

## Supporting Information

Visible-light photoelectrocatalysis/H<sub>2</sub>O<sub>2</sub> synergistic degradation of organic pollutants by magnetic Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@mesoporous TiO<sub>2</sub> catalyst-loaded photoelectrode

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## Preparation of FST and TiO<sub>2</sub>

Preparation of FST: (1) Fe<sub>3</sub>O<sub>4</sub> nanoparticles were prepared by a co-precipitation method. Briefly, 25 mL 1.00 mol·L<sup>-1</sup> FeCl<sub>3</sub> and 0.50 mol·L<sup>-1</sup> FeSO<sub>4</sub> solutions were evenly mixed in a beaker. Under stirring, 50 mL of 1.00 mol/L NaOH solution was added dropwise, then about 10 mL of NH<sub>3</sub>·H<sub>2</sub>O was added until the solution completely turned black and the pH was 10.0. Finally, the mixed solution was stirred at 30 °C for 2 h. The black solids obtained by magnetic separation were washed thrice using absolute ethanol and ultrapure water, and were dried at 80 °C to obtain Fe<sub>3</sub>O<sub>4</sub> nanoparticles. (2) Magnetic Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> was prepared. 0.5 g of Fe<sub>3</sub>O<sub>4</sub> nanoparticles were dispersed ultrasonically in 100 mL absolute ethanol. Then 100 mL ethanol, 50 mL ultrapure water and 2.5 mL NH<sub>3</sub>·H<sub>2</sub>O were added successively, and the pH value was adjusted to 9.0. After stirring the suspension for 0.5 h at 80 °C, 0.5 g of TEOS was slowly added dropwise, and then the reaction solution was stirred and refluxed for 2 h at 80°C. The reacted solution was centrifuged to obtain a solid product, which was washed thrice using absolute ethanol and ultrapure water, and dried after magnetic separation to obtain magnetic Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> cores. (3) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@mesoporous TiO<sub>2</sub> crystals were synthesized using a hydrothermal method with PPG 1000 as the template reagent. Under vigorous stirring, 4 g titanium butoxide was added dropwise to 50 mL 10% (v/v) acetic acid solution, followed by 0.4 g magnetic Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> cores and the mixture stirred in a sealed state for 4 h to form a solution (A). Under intense mixing, the PPG 1000 was dissolved in 45 mL ethanol to obtain solution (B) (containing 10% (v/v) PPG). Solution (B) was added

dropwise to solution (A), after which the mixture was sealed and stirred at 25 °C for 24 h, and subjected to a hydrothermal reaction at 120 °C in a Teflon reactor for 48 h. The obtained colloid after centrifugation of the reaction product was dried at 80 °C for 24 h, and was calcined in a muffle furnace at 400 °C for 2 h to remove the template agent and to obtain FST ( $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{mesoporous TiO}_2$ ).

Preparation of  $\text{TiO}_2$ : As mentioned at the above step (3) of synthesizing FST, magnetic  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  core was not added when preparing the solution (A), all other operations were identical, and finally  $\text{TiO}_2$  catalyst was obtained.

### **Analysis of mesoporous structure**

Fig. S1 showed the isotherms of  $\text{N}_2$  adsorption-desorption of FST. FST exhibited adsorption-desorption isotherms characteristic of type IV, indicating that it had a representative mesoporous structure. The specific surface area and pore volume of FST were  $117.54 \text{ m}^2\cdot\text{g}^{-1}$  and  $0.3485 \text{ cm}^3\cdot\text{g}^{-1}$ , respectively. Based on the Barrett-Joyner-Halenda (BJH) method, the pore size distribution (Fig. S1 insert) was centered at 6.5 nm for the adsorption branch. FST microspheres maintained a large specific surface area and a high pore volume, which were beneficial for adsorbing more pollutant molecules. These have been reported in the literature that the small radial size and large specific surface area of the catalyst promote rapid diffusion of photogenerated  $\text{h}^+-\text{e}^-$  to the catalyst surfaces prior to recombination, thereby improving the separation efficiency of charge carriers<sup>1</sup>.

