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Enhancing Visible-Light Photoelectrochemical Water Splitting through Transition-Metal Doped TiO$_2$ Nanorod Arrays

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Abstract

Extending the photoresponse from the ultraviolet (UV) to the visible light region while maintaining a high photocatalytic activity has been an important challenge for TiO$_2$. We demonstrate the use of transition-metal doping treatment as a facile and effective strategy to substantially improve the performance of TiO$_2$ nanorods in the visible light region for photoelectrochemical (PEC) water splitting. The effect of Fe, Mn and Co as dopants on the PEC performance of the TiO$_2$ nanorods was investigated, wherein the Fe doping is the most effective route to enhance the photoactivity of TiO$_2$. The photocurrent density of Fe-TiO$_2$ sample increases significantly with bias voltage and reaches 2.92 mA/cm$^2$ at 1.25 V vs. RHE, which are five times higher than that of the undoped TiO$_2$. Even under visible light illumination (>420 nm), the photocurrent density of Fe-TiO$_2$ is as high as 0.96 mA/cm$^2$ at 1.25 V vs. RHE. Incident-photon-to-current-conversion (IPCE) efficiency (up to ~ 18%) measurements reveal that the Fe-TiO$_2$ nanorod sample significantly
improve the photoresponse not only in the UV region but also in the visible light region. Fe doping not only enhances the visible light absorption of TiO$_2$ nanorods by creating impurity states near the conduction band, but also obviously increases carrier density of TiO$_2$, leading to effective carrier separation and transportation and relatively long electron lifetime. Due to their relatively high photocatalytic activity, the Fe-TiO$_2$ nanorods can serve as a promising candidate for various areas, such as solar water splitting, dye-sensitized solar cells, and photocatalysis.

1. Introduction

Photocatalytic hydrogen generation by water splitting has attracted extensive research interest in the past decade because of the increasing concern on energy and environmental issues.$^{1-21}$ The photocatalytic water-splitting systems can be classified into two main categories: suspended photocatalysts and photoelectrochemical (PEC) cells. Since Fujishima and Honda reported on the photoelectrolysis of water into hydrogen and oxygen on a TiO$_2$ photoelectrode,$^{22}$ semiconductor-based PEC water splitting by solar energy has been regarded as one of the most important ways for hydrogen generation.$^{2,9}$ Generally, realizing the PEC water splitting requires the semiconductor to meet the following property criteria: stability, appropriate band gap, efficient visible light absorption,
and suitable band-edge positions to straddle the water redox potentials. Since most of narrow gap semiconductors suffer from photo-corrosion, photocatalytic materials still are limited to a few wide band gap oxide semiconductors such as TiO$_2$$^{10,14,17,18}$, SrTiO$_3$$^{10}$, and WO$_3$$^{10}$. Among various wide band gap semiconductors, TiO$_2$ is one of the most promising materials due to its low cost, good photocatalytic activity, and chemical stability.$^{10}$ However, the efficiency of solar PEC water splitting based on TiO$_2$ is very low due to its wide band gap, resulting in response only under UV light. Numerous approaches have been developed to enhance the visible light response of TiO$_2$, such as metal or non-metal doping, quantum dot or dye sensitization, composite semiconductors and so on.$^{23}$ Hereinto, doping serves as an effective route in the modifications of TiO$_2$ because it can keep the integrity of the crystal structure and make favorable changes in the electronic structure. Up to now a great deal of theoretical and experimental efforts have been devoted to 3d transition-metal (TM) doped TiO$_2$.$^{23,24}$ Theoretical researches predict that the formation of new states closed to the valence band and conduction band induced by 3d TM dopants results in significant energy gap narrowing together with enhanced optical absorption.$^{24,25}$ However, many experimental reports indicate that the effect of red shift by 3d TM dopants is not obvious, and these dopants in TiO$_2$ will act as recombination centers, which result in the limited enhancement of photocatalytic activity.
or even lower than pure TiO$_2$. Until recently, to improve the visible light absorption while maintaining a high photocatalytic activity has been challenging.

