### Enhancing Visible-Light Photoelectrochemical Water Splitting

## through Transition-Metal Doped TiO<sub>2</sub> Nanorod Arrays

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### **Supporting information**

#### Materials:

Titanium tetrachloride (GR), Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (98.5%), Mn(NO<sub>3</sub>)<sub>2</sub> (50 wt. % in H<sub>2</sub>O) and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (AR) were purchased from Aladdin Reagent Inc. in Shanghai, and hydrochloric acid (36%-38% by weight), KOH (AR) and urea (AR) were purchased from Beijing chemical company without any further purification. Deionized water was purchased from Weisi chemical company.

## Experimental section

TiO<sub>2</sub> nanorod arrays were grown as described by Liu et al.<sup>39</sup> In a typical growth process, 5-10 mL of deionized water was mixed with 5-10 mL of concentrated hydrochloric acid (36%-38% by weight) in a 20mL Teflonlined stainless steel autoclave. 0.3 mL of titanium tetrachloride (TiCl<sub>4</sub>) was added into the mixture, and then the mixture was stirred at ambient conditions for 5 min. After that, a piece of FTO substrates (F:SnO<sub>2</sub>, 14

 $\Omega/\Box$ ) were placed at an angle against the wall of the Teflon-liner with the conducting side facing down. The hydrothermal synthesis was conducted at 150 °C for 12 h in an electric oven. After the autoclave was cooled to room temperature, the FTO substrate was taken out, washed with deionized water and dried it in air.

#### **1.** The EDS results of the TM-TiO<sub>2</sub> nanorods.

Fe Mn Co 10m 50m 100m 100m 10m 100m 10m 50m 50m М М Μ М М Μ М Μ М 1# 0.99 0.79 1.15 1.52 0.29 0.48 0.08 0.11 0.14 2# 1.09 1.23 1.61 0.31 0.51 0.82 0.05 0.09 0.17 3# 1.28 0.13 1.07 1.34 0.43 0.62 0.55 0.09 0.13 4# 1.11 1.12 0.59 1.43 0.38 0.66 0.07 0.12 0.11 5# 1.03 1.17 1.42 0.51 0.81 0.49 0.06 0.07 0.13 6# 1.07 1.26 1.52 0.37 0.88 0.52 0.08 0.09 0.14 Mean 1.06 1.20 1.47 0.38 0.66 0.63 0.07 0.11 0.13 SD(±) 0.06 0.10 0.03 0.04 0.08 0.16 0.14 0.01 0.03

Table S1. The EDS results of the TM-TiO<sub>2</sub> nanorods (atomic ratio %).



Figure S1. TEM and EDS mapping images of single Mn-TiO<sub>2</sub> nanorod.



Figure S2. TEM and EDS mapping images of single Co-TiO<sub>2</sub> nanorod.

#### 2. The effect of light intensity on the photocurrents of $Fe-TiO_2$ sample.

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<sub>2</sub> were investigated at an external bias 0.6 V vs. RHE under illumination using a 150 W Xe solar simulator (Newport 94021A) with AM 1.5G filter for a range of 10~100 mW/cm<sup>2</sup> and a Xe solar simulator PLS-SXE300 (output optical power up to 50 W) with AM 1.5G filter for a range of 200~600 mW/cm<sup>2</sup> as light sources, respectively. The light intensity was double checked by a standard Si solar cell (SRC-1000-TC-QZ, SN 10510-0309) and a power meter (LPE-1A). All of other test conditions were fixed as described in the main text.