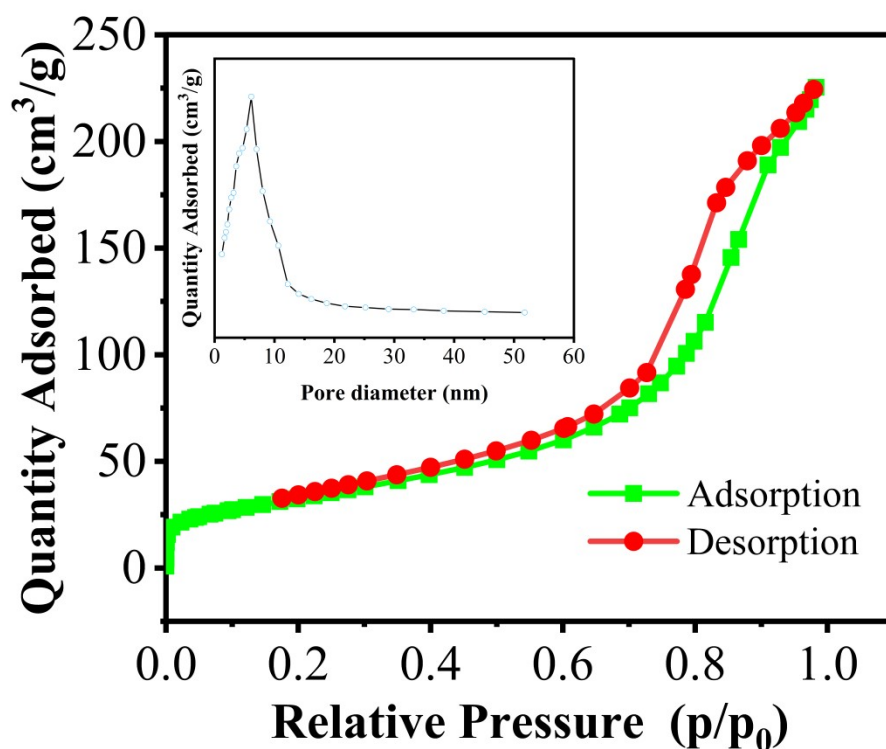


Fig S1 N<sub>2</sub> adsorption-desorption isotherms, Inset: pore size distribution of FST microspheres

### Magnetic response

As shown in Fig. S2, FST microspheres exhibited the typical ferromagnetic hysteresis loop. Magnetic saturation ( $M_s$ ) of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, and FST were 44.24, 19.02, and 9.39 emu·g<sup>-1</sup>, respectively. With the encapsulation of SiO<sub>2</sub> and TiO<sub>2</sub> in the outer layer of Fe<sub>3</sub>O<sub>4</sub>, the  $M_s$  of these composites decreased gradually. But the magnetization of the FST was strong enough that the applied magnetic field could effectively separate FST from the suspension (Fig. S2 insert). Through oscillation and ultrasonic vibration, FST could be uniformly dispersed again. The FST photocatalysts could be fixed on the ITO electrode surface by magnets, and FST-loaded ITO working electrodes would be reused. When FST catalysts were fixed, the addition of other adhesives was not necessary. This method will not affect the effective working

area of the FST photocatalysts, and overcome the limitations of high cost, complicated operation and easy peeling of the materials by other fixing methods.