Additionally, the photocatalytic performance of TiO$_2$ can be improved by rationally controlling its morphology and orientation etc. For example, vertically aligned TiO$_2$ nanorod arrays as photoanode not only provide large surface area and efficient light trapping, but also have short diffusion distance for photogenerated minority carriers, which is expected to facilitate the charge separation and reduce the loss due to electron-hole recombination. Recently, considerable efforts have been devoted to growing various oriented TiO$_2$ nanostructures and modifying their properties, such as oriented single-crystalline rutile TiO$_2$ nanorods or nanowires, hydrogen-treated TiO$_2$ nanowires, Sn doped TiO$_2$ nanowires, branched TiO$_2$ nanorods, and W doped TiO$_2$ nanowires etc. However, most of these efforts only improve the PEC performance of TiO$_2$ nanowires in the UV region, and the improvement in the visible light region is very limited. For example, the IPCE values of H:TiO$_2$ and H, N-TiO$_2$ nanowires are below 0.7% from 440 nm to 650 nm and 4% from 420 nm to 550 nm, respectively. To our knowledge, there have been no reports on the 3d-TM doped TiO$_2$ nanorod arrays with both improved PEC performance and strong visible light response.

Here, we demonstrate that a significant improvement of the PEC water
splitting activity under visible light irradiation based on TiO₂ nanorod arrays can be achieved by doping 3d TM using a facile solution method. The PEC performance of the TM doped TiO₂ nanorods can further be adjusted by the concentration of TM ion in the solution. The effect of Fe, Mn and Co as dopants on the PEC performance of TiO₂ nanorods was investigated in which Fe doping is the most effective route to enhance the photoactivity of TiO₂. The photocurrent density of Fe-TiO₂ sample increases significantly with bias voltage and reaches 2.92 mA/cm² at 1.25 V vs. RHE, which is five times higher than that of the undoped TiO₂. Even under visible light illumination (>420 nm), the photocurrent density of Fe-TiO₂ is as high as 0.96 mA/cm² at 1.25 V vs. RHE. Incident-photon-to-current-conversion efficiency (IPCE) (up to ~ 18%) indicates that Fe doped TiO₂ nanorod arrays show substantially enhanced photoresponse not only in the UV region but also in the visible light region in comparison to the undoped TiO₂ nanorod sample, and exhibit long-term stability. The transition-metal doping hydrothermal treatment we developed is a facile and effective strategy to substantially improve the performance of TiO₂ nanorods for photoelectrochemical (PEC) water splitting. The relatively high PEC performance of the Fe-TiO₂ nanorods opens new opportunities in various areas, such as solar water splitting, dye-sensitized solar cells, and photocatalysis.
2. Experimental section

TiO$_2$ nanorod arrays on a fluorine-doped tin oxide (FTO) glass substrate were grown by a hydrothermal method previously reported by Liu et al.$^{39}$ For doping TM in TiO$_2$, 1g of urea and 10-100 mM TM nitrate were dissolved in 15 mL aqueous solution. The solution and the FTO substrate with TiO$_2$ nanorod arrays were transferred to a 20mL Teflon-lined stainless steel autoclave. The autoclave was sealed and put into an electric oven at 150 °C for 2 h. When the autoclave was cooled down to room temperature, these samples were cleaned with deionized water and were dried in air. The colors of the samples were obviously different than that of TiO$_2$ nanorod arrays without dopants, and depended on the doping metal ion. Finally the samples were annealed in a furnace at 450 °C for 30 min.

The morphologies and structures of the samples were characterized by X-ray diffraction (XRD, Philips X’pert Pro diffractometer), field-emission scanning electron microscope (FESEM, Hitachi S-4800), energy dispersive X-Ray spectrometry (EDS), X-ray photoelectron spectroscopy (XPS, PerkinElmer Physics PHI 5300), and field-emission transmission electron microscope (HRTEM, Tecnai F20). For TEM analysis, samples were prepared by scratching off nanorod flakes on a Ni
grid.

