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Supporting Information

Magnetic Composite Microspheres with Exposed {001} Facets TiO_2 Shell: A Highly Active Visible-light and Selectivity Photocatalyst

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Chemicals. Poly(allylamine hydrochloride) (PAH) was purchased from Sigma-Aldrich Chemicals Co. Anhydrous $FeCl_3$, trisodium citrate, sodium acetate (NaAc), ethylene glycol, tetraethyl orthosilicate (TEOS), $HAuCl_4 \cdot 3H_2O$, absolute ethanol, NH_4F, concentrated ammonia solution (28 wt %), $NaBH_4$, carboxymethyl cellulose sodium (CMC, 99%), tetrabutyl orthotitanate (TBOT, 99%), methylene blue (MB, pure) and methyl orange (MO, pure) are of analytical grade and purchased from Shanghai Chemical Corp. P25 aeroxide was obtained from Degussa AG, Frankfurt. All chemicals were used as received. Ultrapure water (18 MU cm) was used for all experiments.

Materials for synthesis of $Fe_3O_4/SiO_2/Au$ (MG) microspheres. In a typical liquid phase synthesis, 1.3 g anhydrous $FeCl_3$, 0.5 g trisodium citrate, and 2.0 g NaAc were dissolved in 40 mL ethylene glycol with magnetic stirring. The yellow solution was then transferred into a 100 mL Teflon-lined stainless-steel autoclave and heated at 200 ^{o}C for 10 h, then cooled to room temperature, and the black products were washed by ethanol and ultrapure water. An aqueous dispersion of the above-mentioned magnetite particles was added to a three-neck round-bottom flask charged with absolute ethanol and concentrated ammonia solution under mechanical stirring for 15 min at room temperature. Then 2 mL TEOS was added dropwise in 1 min, and the reaction proceeded for 10 h under continuous mechanical stirring. The resultant core-shell Fe_3O_4/SiO_2 microsphere product was separated and collected with a magnet. Au nanoparticles (AuNPs) on the composite microspheres were prepared using a modification of the method by our group which was adopted to absorb PAH and $AuCl_4^-$ onto the Fe_3O_4/SiO_2 microsphere. In an optimized deposition process, 40 mg Fe_3O_4/SiO_2 were soaked in 60 mL PAH solution (0.2 wt %) under ultrasonication for 30 min. The precipitate was washed with ultrapure water, and then immersed in 10 mL $HAuCl_4$ aqueous solution (1.71 mM) under ultrasonication for 30 min to combine $AuCl_4^-$ with the $–CH_2NH_3^+$ group via electrostatic attraction. Separated with a magnet and washed, the resulting microspheres were redispersed in 0.1

M $NaBH_4$ solution for reduction of $AuCl_4^-$. The color of the suspension rapidly changed from buff to wine red, indicating the formation of AuNPs on the microspheres surface.

Characterization. To demonstrate the overall uniformity and morphology of the particles, the samples were examined by scanning electron microscopy (SEM) using a JEOL SM-6360LV microscope and a Hitachi-4800S microscopy (Hitachi, Japan). Transmission electron microscopy (TEM) images were taken with a JEOL 2011 microscope (Japan) operated at 200 kV equipped with a Bruker X-flash silicon drift detector (SDD) detector. All samples were placed on a carbon-coated copper grid and dried at room temperature overnight. The crystalline structure was investigated by X-ray power diffraction (RIGAK, D/MAX 2550 VB/PC, Japan) and the magnetization curve of the product was measured with a Vibrating Sample Magnetometer (LAKE SHORE, 7407). The porosity of the products was measured by the nitrogen adsorption–desorption isotherm and Barrett–Joyner–Halenda (BJH) methods on a Micromeritics ASAP 2020M accelerated surface area and porosimetry system. UV/Vis-NIR diffuse reflectance spectra were measured on a Shimadzu UV 3101PC double-beam, double-monochromator spectrophotometer. $BaSO_4$ powder was used as a reference (100 % reflectance). The UV-Vis absorption spectra of the solution to monitor the concentration of MB and MO at different time intervals were recorded on a UV-vis spectrometer (UNICO UV-2102PC) at 25 ^{o}C. The photocurrent measurements were carried out with a CHI 660C workstation, an ultraviolet lamp (365 nm, 70 $mWcm^{-2}$) and a Xenon lamp with a cutoff filter (< 400 nm). A three-electrode configuration was employed, consisting of an ITO working electrode, Ag/AgCl (3 M KCl) and a platinum wire serving as the reference and counter electrodes respectively. The ITO electrodes were modified with different kinds of catalysts dispersion by spin-coating.

