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## Supporting Information

## Hierarchical TiO<sub>2</sub> nanonetwork-porous Ti 3D hybrid

## photocatalysts for continuous-flow photoelectrodegradation of

## organic pollutants

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Scheme 1. The transformation process from original porous Ti to  $TiO_2$ /porous Ti, the quartz box equipped with  $TiO_2$ /porous Ti, and the real reactor.

Scheme 1 shows the transformation process from original metallic porous Ti to  $TiO_2$ /porous Ti, the model of quartz box for continuous flow photocatalysis, and the real reactor. Firstly, from a visual observation, it can be seen that the porous Ti is silver in colour, the as-obtained  $TiO_2$ /porous Ti turns to gray after a series of treatment. The real reactor is equipped with  $TiO_2$ /porous Ti and Pt wire fixed in the porosity of the PMMA upper cover.



**Fig. S1.** Raman spectra with excitation line at 633 nm: porous Ti, TiO<sub>2</sub>/porous Ti-60, TiO<sub>2</sub>/porous Ti-110, respectively.

We had tried different hydrothermal temperature, including 60 °C and 110 °C. The other steps were the same. In order to further distinguish between the surface of the TiO<sub>2</sub>/porous Ti-60 and that of TiO<sub>2</sub>/porous Ti-110 (Fig. S1). First, it shows that the original porous Ti presents almost no Raman peaks, compared to TiO<sub>2</sub>/porous Ti-60 and TiO<sub>2</sub>/porous Ti-110. It is obvious that the mixed phases of anatase and rutile coexist in the surface of the TiO<sub>2</sub>/porous Ti-110, and Raman peaks from anatase show much stronger intensity than that from rutile, similar with P25 TiO<sub>2</sub>. However, the Raman peaks belong to rutile in the TiO<sub>2</sub>/porous Ti-60 is unconspicuous. Owing to better crystallinity of TiO<sub>2</sub>/porous Ti-110 and superior photocatalytic efficiency on formation of surface phase [1-4], we chose hydrothermal temperature at 110 °C to prepare TiO<sub>2</sub>/porous Ti.



Fig. S2.SEM images of cross section of TiO<sub>2</sub>/porous Ti with different magnifications.

The cross section of TiO<sub>2</sub>/porous Ti with different magnifications is shown in Fig. S2. It is noted that TiO<sub>2</sub>/porous Ti is a hierarchical 3D porous nanostructure with two levels, and the skeleton of porous Ti has no change (Fig. S2(a)). The self-assembly TiO<sub>2</sub> nanowire networks are uniform with length about 2-3 $\mu$ m (Fig. S2(b)), providing complete overcoat layers and 2-3  $\mu$ m of thickness.



Fig. S3. TEM and HRTEM images of TiO<sub>2</sub>/porous Ti with different magnification.

Fig. S3(a) and the inset present that typical as-prepared  $TiO_2$  nanowires are constituted particles and  $TiO_2$  nanorods self-assembly, the diameter of the nanorod is around 10-20 nm, which is consistent with the result from SEM. From the HRTEM image of  $TiO_2$  nanorod (Fig. S3(b)), it can be seen that the spacing of 0.351 nm and 0.205 nm are corresponding (101) plane of anatase, (210) plane of rutile, respectively. This suggests the surface-phase junction between the anatase and the rutile, supporting a structural model derived from Raman spectroscopy. It plays a key role on the degradation activity of the  $TiO_2$ /porous Ti.



**Fig. S4**. Degradation degree of Rh B (20 mg·L<sup>-1</sup>, a) and MB (20 mg·L<sup>-1</sup>, b) using TiO<sub>2</sub>/porous Ti under PEC conditions. The illustrations are the variations of Rh B and MB during degradation processunder UV irradiation with the bias at different time intervals. ( $I_0$ =110 mW cm<sup>-2</sup>)

To further study the degradation activity of the TiO<sub>2</sub>/porous Ti, the similar investigation was carried out. Fig. S4 present the degradation extents of Rh B (20 mg·L<sup>-1</sup>) and MB (20 mg·L<sup>-1</sup>) employing TiO<sub>2</sub>/porous Ti under photocatalysis and PEC conditions in acidic solutions. Different from MO, Rh B and MB are both cationic type dyes. The light intensity of the UV-LED lamp used in the experiment was 110 mW cm<sup>-2</sup>. Firstly, it can be observed that the degradation efficiencies were enhanced under PEC condition compared that under UV-LED irradiation only, but the enhancement degree of degradation of both organic dyes were different. In Fig. S4(a), Rh B was degraded 40%, 85% under 0.4 V&LED and 0.6 V&LED conditions within 60 min, respectively. While in Fig. S4(b) the corresponding percentages of degradation of MB were about 98% and 96% under similar conditions, separately. That is to say the photoelectrocatalytic degradation efficiencies were superior to photocatalytic degradation using TiO<sub>2</sub>/porous Ti as photocatalyst, which illustrates its high performance when used as photoelectrocatlytic electrode material. Moreover, at various bias potentials the synergetic effects for both organic dyes were disparate,

maybe the degradation pathway of MO<sub>5</sub> Rh B and MB was different from each other[5], and it needs to be studied further.



**Fig. S5**. The Raman spectra with an excitation line at 633 nm: the prepared  $TiO_2$ /porous Ti before and after reaction, respectively.



Fig. S6. SEM images of TiO<sub>2</sub>/ porous Ti (a,b) after reaction with different magnifications.

The corresponding crystal structure and morphology of the TiO<sub>2</sub>/porous Ti were characterized by Raman spectra and SEM images. The Raman spectra are shown in Fig. S5. Compared with the TiO<sub>2</sub>/porous Ti before and after reaction, it is obvious that the Raman peaks are consistent. The morphologies and microstructures of the catalyst before and after reaction were observed via SEM images (Fig. S6). After reaction, the nanostructures on the surface of channel of the porous Ti still maintained their nest-

network morphology, corresponding to the Raman results. So it is proved that the stability of the  $TiO_2$ /porous Ti is very good.

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