The photoelectrochemical measurement was performed in 1 M KOH solution using a three-electrode configuration. TiO$_2$ nanorod arrays with or without 3d TM dopants were used as the working electrodes (photoanodes), saturated Ag/AgCl as the reference electrode, and a platinum foil as a counter electrode. The photocurrent measurements were carried out by applying an external bias to the cell using an electrochemical station (Zahner IM6e, Germany) with a scan rate of 10 mV/s and using a 150 W Xe solar simulator (Newport 94021A) with AM 1.5G filter as light source. Incident-photon-to-current-conversion efficiency (IPCE) spectra were measured on a QE/IPCE Measurement Kit (Crowntech QTest Station 1000AD) with a tungsten halogen lamp (CT-TH-150), a calibrated silicon diode and a monochromator (Crowntech QEM24-S 1/4 m).

3. Results and Discussion

The TM-doped TiO$_2$ nanorod arrays on FTO were prepared using a hydrothermal method. After the doping treatment, the color of the samples will change from gray-white (for pure TiO$_2$) to light red (for Fe doped TiO$_2$ denoted by Fe-TiO$_2$), brown-red (for Mn doped TiO$_2$ denoted by Mn-TiO$_2$) and yellow (for Co doped TiO$_2$ denoted by Co-TiO$_2$), respectively, as shown in Figure 1. SEM images reveal that vertically or
slantingly aligned nanorod arrays were uniformly grown in high density on the FTO substrate (Figure 1). These nanorods are uniform with a rectangular cross section. The nanorod diameters are in the range of 50-300 nm and the typical nanorod lengths are around 5 μm. There are no obvious changes in morphology by comparing with SEM images of the samples before and after doping. From the insets in Figure 1, it can be seen that the color is uniform, implying uniform distribution of dopants in the TiO$_2$ nanorods. The EDS results of the TM-TiO$_2$ nanorods are shown in Table S1 (see supporting information).

![Figure 1. SEM images of (a) TiO$_2$, (b) Fe-TiO$_2$, (c) Mn-TiO$_2$ and (d) Co-TiO$_2$ nanorod arrays on FTO substrates. Insets are the corresponding digital pictures, respectively. All scale bars are 1μm.](image)

To investigate the effect of doping on the crystal structure, XRD spectra were collected from the TiO$_2$ nanorods and TM doped TiO$_2$ nanorods grown at various metal salt concentrations (50mM for Fe- and Mn-TiO$_2$, 10mM for Co-TiO$_2$), as shown in Figure 2. If no special explanation, all the following samples were prepared under these conditions. All the XRD
patterns have two diffraction peaks at 2θ angles of 36.5° and 63.2°, which can be indexed as the (101) and (002) reflection of tetragonal rutile TiO$_2$ (JCPDS No. 88-1175). The (002) diffraction peak dominating over the (101) peak indicates that the nanorods grew preferentially along the <001> direction. Other peaks can be contributed to the FTO substrate. Obviously, there is no impurity peak after doping. The decrease of the (002) peak intensity depends on the doping metal element in which the most decrease is Co, the second for Mn and the least for Fe. These decreases may be due to the increase of defect density in TiO$_2$ structures, which has also been observed in the hydrogen-treated TiO$_2$ nanowire arrays\textsuperscript{33}.

![XRD spectra of TiO$_2$, Co-TiO$_2$, Fe-TiO$_2$, and Mn-TiO$_2$ nanorod arrays on FTO substrates.](image)

Figure 2. XRD spectra of TiO$_2$ (gray curve), Co-TiO$_2$ (green-yellow curve), Fe-TiO$_2$ (wine curve) and Mn-TiO$_2$ (orange curve) nanorod arrays on FTO substrates.