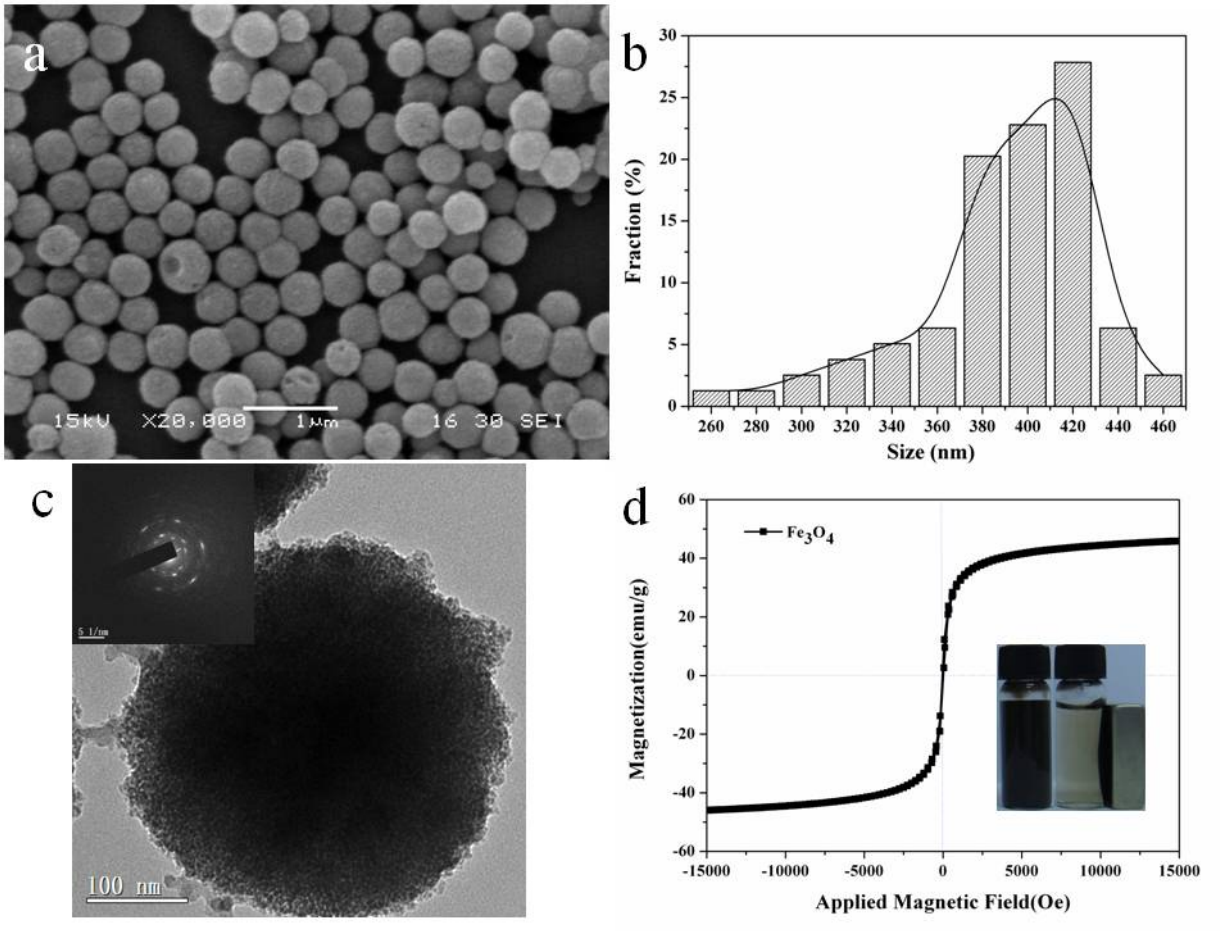

Fig. S1 a) SEM images of Fe_3O_4 particles. b) Diameter distribution of Fe_3O_4 particles. c) TEM images of a Fe_3O_4 particle, inset is the SAED pattern recorded on single particle. d) the inset is a photograph of Fe_3O_4 under an external magnetic field.

