was then photoelectrodeposited on the surface of the photoanodes to further improve the charge separation ability under visible light illumination. Compared to the disordered Fe_2TiO_5 film, more than one order of magnitude enhanced activity at 1.23 V vs. NHE was achieved. This work not only provides a principal method for tackling the low charge transport property of hematite and the limited absorption of TiO_2 , but also demonstrates a promising design for the development of novel nanoarchitectures for efficient PEC applications.

Results and discussion

Scheme 1 shows the procedure for the fabrication of 3-D Fe_2TiO_5 -based inverse opal nanostructures. Firstly, polymeric PS colloidal crystal films were deposited onto the FTO substrate through a colloidal self-assembly method (Step I). Subsequently, the solution consisting of Fe and Ti precursors was fully infiltrated through the interstitial sites of the PS opal template (Step II). After infiltration

with the mixture solution, the samples were calcined under an air atmosphere to remove the polymer template (Step III). For the efficient charge separation, the surface of the Fe_2TiO_5 inverse opals was further modified through co-catalyst deposition (Step IV).

Fig. 1 shows the XRD pattern of the as-synthesized Fe_2TiO_5 inverse opals. Besides those corresponding to the FTO substrates (Fig. S1, ESI[†]), typical characteristic peaks from Fe_2TiO_5 (JCPDS no. 41-1432) can be observed. The strong diffraction peaks located at $2\theta = 26.7^\circ$, 32.7° and 54.7° confirm the formation of pure pseudobrookite Fe_2TiO_5 with orthorhombic phase structures.¹⁹

To study the effect of pore size on the PEC performance, opal templates composed of PS spheres with diameters of 200, 250 and 350 nm were prepared by a self-assembly method. Fig. 2a and Fig. S2a (ESI[†]) show SEM images of the colloidal crystal templates fabricated from PS spheres of 250 nm. The top-view image clearly demonstrates the face-centered cubic (fcc) arrangement of the monodispersed PS spheres, with the close-packed plane (111) parallel to the underlying substrate. In Fig. S2b (ESI[†]), an enlarged view shows that the PS microspheres are arranged closely, with a high degree of perfection in the colloidal order. The morphology of the inverse opals fabricated from three opal templates can be seen in Fig. 2b–d. When 250 nm PS-sphere arrays were used, ordered hexagonal arrays with spherical pores arranged three dimensionally were easily obtained (Fig. 2b). The average pore size is determined to be 190 nm. Due to thermal effects during template removal, there was 24% shrinkage in comparison to the original PS spheres. The elemental composition of the film can be confirmed by the EDS spectrum in Fig. S3 (ESI[†]). Other than the signal of Sn originating from the FTO substrate, titanium, iron and oxygen elements were detected, confirming the formation of the Fe–Ti–O nanostructures. As shown in Fig. S4 (ESI[†]), the high-resolution TEM image shows the well-defined crystallinity of the nanoparticles with a lattice spacing of 0.48 nm, which can be ascribed to the (200) planes of orthorhombic Fe_2TiO_5 . These results confirm the successful transformation of the PS-sphere arrays into Fe_2TiO_5 inverse opals without changing the highly ordered structures. After similar procedures, Fe_2TiO_5 inverse

Scheme 1 Schematic illustration of the procedure for the design of Fe_2TiO_5 -based inverse opal photoanodes.

Fig. 1 XRD pattern of the Fe_2TiO_5 inverse opals on FTO substrates.

Fig. 2 SEM images of (a) the colloidal crystal template self-assembled from PS spheres with diameters of 250 nm; (b) Fe_2TiO_5 IO-250; (c) Fe_2TiO_5 IO-200; (d) Fe_2TiO_5 IO-350.

opals with different pore sizes can be fabricated through changing the diameter of the PS spheres. For convenience, the Fe_2TiO_5 products synthesized from 200, 250 and 350 nm PS-sphere arrays are denoted as IO-200, IO-250 and IO-350, respectively.