Structural characterizations of the TM-doped TiO$_2$ nanorods were performed by TEM and HRTEM. Figure 3a shows a TEM image of the Fe-TiO$_2$ nanorod. Basically, the diameters of the nanorods under TEM
observation are consistent with the SEM results. The HRTEM image shown in Figure 3b reveals the single-crystalline structure of the nanorod, and gives a lattice fringe of about 0.32 nm, corresponding to the $d_{110}$ space of the bulk rutile TiO$_2$. The dopant distribution in the nanorod was further analyzed by EDS. Variations of the O Lα, Ti Lα, Ti Kα, Fe Lα and Fe Kα signals along the nanorod are given in Figure 3c. Clearly, the distribution of Fe element along the nanorod axial and radial direction is uniform. The analysis of EDS mapping was also applied to Mn- and Co-TiO$_2$ nanorods, which confirm that the distribution of Mn and Co in nanorods is also uniform (see Figure S1 and S2 in Supporting Information).

Figure 3. (a) TEM, (b) HRTEM and (c) EDS mapping images of single Fe-TiO$_2$ nanorod.
XPS was employed to explore the chemical states of surface elements of the 3d-TM doped TiO$_2$ nanorod arrays. Two peaks at 464.3 and 458.5 eV were observed from the fully scanned TiO$_2$ spectrum (Figure 4a), which can be assigned to Ti 2p$_{1/2}$ and Ti 2p$_{3/2}$ spin-orbital components in TiO$_2$, respectively.$^{40,41}$ After the doping treatments, the high-resolution Mn, Fe and Co 2p XPS spectra of the samples are shown in Figures 4b, 4c and 4d, respectively. Figure 4b shows the Mn 2p core-level XPS spectrum with two peaks at 653.5 (Mn 2p$_{1/2}$) and 641.6 eV (Mn 2p$_{3/2}$). The binding energies of Mn 2p are consistent with that of Mn$_2$O$_3$. The Fe 2p XPS spectrum is identical with Fe 2p$_{1/2}$ and 2p$_{3/2}$ peaks centered at binding energies of 724.4 and 710.6 eV, which are consistent with the typical values for Fe$_2$O$_3$. In the Co 2p spectrum (Figure 4d), the doublet peaks at 796.6 and 780.2 eV could be indexed to Co 2p$_{1/2}$ and Co 2p$_{3/2}$, respectively. The peaks could be assigned to the bivalent cobalt corresponding to the standard CoO.$^{44,45}$ The above results clearly indicate that Mn, Fe and Co have been successfully incorporated into the TiO$_2$ nanorods.
Figure 4. (a) XPS spectra of TiO$_2$ nanorod and high-resolution (b) Mn, (c) Fe and (d) Co 2p core-level XPS spectra of the TiO$_2$ nanorod doped with Mn, Fe and Co, respectively.