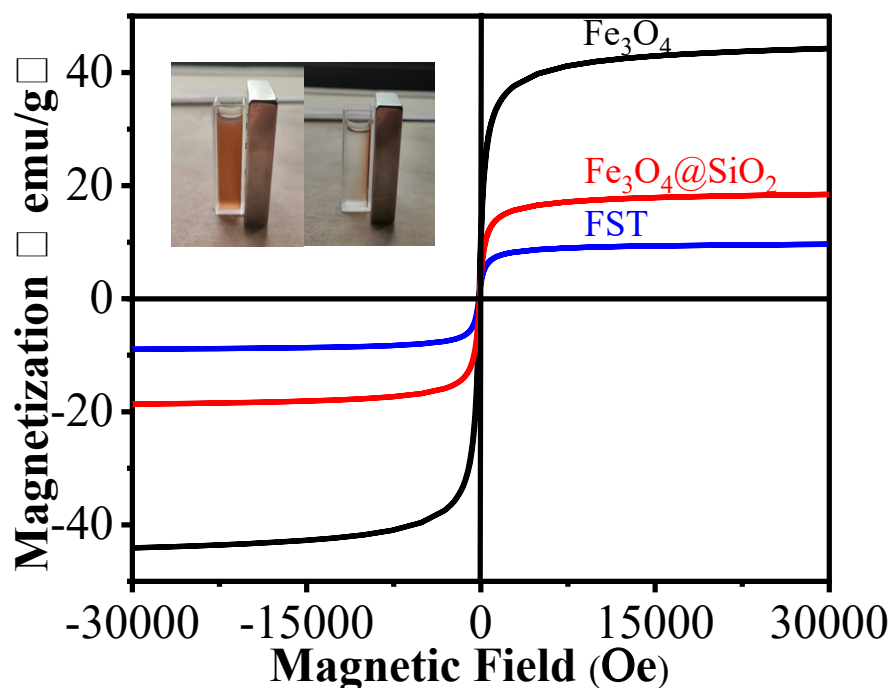


Fig. S2 Magnetic hysteresis loop of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, and FST, Inset: Magnetic separation photo

### XPS analysis

The FST catalysts were characterized using XPS to identify surface elements and valence states (Fig. S3). Fig. (a) displayed the high-resolution full spectrum of FST. The prepared FST was composed of four elements: Fe, Si, Ti and O. The C peak was attributed to the use of C as the binding energy reference calibration during the test process. As seen in O 1s spectra (Fig. (b)), the binding energy of O 1s could be fitted into two distinctive peaks, 530.01 eV for O<sup>2-</sup>, 532.69 eV for the surface hydroxyl groups (OH)<sup>-</sup>, respectively. The Fe 2p spectra (Fig. (c)) revealed characteristic peaks at 710.43 eV and 724.61 eV for Fe 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub>. As previously reported<sup>3</sup>, these

two characteristic peaks indicated that the surface of the FST composites contained  $\text{Fe}_3\text{O}_4$ . Fig. (d) displayed a peak at 102.15 eV for Si 2p while a peak at 532.69 eV for O 1s shown in Fig. (b), which could be ascribed to  $\text{SiO}_2$ . Double peaks of Ti at 456.68 eV and 464.33 eV in Fig. (e) corresponded to  $\text{Ti } 2p_{1/2}$  and  $\text{Ti } 2p_{3/2}$  in anatase  $\text{TiO}_2$ . The distance between the two peaks was 5.7 eV, indicating that its existence form was  $\text{Ti}^{4+}$ .