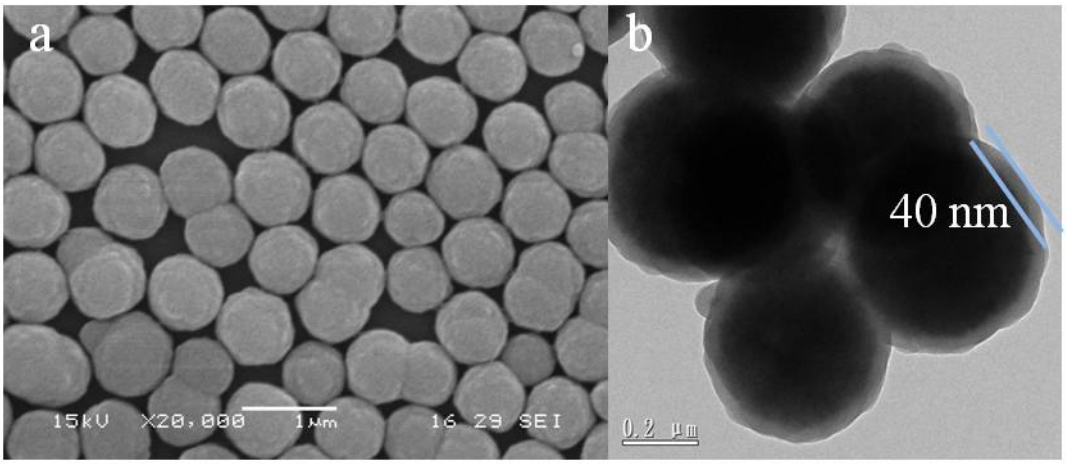

Fig. S2 a) SEM images of Fe_3O_4/SiO_2 particles. b) TEM images of Fe_3O_4/SiO_2 particles.