The elemental compositions and chemical states of the Fe_2TiO_5 films were further investigated by XPS. As shown in Fig. 3a, the existence of Ti 2p, Fe 2p, Sn 3d and O 1s can be confirmed by the XPS survey spectrum of the sample. Besides the Sn 3d peak derived from the FTO substrates, no other impurity was detected. In Fig. 3b, the typical Fe $2p_{3/2}$ and Fe $2p_{1/2}$ peaks can be found at 711.05 eV and 724.97 eV, which is consistent with those of Fe_2TiO_5 .²⁰ The Ti 2p spectrum in Fig. 3c can be deconvoluted into two peaks, which are assigned to Ti $2p_{1/2}$ and Ti $2p_{3/2}$. The XPS signals at 464.30 eV and 458.50 eV indicate the existence of the Ti^{4+} oxidation state in the photoanodes. In Fig. 3d, the binding energy of the O 1s peak is mainly located at 529.9 eV, attributed to the lattice oxygen bound to Ti and Fe.

Fig. 3 (a) The survey XPS spectrum of Fe_2TiO_5 IO-250; high resolution XPS scans of the Fe 2p (b), Ti 2p (c) and O 1s peaks (d) of Fe_2TiO_5 IO-250.

Fig. 4 (a) Transmission spectra of the PS opals with different sizes; (b) light absorption spectra of the Fe_2TiO_5 inverse opals and disordered photoanodes.

Essentially, the formation of high-quality inverse opal structures can provide photon trapping regions that readily improve the interactions between the constituent semiconductors and light. Light in a photonic crystal usually undergoes strong coherent multiple scattering and travels with a very low group velocity near the photonic stop-band edges.²¹ Thus, tuning the optical structure of the Fe_2TiO_5 inverse opals should be an efficient strategy to enhance light absorption. In this study, the inverse opals are finely tuned by varying the sizes of the photonic crystals, with their stop-bands estimated to be encompassed by, overlapped with and beyond the absorption edge of Fe_2TiO_5 . The transmission spectra of the opal templates with different sizes are shown in Fig. 4a. When the diameter of the PS spheres increases from 200 to 350 nm, sharp transmission dips corresponding to the stop-bands are always observed, indicating the highly ordered opal lattice in these samples.²² The corresponding stop-band peaks are located at 430, 540 and 740 nm, respectively. Fig. 4b presents the light absorption spectra of the different types of Fe_2TiO_5 film. All of the samples absorb light at a wavelength shorter than 600 nm, corresponding to the bandgap of 2.06 eV. This value is in agreement with the reported value for Fe_2TiO_5 , indicating its considerable ability for visible light absorption.²³ Furthermore, differences in the absorption intensity of the Fe_2TiO_5 films can be clearly observed. Due to the multiple scattering of light in the porous structures, the Fe_2TiO_5 inverse opals exhibit much stronger light absorption than the disordered sample.

To investigate the contribution of the highly ordered structure to the photoactivity, the PEC performance of different Fe_2TiO_5 inverse opals was evaluated. Fig. 5a shows the linear sweep voltammetry (LSV) curves measured under UV-vis light irradiation. Obviously, all of the inverse opal samples exhibit superior photocurrents to the

Fig. 5 (a) Linear scan voltammetry (LSV) of the different Fe_2TiO_5 -based photoanodes under chopped UV-vis illumination; (b) linear scan voltammetry (LSV) of the different Fe_2TiO_5 -based photoanodes under visible light illumination.