To evaluate the effect of dopants on the PEC properties of TiO$_2$, we measured the photocurrents of colored Fe-, Mn- and Co-TiO$_2$ nanorod photoanodes and compared them with those of the undoped TiO$_2$ nanorods. All TiO$_2$ nanorod samples were fabricated into photoanodes with a well-defined area of 0.2 cm$^2$. The PEC measurements were conducted in 1 M KOH electrolyte (pH = 13.5), under simulated sunlight illumination at 100 mW/cm$^2$ from a 150 W xenon lamp coupled with an AM 1.5G filter. The linear sweeps of TiO$_2$ (gray) and TiO$_2$ nanorods doped with Fe (wine), Mn (orange), and Co (green-yellow), in a potential range of 0 to 1.75 V vs RHE, are shown in Figure 5a. It is seen that the
dark current densities are essentially negligible (3-7 μA/cm²) even at high potentials of 1.75 V vs RHE. The photocurrent densities increase significantly with bias voltage and reach 0.76 mA/cm² for Co-TiO₂, 1.25 mA/cm² for Mn-TiO₂ and 2.92 mA/cm² for Fe-TiO₂ at 1.25 V vs RHE, which are two and five times higher than the photocurrent density of 0.56 mA/cm² for the undoped TiO₂, respectively, except a slight increase for Co-TiO₂. It is obvious that Fe doping by a simple hydrothermal method greatly improves the PEC properties of TiO₂ and yields a maximum photocurrent density of 2.92 mA/cm² at 1.25 V vs RHE. This value is slightly better than the best reported values of 2.8 mA/cm² for TiO₂ photoanodes⁴⁶, 2.5 mA/cm² at 1.23V vs RHE for hydrogen-treated TiO₂ nanowire arrays⁴³ and 2.0 mA/cm² at 1.65V vs RHE for Ti-Fe-O nanotube arrays.⁴⁷ The TiO₂, Mn-TiO₂ and Fe-TiO₂ samples exhibit an obvious increase in photocurrent density at an onset potential of 0.25 V vs RHE and reach their saturated photocurrents at a low potential of 0.6 V vs RHE, except that the photocurrent density of Co-TiO₂ sample increases near-linearly with the applied potential and doesn't reach saturation at the scanning voltage range.

To test the photoresponse of TM-doped TiO₂ samples in the visible light region, photocurrents were measured with the use of a 420 nm long-pass filter, as shown in Figure 5b. The onset potentials for the four samples positively shift to 0.36 V vs RHE due to the decrease of the
photogenerated carrier. The photocurrent densities of TM-doped TiO$_2$ samples are higher than that of TiO$_2$ (gray). Under visible light illumination, the photocurrent density of Fe-TiO$_2$ is as high as 0.96 mA/cm$^2$ at 1.25 V vs RHE. For Mn- and Co-TiO$_2$, the photocurrent densities are 0.34 and 0.14 mA/cm$^2$ at 1.25 V vs RHE, respectively. These results indicate that in this case Fe doping is an effective method to promote the PEC performance of TiO$_2$ in the visible light region. However, the enhancement induced by Co doping is relatively limited, which probably results from the increase of defect density supported by XRD data. For enhancing photocatalytic activity, effective carrier transfer to the catalyst/solution interface is another important factor, in addition to broad and strong optical absorption. Only if the electron and hole excited by photon are transferred to the surface, photocatalytic reactions could occur. In case of doping, metal ions could enhance optical absorption, but they likely behave as recombination centers, which would hinder electron/hole transferring to the surface. Therefore, there exists an optimum concentration of doped metal ion, below which the improvement of optical absorption is negligible, and above which the photocatalytic activity decreases due to the increase in recombination. Figure 5c shows the photocurrent densities of Fe-, Mn- and Co-TiO$_2$ nanorod arrays at 1.25 V vs Ag/AgCl as a function of metal ion concentration. The Fe- and Mn-TiO$_2$ nanorod arrays prepared using
50mM Fe(NO₃)₃ and Mn(NO₃)₂ solutions, respectively, yield a maximum photocurrent density. The photocurrent density of Co-TiO₂ nanorod arrays decreases as the Co ion concentration increases. By optimizing the metal ion concentration, the condition for maximum photocurrent density was obtained.

![Graphs showing photocurrent density vs applied potential](image)

Figure 5. (a,b) Photocurrent density vs applied potential curves of four nanorod photoanodes under AM 1.5G solar illumination (a) and visible light illumination >420nm (b): the TiO₂ nanorods (gray curve), the Fe-TiO₂ nanorods (wine curve), the Mn-TiO₂ nanorods (orange curve), and the Co-TiO₂ nanorods (green-yellow curve). The dark currents of the four samples are plotted as a black dotted line for comparison. (c) Photocurrent density vs metal ion concentration at 1.25 V vs RHE. (d) Calculated photoconversion efficiencies for the four samples, as a function of applied potential vs RHE.