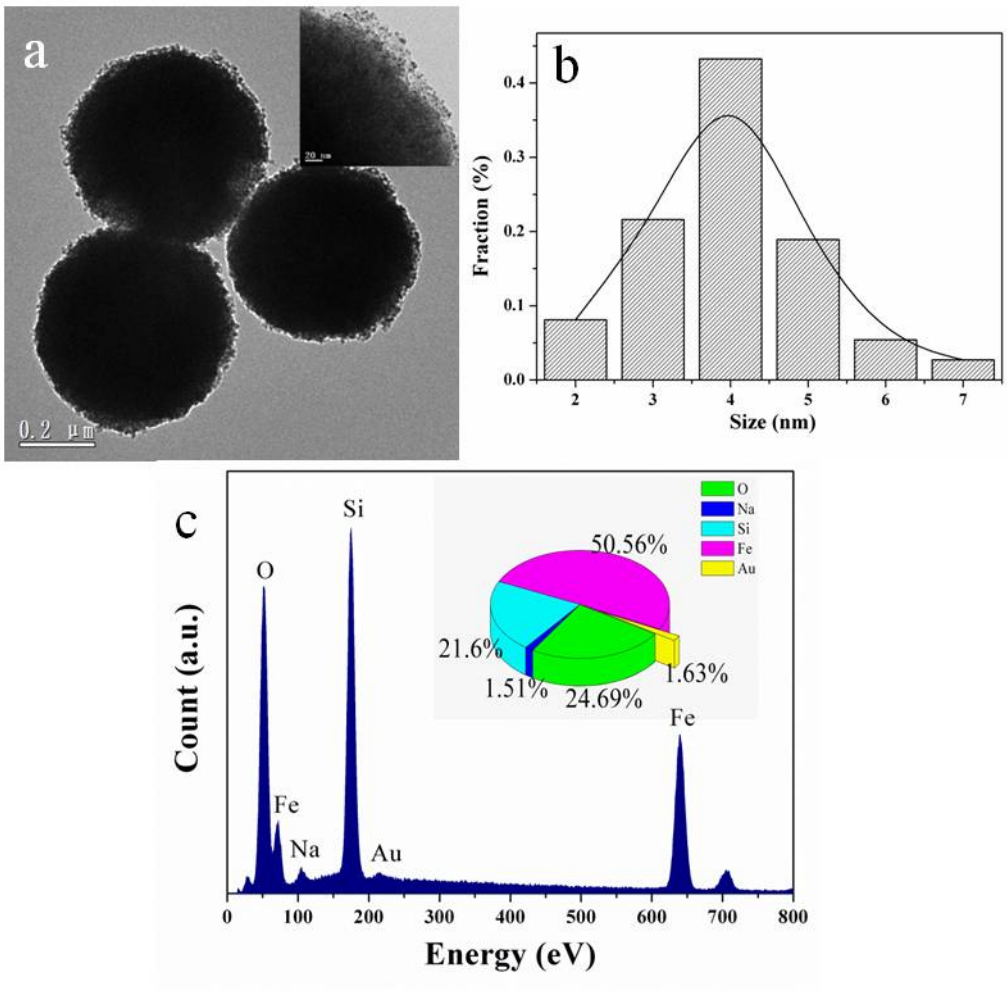

Fig. S3 a) TEM images of MG microspheres, inset is the enlarged TEM image. b) Column plot of gold nanoparticles size distribution on MG. c) EDX spectra of MG. Inset is a pie chart showing the element distribution, and the gold content is ca. 1.63 wt%.

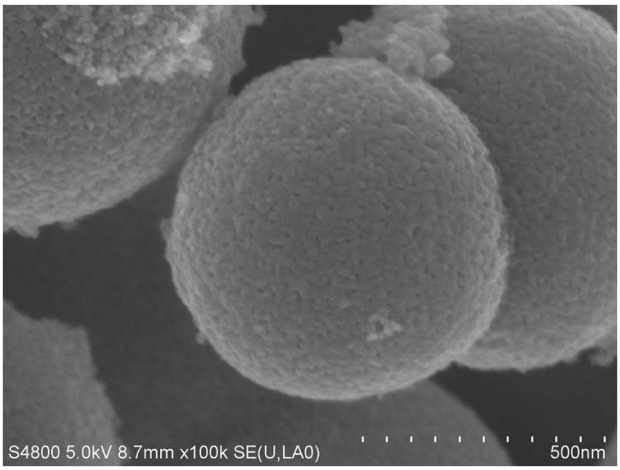

Fig. S4 SEM images of a single MG/TiO_2 microsphere.

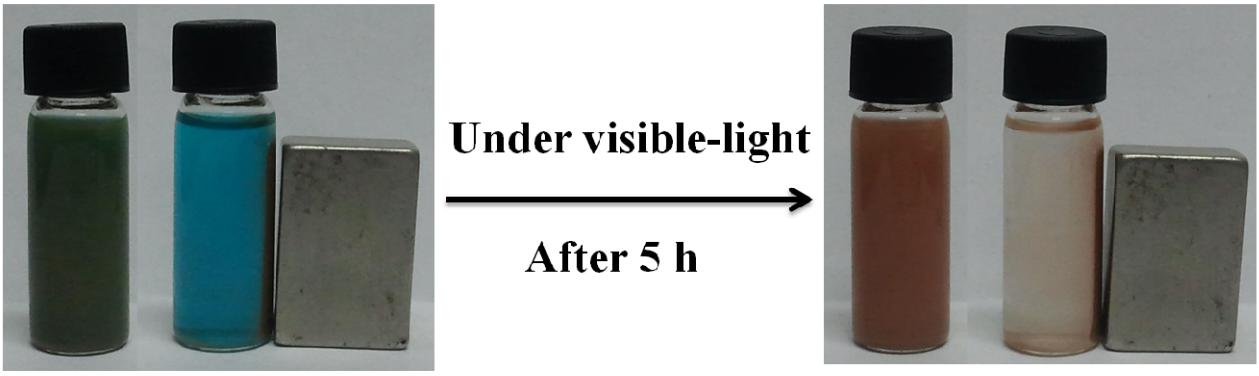

Fig. S5 The photographs of aqueous slurry with MG/TiO_2 and MB before and after the degradation under visible-light after 5h.