disordered sample fabricated without the assistance of PS templates. Due to the maximum overlap of the stop-band of the inverse opal structure with the absorption edge of Fe_2TiO_5 , Fe_2TiO_5 IO-250 presented a significantly enhanced photoresponse. However, the stop-band of PS-350 is beyond the light absorption region of Fe_2TiO_5 , and the weak interaction between light and the semiconductor matrix results in a relatively lower photocurrent. The photocurrent intensity of Fe_2TiO_5 IO-250 is more than 3 times higher than that of the disordered sample, and even 2 times higher than that of Fe_2TiO_5 IO-350. As a result, the applied bias photon-to-current efficiency (ABPE) of the optimized Fe_2TiO_5 inverse opal photoanode was calculated to be 0.02% at 1.05 V vs. RHE. To demonstrate the contribution of the highly ordered opal structure to the photoactivity, a disordered porous Fe_2TiO_5 film was also fabricated, using disordered PS nanoparticles as the template (Fig. S5, ESI†). As shown in Fig. S6 (ESI†), the superior photoresponse of Fe_2TiO_5 IO-250 to that of the disordered porous film proves the beneficial effect of inverse opal structures. The PEC performance of the photoanodes under visible light ($\lambda > 420$ nm) irradiation was further evaluated. Fe_2TiO_5 IO-250 presents the highest photoactivity among all samples (Fig. 5b), indicating the importance of structural modulation during the fabrication of inverse opals.

To illustrate the superiority of the Fe–Ti–O system over separate semiconductors, Fe_2O_3 and TiO_2 inverse opal structures were fabricated through changing the precursor components. As expected, TiO_2 exhibits the highest photocurrent density, with a much lower onset potential under full-arc irradiation (Fig. S7a, ESI†). Meanwhile, the Fe_2TiO_5 inverse opals show significantly enhanced photoactivity over Fe_2O_3 , indicating the improved charge mobility through Ti incorporation. However, no obvious photoresponse is observed for the TiO_2 photoanodes after exposure to visible light irradiation ($\lambda > 420$ nm). The superior photoactivity of the Fe_2TiO_5 inverse opals clearly demonstrates their great potential for visible light-driven PEC applications (Fig. S7b, ESI†). As the photochemical stability of the materials is an important technical aspect of photoanodes, photocurrent–time (i – t) measurements of Fe_2TiO_5 IO-250 at a potential of 0.3 V vs. Ag/AgCl were carried out. As shown in Fig. 6a, no apparent loss of photocurrent was observed over the entire testing duration.

To develop more efficient Fe_2TiO_5 -based photoanodes, the feasibility of cocatalyst loading onto the surface was investigated.

Fig. 6 (a) Transient photocurrent curve of the Fe_2TiO_5 IO-250 photoanodes performed with chopped UV-vis light at 0.3 V vs. Ag/AgCl; (b) LSV curves of the Fe_2TiO_5 -based photoanodes with or without cocatalyst loading under visible light irradiation.

Fig. 7 (a) Electrochemical impedance spectra (EIS) of the Fe_2TiO_5 -based photoanodes with or without cocatalyst loading. (b) Stability of the $\text{Fe}_2\text{TiO}_5/\text{FeOOH}$ photoanodes at 0.3 V vs. Ag/AgCl under visible light irradiation.

In a typical photoelectrodeposition experiment, FeOOH electrocatalysts can be photodeposited onto Fe_2TiO_5 IO-250 at 0.2 V versus Ag/AgCl in 0.1 M FeSO_4 solution with stirring. Based on the LSV curves in Fig. 6b, the performance of the Fe_2TiO_5 photoanodes under visible light irradiation is obviously improved in the presence of FeOOH cocatalysts.²⁴ At a potential of 0.8 V vs. Ag/AgCl, the photocurrent intensity of the $\text{Fe}_2\text{TiO}_5/\text{FeOOH}$ photoanodes is about 2 times higher than that of pristine Fe_2TiO_5 . Based on the Nyquist spectra and the suggested equivalent model shown in the inset of Fig. 7a, the high-frequency intercept on the real axis represents the ohmic series resistance (R_s), corresponding to the bulk resistance of the electrolyte and electrodes. The semicircle at high frequency can be ascribed to the resistance (R_{ct}) and chemical capacitance (CPE) of the solid state interface layer. Compared to blank Fe_2TiO_5 , the much smaller internal impedances (*i.e.* R_s and R_{ct}) of the $\text{Fe}_2\text{TiO}_5/\text{FeOOH}$ photoanodes indicate a decreased solid state interface layer resistance and charge transfer resistance.^{25,26} A 24 h stability test of $\text{Fe}_2\text{TiO}_5/\text{FeOOH}$ was further performed at 0.3 V vs. Ag/AgCl under full-arc irradiation. As can be seen from Fig. 7b, the cocatalyst-loaded photoanode retains acceptable stability in the experimental time duration. Thus, cocatalyst loading is an effective strategy to improve the photoelectrochemical performance of Fe_2TiO_5 , while more efficient photoanodes can be rationally developed through cocatalyst selection.²⁷

