## **Electronic supplementary information**

## **Experimental Section**

**Preparation of hematite microcubes and submicrocubes.** For the synthesis of hematite microcubes, 1 mmol FeCl<sub>3</sub>·6H<sub>2</sub>O was dissolved in a mixed solvent consisting of 16 mL distilled water and 4 mL ethanol. Then, the homogenous solution was transferred to a 25 mL Teflon-lined autoclave, which was kept in an oven at 140 °C for 24 h, and allowed to cool to room temperature naturally. Afterwards, the precipitate was collected by centrifugation and washed more than three times with distilled water and ethanol, respectively, and then dried overnight in an oven at 60 °C. The synthesis of hematite submicrocubes was carried out under identical conditions except that the quantity of FeCl<sub>3</sub>·6H<sub>2</sub>O was decreased from 1 mmol to 0.6 mmol.

**Preparation of porous hematite mesocrystals through HCl etching.** In a typical etching process, 25 mL of concentrated HCl solution (36-38 wt%) was mixed with 20 mL of distilled water in a three-neck round bottom flask, which was heated in an oil bath at 60 °C. Meanwhile, 170 mg of as-prepared hematite microcubes or submicrocubes were dispersed in 5 mL of distilled water, and then the suspension was added into the flask quickly. After etching for a certain time, 2 mL of solution was taken out and mixed quickly with 5 g ice to stop the etching reaction. Afterwards, the product was collected by centrifugation and washed more than three times with distilled water and ethanol, respectively, and then dried overnight in an oven at 60 °C.

**Characterization.** The products were characterized by powder X-ray diffraction (XRD, Rigaku Dmax-2000, Cu K $\alpha$  radiation), scanning electron microscopy (SEM, Hitachi S4800, 5 kV), transmission electron microscopy (TEM) and high-resolution TEM (HRTEM, FEI Tecnai F30, 300 kV). The Brunauer–Emmett–Teller (BET) specific surface area was measured using a Micromeritics ASAP 2010 instrument. The UV-vis spectra were recorded on a Hitachi U-4100 spectrophotometer. The chromium concentration was measured using an Inductively Coupled Plasma (ICP)-atomic emission spectrometer (PROFILE SPEC). Magnetic measurements were performed

with a commercial superconducting quantum interference device (SQUID) magnetometer (MPMS-7, Quantum Design Corp.).

**Visible-light photocatalysis measurement.** The photocatalytic activity of the products was evaluated by the degradation of rhodamine B (RhB) in aqueous solutions under visible light. Prior to irradiation, 10 mg photocatalyst was mixed with 50 mL of 0.02  $\mu$ M RhB solution in a quartz flask and stirred in the dark for 30 min, which was followed by the addition of 0.255 mL of hydrogen peroxide solution (H<sub>2</sub>O<sub>2</sub>, 30 wt%). Then, the suspension was exposed to visible-light irradiation from a 300 W Xe lamp equipped with cutoff filter of 420nm (PLS-SXE 300C). 3.0 mL of solution was taken out at certain time intervals, and the photocatalyst was separated from the solution by centrifugation. The UV-vis spectra of the remaining solutions were measured to evaluate the RhB concentration.

**Cr(VI) removal experiments.** Aqueous solutions containing different concentrations of Cr(VI) were prepared using  $K_2Cr_2O_7$  as the Cr(VI) source and adjusted to pH 4 by HCl solution. Then, 10 mg of adsorbent samples were suspended in 5 mL of the above solution, and then stirred under ambient conditions for 5 h to reach adsorption equilibrium. The resultant solid and liquid were separated by centrifugation and the chromium concentration in the remaining solutions was measured by ICP-atomic emission spectroscopy.



**Fig. S1** SEM (a) and TEM (b) images, and schematic illustration (c) of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> microcubes with a pseudocubic morphology. Inset in (b) shows the SAED pattern corresponding to the circled area.



Fig. S2 XRD patterns of α-Fe<sub>2</sub>O<sub>3</sub> submicrocubes before etching and microdiscs after etching.



**Fig. S3** SEM images of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> products obtained after etching submicrocubes for different times: (a,b) 4 min, (c,d) 14 min.



Fig. S4 Temperature dependence of magnetization (*M*) for hematite microcubes (a) and microcones (b). The Morin transition temperature ( $T_M$ ) is determined by the main peak in the dM/dT curves shown in the insets.