To quantitatively determine the conversion efficiency of photon energy to chemical energy from TM doped TiO₂ samples, the photoconversion efficiency is calculated based on the equation, \( \eta = \frac{I (1.23 - V)}{J_{\text{light}}} \).
where \( V \) is the applied voltage versus reversible hydrogen electrode (RHE), \( I \) is the photocurrent density at the measured potential, and \( J_{\text{light}} \) is the irradiance intensity of 100 mW/cm\(^2\) (AM 1.5G). As shown in Figure 5d, the Fe-TiO\(_2\) exhibits the highest efficiency of 1.35% at a low bias of 0.6 V vs RHE, the Mn-TiO\(_2\) achieves 0.58% at a voltage of 0.6 V vs RHE, and the Co-TiO\(_2\) shows 0.24% at 0.7 V vs RHE. Compared to the photoconversion efficiency of 0.26% at 0.6 V vs RHE measured from the undoped TiO\(_2\), the Fe doping can significantly increase the maximum photocurrent at a similar saturation potential and greatly improve the photoresponse under visible light, thus leading to a much improved photoconversion efficiency. Although the photocurrent density of Co-TiO\(_2\) is higher than that of pure TiO\(_2\) especially under visible light illumination, the photoconversion efficiency is slightly lower than that of pure TiO\(_2\) due to the high saturation potential.

Considering that the TiO\(_2\) nanorods doped with different metal ions exhibit different colors, to further investigate their wavelength-dependent photoelectrochemical properties is important for understanding the interplay between the photocatalytic activity and the light absorption of these samples. IPCE is powerful to quantitatively reveal their photocatalytic activity as a function of wavelength of incident light. We have performed IPCE measurements of the TM-TiO\(_2\) nanorod samples at 0.6 V vs RHE, as shown in Figure 6a. IPCE can be expressed by the
following equation,

\[ \text{IPCE} = \frac{1240I}{\lambda J_{\text{light}}} \]

where I is the measured photocurrent density at a specific wavelength, \( \lambda \) is the wavelength of incident light, and \( J_{\text{light}} \) is the measured irradiance at a specific wavelength. The IPCE values of the Fe-TiO\(_2\) nanorod sample increase slowly from almost zero at 560 nm to 3.0% at 500 nm, and then rapidly increase to 15.6% at 430 nm, and finally maintain relatively high efficiencies of 16-18.3% at 300-430 nm. Clearly, the Fe-TiO\(_2\) nanorod sample significantly improves the photoresponse not only in UV region but also in the visible light region compared to the undoped TiO\(_2\) nanorods. Although the Mn-TiO\(_2\) nanorods also exhibit obviously enhanced photoactivity in the visible light region, the IPCE values decrease gradually from 7% at 400 nm to 0.6% at 300 nm. For the Co-TiO\(_2\) nanorod sample, the photoresponse is also extended to the visible light region, but the IPCE values are lower than those of TiO\(_2\). In the present circumstances, Fe doping is the most effective route to enhance the photoactivity of TiO\(_2\).

The IPCE values are relatively low compared to the overall photocurrents. To understand why there is such a discrepancy between the photocurrents and the integration of the IPCE results, the effect of light intensity on the photocurrents of Fe-TiO\(_2\) were investigated at an external bias 0.6 V vs. RHE (see in supporting information). Figure S3 shows the
variation of the photocurrents with the incident optical power. In the relatively low power range, the photocurrent is low partly due to the more important contribution of trap recombination. Trap filling can enhance the lifetime of the photogenerated charge carriers and can improve the quantum yield at higher light intensities.\textsuperscript{47-49} With increased intensity, the traps can be saturated, leading to enhanced photocurrent. Therefore, we think that the relatively low IPCE values should be attributed to trap filling effect due to weaker light intensity at IPCE measurements.