Conclusion

In summary, we demonstrated that the multiple scattering of light in the porous structure of inverse opals could contribute to the photoactivity of Fe_2TiO_5 photoanodes. Due to the matching between the low light wavelength and the absorption edge of the semiconductors, Fe_2TiO_5 IO-250 exhibited significantly increased photocurrent density under either full arc or visible light irradiation. The Fe_2TiO_5 inverse opals also showed superior photoactivity compared to Fe_2O_3 and TiO_2 , indicating the great potential of Fe–Ti–O systems for high-efficiency PEC applications. Further investigation indicated that the charge recombination occurring at the surface could be suppressed through the photodeposition of FeOOH as an efficient electrocatalyst, resulting in more than one order of magnitude enhanced activity at 1.23 V vs. NHE over the disordered Fe_2TiO_5 film. This work provides a principal method to develop visible light-driven photonic crystals, and a feasible route to obtain more efficient materials for solar fuel production.

Experimental

Fabrication of the PS templates

Suspensions of commercial monodisperse PS spheres ($d = 200, 250$ and 350 nm, dispersed in water) with desired concentrations were used as precursors. For the self-assembly of the opal templates, cleaned FTO substrates were fixed in a glass vial filled with a suspension of PS spheres. The vial was kept in a temperature-controlled oven and heated to $60\text{ }^{\circ}\text{C}$ to initiate self-assembly of the opals. The hexagonally packed PS film was then heated at $90\text{ }^{\circ}\text{C}$ for 1 h to improve the adhesion and structural stability of the opal structures.

Fabrication of the Fe_2TiO_5 inverse opals

The Fe_2TiO_5 inverse opals were fabricated through the infiltration method. In a typical experiment, tetrabutyl titanate and ferrous nitrate dissolved in ethanol solutions were prepared and used as Ti and Fe precursors, respectively. The precursor solutions were quickly mixed with stirring. A certain amount of cetyltrimethylammonium bromide was added to achieve a homogeneous suspension. Then, substrates with the PS opal templates were immersed vertically into the suspension solutions for 10 min to make the solution infiltrate into the PS opals. This procedure was repeated several times to achieve sufficient filling. Finally, the Fe_2TiO_5 inverse opals were obtained by heating the samples at $500\text{ }^{\circ}\text{C}$ for 2 hours and then $750\text{ }^{\circ}\text{C}$ for 10 minutes. For comparison, Fe_2O_3 and TiO_2 inverse opal structures were also prepared as controls by changing the precursors.

Characterization

X-ray diffraction (XRD) data were collected on a Bruker D8 focus Advance diffractometer ($\text{CuK}\alpha$ radiation). The morphology of the products was characterized by field emission scanning electron microscopy (JSM-7600F, JEOL) and high-resolution transmission electron microscopy (HR-TEM, JEOL-2010). X-ray photoelectron spectroscopy (XPS) was carried out using XPS spectrometers (ESCA Lab 220I-XL). The diffuse reflectance spectra and absorption spectra were characterized by UV-vis-NIR spectrophotometry (Cary 5000).

Photoelectrochemical measurements

PEC measurements were performed using a three-electrode configuration with a 300 W Xe lamp as a light source. The intensity of the light was determined to be about 250 mW cm^{-2} . FTO glass loaded with the samples was used as the working electrode. A platinum plate and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively. 1 M NaOH aqueous solution was used as the electrolyte. The photocurrent was measured with linear sweep voltammetry (Gamry electrochemical workstation, Interface 1000). Electrical impedance spectroscopy (EIS) was measured in the dark at 0 V vs. Ag/AgCl, under an AC perturbation signal of 5 mV over the frequency range of 1 MHz to 100 mHz.

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