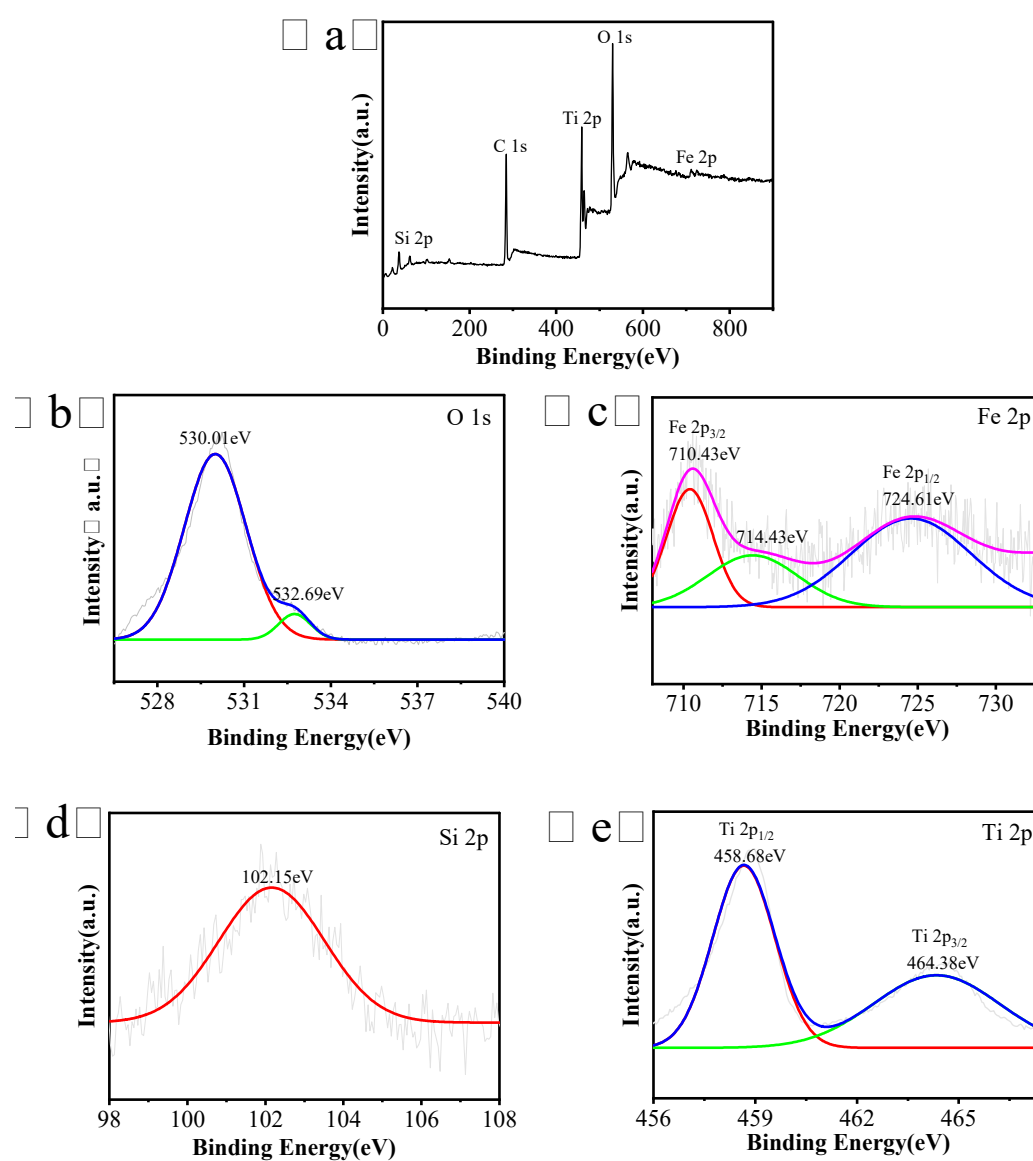


Fig. S3 XPS spectra: (a) survey, (b) O 1s, (c) Fe 2p, (d) Si 2p, (e) Ti 2p for the FST photocatalysts

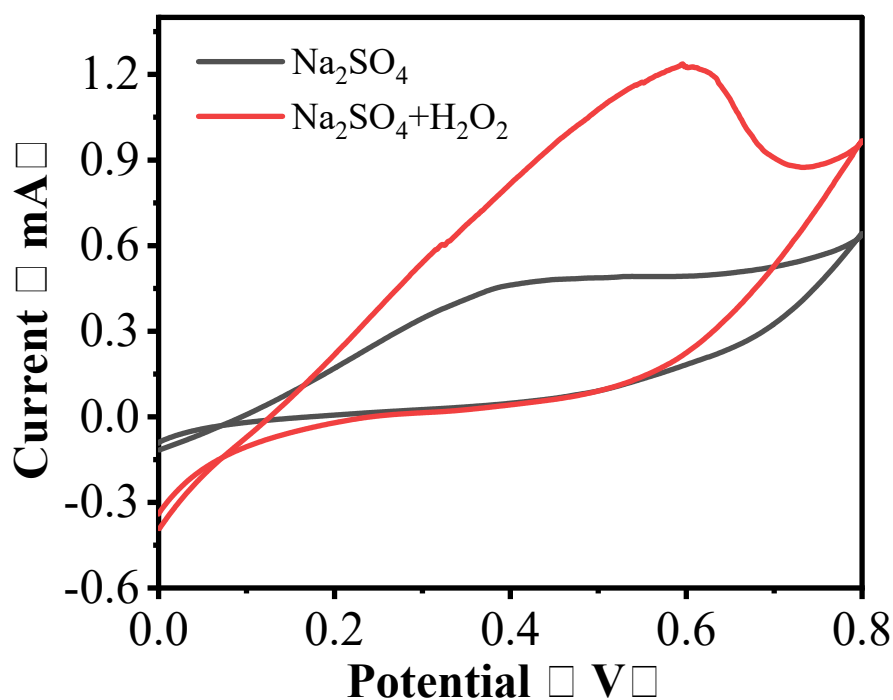


Fig. S4 Cyclic voltammety curve ( $1.00 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1} \text{ H}_2\text{O}_2$  and  $0.500 \text{ mol} \cdot \text{L}^{-1} \text{ Na}_2\text{SO}_4$  solution, scan rate  $0.05 \text{ V} \cdot \text{s}^{-1}$ )

#### References:

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