The optical absorption of TM-doped TiO\textsubscript{2} samples was measured to further analyze the contribution for their PEC performance, as shown in Figure 6b. All absorption spectra of the TM-doped TiO\textsubscript{2} show an obviously red shift, which can be attributed to the charge transfer transitions between the metal ion d electrons and the TiO\textsubscript{2} conduction or valence band. The band gaps of the TM-doped TiO\textsubscript{2} and undoped TiO\textsubscript{2} estimated by their absorption spectra (see in supporting information Fig. S5) are 2.15 eV (for Fe doped TiO\textsubscript{2}), 2.17 eV (for Mn doped TiO\textsubscript{2}), 2.34 eV (for Co doped TiO\textsubscript{2}), and 3.01 eV (for undoped TiO\textsubscript{2}), respectively. Although all TM-doped TiO\textsubscript{2} samples exhibit a broader and stronger absorption than the undoped TiO\textsubscript{2}, only the Fe-TiO\textsubscript{2} sample achieves the significant enhancement of the PEC performance. Relatively limited improvement for Mn-TiO\textsubscript{2} and negligible enhancement for Co-TiO\textsubscript{2} probably results from the inefficient separation and transportation of
photoexcited charge carriers.

Figure 6. (a) IPCE spectra of the TiO$_2$ (gray), Fe-TiO$_2$ (wine), Mn-TiO$_2$ (orange) and Co-TiO$_2$ (green-yellow) nanorod photoelectrodes measured at an applied bias of 0.6 V (vs RHE) in 1M KOH solution. (b) Optical absorption spectra of the TiO$_2$ (gray), Fe-TiO$_2$ (wine), Mn-TiO$_2$ (orange) and Co-TiO$_2$ (green-yellow) nanorod arrays on the FTO substrates.

To further understand the different PEC performance of the TiO$_2$ nanorods doped with different TM ions, electrochemical impedance spectroscopy measurements were conducted at a frequency of 1 kHz in the dark. The Mott Schottky plots of the undoped and TM doped TiO$_2$ nanorods are displayed in Figure 7. All four TiO$_2$ nanorod samples exhibit
a positive slope in the corresponding Mott Schottky plots, as expected for n-type semiconductor. According to the Mott Schottky equation,

\[ \frac{1}{c^2} = \left( E - E_{FB} - kT/e \right)/N_d e \varepsilon_0 \varepsilon \]

where \( c \) is the space charge capacitance in the semiconductor, \( E \) is the applied potential, \( E_{FB} \) is the flat band potential, \( T \) is the temperature, and \( k \) is the Boltzmann constant, \( e \) is the elemental charge, \( N_d \) is the charge carrier density, and \( \varepsilon_0 \) and \( \varepsilon \) are the vacuum permittivity and the relative permittivity of the TiO\(_2\) (\( \varepsilon = 170 \)),\(^{50}\) respectively. The charge carrier densities (\( N_d \)) of the TiO\(_2\) nanorod samples were calculated from the Mott Schottky plots using the following equation:

\[ N_d = 2 \left( \frac{dE}{d \left( \frac{1}{c^2} \right)} \right) / \left( e \varepsilon_0 \varepsilon \right) \]

The calculated carrier densities of the Fe-TiO\(_2\), Mn-TiO\(_2\), Co-TiO\(_2\) and TiO\(_2\) nanorods were \( 2.32 \times 10^{19} \), \( 1.81 \times 10^{18} \), \( 5.31 \times 10^{17} \) and \( 9.12 \times 10^{18} \) cm\(^{-3}\), respectively. Obviously, Fe doping leads to a significant enhancement of carrier density in TiO\(_2\). As the donor concentration increases so does the electron concentration in the conduction band, with the Fermi level energy moving closer to the conduction band edge, which facilitates the charge separation at the TiO\(_2\)/electrolyte interface by increasing the degree of band bending at the TiO\(_2\) surface.\(^{33}\) The effective charge separation and transportation and enhancement of visible light absorption are inferred to be the major reasons for the IPEC improvement.
of the Fe-TiO₂ nanorods. In addition, both the Mn-TiO₂ and the Co-TiO₂ samples show a decrease of charge carrier density compared to that of the undoped TiO₂ sample. Mn and Co doping probably induces more defects in TiO₂ structures than Fe doping, which acts as recombination centers and results in ineffective charge separation and transportation. It may be responsible for the relatively limited PEC performance improvement for Mn-TiO₂ and negligible enhancement for Co-TiO₂ compared to that of the undoped TiO₂.