Figure S3 shows the variation of the photocurrents with the incident optical power. Three domains clearly appear in this curve: at low power densities ( $10\sim30$  mW/cm<sup>2</sup>), the photocurrent increases slowly with the

optical power. At middle power densities (40~90 mW/cm<sup>2</sup>), the photocurrent increases relatively rapidly with the 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.<sup>1-3</sup> With increased intensity, the traps can be saturated, leading to enhanced photocurrent. At high power densities (100~600 mW/cm<sup>2</sup>), the photocurrent gradually increased and became saturated with the optical power. We plotted the responsivity vs. optical power as shown in Figure S4. Here the responsivity can be expressed as  $R=I_{Photocurrent}/P$ , where  $I_{Photocurrent}$  is the photocurrent and P is light intensity. Obviously, the responsivity gradually increased and reached the maximum at 90 mW/cm<sup>2</sup>, and then gradually decreased with the optical power. In the high power range, the responsivity decreases with increasing power P as P-1/2. This arises from the photocurrent varying with the optical power as  $P^{1/2}$  which demonstrates the existence of intrinsic recombination (electron-hole) at high incident powers. Based on the above results, the discrepancy between the photocurrents and the integration of the IPCE results should be attribute to trap filling effect under illumination with low optical power. In fact, this phenomenon generally exits in various semiconductor materials ( $TiO_2^{4-6}$ ,  $GaN^7$  etc.) and devices, such as solar cells 4-5, photodetectors 7 and photoandoes.8-9



Figure S3. The variation of the photocurrents with the incident optical power.



Figure S4. Responsivity vs optical power density for a Fe-TiO<sub>2</sub> photoanode at 0.6 V vs. RHE.

## 3. The estimated band gaps of the TM-doped $TiO_2$ .



Figure S5. The estimated band gaps of the TM-doped  $TiO_2$  and undoped  $TiO_2$ .

### 4. The photoelectron lifetimes of four samples.

To better understand the enhanced PEC performance, the inherent electronic properties of the TM doped TiO<sub>2</sub> nanorods were characterized by measuring their open-circuit photovoltage decay (OCPD). OCPD was measured to assess photoelectron lifetime in this study 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 (Fig. S6). The  $V_{oc}$ decay rate is directly related to the photoelectron lifetime by the following equation:<sup>10</sup>

$$\tau = \frac{k_B T}{e} \left( \frac{dV_{oc}}{dt} \right)^{-1}$$

where  $\tau$  is the potential dependent photoelectron lifetime,  $k_B$  is Boltzmann's constant, T is the temperature, e is the charge of a single electron, and  $V_{oc}$  is the open-circuit voltage at time t. The calculated photoelectron lifetime is shown in Fig. S4 as a function of  $V_{oc}$ . Clearly, the photoelectron lifetime increases with decreasing  $V_{oc}$ . The Fe doped TiO<sub>2</sub> nanorods showed relatively long electron lifetime, contributing to it's high PEC performances, in good agreement with the previous reported results.



Figure S6. The decay of photovoltage with time of four samples.



Figure S7. The photoelectron lifetimes of four samples.

# 5. The $O_2$ generation of the Fe-Ti $O_2$ photoanode.

Obviously,  $O_2$  bubble produced from the Fe-TiO<sub>2</sub> photoanode under visible light illumination with the current increased. To evaluate the faradaic efficiency, the Fe-TiO<sub>2</sub> electrode with a area of 1 cm<sup>2</sup> was illuminated through a quartz window used a 300 W xenon arc lamp with a 420 nm long-pass filter as the light source. The photoelectrochemical cell was evacuated after pouring the electrolyte solution (1 mol/L KOH) into the reactor (Perfectlight Labsolar III-AG). O<sub>2</sub> production was analyzed by a gas chromatographer (GC-7900). The measured current and the evolved O<sub>2</sub> gas from the Fe-TiO<sub>2</sub> photoelectrode at a constant applied potential of 1.25 V vs RHE for a period of 600 min are shown in Figure S8. The gas production rate is directly proportional to the photocurrent density. The corresponding charge,  $Q(O_2)$ , was obtained via the equation  $Q(O_2)=4Fn$  ( $O_2$ ), where F is the Faraday constant, and n ( $O_2$ ) is the number of moles of  $O_2$ . The calculated faradaic efficiency is around 86%.



Figure S8. The measured current and the evolved  $O_2$  gas from the Fe-TiO<sub>2</sub> photoanode at a constant applied potential of 1.25 V vs RHE for a period of 600 min.

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