Figure 7. (a) Mott Schottky plots collected at a frequency of 1 kHz in the dark for the Fe-TiO₂, Mn-TiO₂, Co-TiO₂ and TiO₂ nanorods. Inset: Mott Schottky plots of the Fe-TiO₂, Mn-TiO₂ and TiO₂
nanorods, measured under the same conditions. (b) Photocurrent densities vs time of the Fe-TiO$_2$, Mn-TiO$_2$, Co-TiO$_2$ and TiO$_2$ nanorods measured at 0.5 V vs RHE under 100 mW/cm$^2$ solar illumination.

To better understand the enhanced PEC performance, the inherent electronic properties of the TM doped TiO$_2$ nanorods were characterized by measuring their open-circuit photovoltage decay (OCPD). OCPD was measured to assess photoelectron lifetime and thus to evaluate the recombination rate of the photoelectrons and holes. OCPD measurement consists of turning off illumination at a steady state and monitoring the subsequent decay of photovoltage, $V_{oc}$, with time (see Fig. S6 in Supporting Information). The $V_{oc}$ decay rate is directly related to the photoelectron lifetime. The calculated photoelectron lifetime is shown in Fig. S7 as a function of $V_{oc}$ (see Supporting Information). Clearly, the photoelectron lifetime increases with decreasing $V_{oc}$. The Fe doped TiO$_2$ nanorods showed relatively long electron lifetime, contributing to its high PEC performances, in good agreement with the above results. The TiO$_2$ photoanode stability was tested at 0.5 V vs RHE under continuous solar illumination for 8000 seconds (Figure 7b). There is no observable degradation, indicating excellent chemical and structural stability of the TM doped TiO$_2$ nanorods for long-term PEC conversion. We further performed the O$_2$ evolution experiment of Fe-TiO$_2$ sample over a period of 600 min to evaluate its O$_2$ generation ability and stability (see in supporting information). The Fe-TiO$_2$ photoanode under visible light
illumination exhibited a stable $O_2$ generation ability, as shown in Figure S8. The calculated faradaic efficiency is around 86%.

4. Conclusion

We report the first demonstration of transition-metal doping treatment as a facile and effective strategy to substantially improve the performance of TiO$_2$ nanorods for photoelectrochemical (PEC) water splitting. The effect of Fe, Mn and Co as dopants on the PEC performance of the TiO$_2$ nanorods were investigated in which the Fe doping is the most effective route to enhance the photoactivity of TiO$_2$. The photocurrent density of Fe-TiO$_2$ sample increases significantly with bias voltage and reaches 2.92 mA/cm$^2$ at 1.25 V vs RHE, which are five times higher than that of the undoped TiO$_2$. Even under visible light illumination (>420 nm), the photocurrent density of Fe-TiO$_2$ is as high as 0.96 mA/cm$^2$ at 1.25 V vs RHE. Incident-photon-to-current-conversion efficiency (up to ~ 18%) measurements reveal that the Fe-TiO$_2$ nanorod sample significantly improves the photoresponse not only in the UV region but also in the visible light region. Fe dopants not only enhance visible light absorption of TiO$_2$ nanorods by creating impurity energy levels near the conduction band, but also obviously increase carrier density of TiO$_2$, leading to effective carrier separation and transportation and relatively long electron lifetime. Due to their relatively high photocatalytic activity, Fe-TiO$_2$
nanorods can serve as a promising candidate for various areas, such as solar water splitting, dye-sensitized solar cells, and photocatalysis.

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