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Supporting Information

Self-templated Formation of $ZnFe_2O_4$ Double-shelled Hollow Microspheres for Photocatalytic Degradation of Gaseous *o*-dichlorobenzene

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Experimental Section

Materials synthesis: In a typical synthesis of $ZnFe_2O_4$ double-shelled hollow microspheres, 16 mL of glycerol was dissolved into 80 mL of isopropanol to form a transparent colorless solution. Then 0.25 mmol of $Zn(NO_3)_2·6H_2O$ and 0.5 mmol $Fe(NO_3)_3·9H_2O$ were added into the above solution under vigorous stirring. After about 20 min, the obtained solution was then transferred into a 100 mL Teflon-lined stainless steel autoclave and kept at 180 °C for 6 h. The autoclave was cooled down naturally, and then the faint yellow precipitate was collected by centrifugation and washed with absolute ethanol for several times, followed by drying in an oven at 60 °C. Finally, the sample was annealed at 350 ºC for 2 h with a heating rate of 20 ºC/min. Other interior hollow spheres, such as solid and yolk-shelled spheres, were synthesized by a similar procedure with different calcination rates.

Materials Characterization*:* The X-ray diffraction (XRD) patterns were performed by an X-Ray diffractometer with Cu Ka radiation (Rigaku Corporation D/max-2400, Japan). The morphology images were captured by using a field emission scanning electron microscope (FESEM, Hitachi SU8010, Japan). The transmission electron microscopy (TEM) images were acquired by using a FEI Tecnai G20 (USA). The surface elements compositions were conducted by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI). The specific surface area of fabricated material was investigated by nitrogen adsorption/desorption isotherms on a Quantachrome instrument (NOVA 4200e, USA). Thermogravimetric (TG) analysis was conducted by using an EXSTAR TG/DTA6300 thermal analyzer (Seiko, Japan) with a heating rate of 10 °C/min in air. The electron paramagnetic resonance (EPR) spectra were recorded on a Bruker ECS106 X-Band spectrometer (Bruker A200, Germany) for capturing $O_2^{\bullet -}$ free radicals.

***Photocatalytic evaluation*:** To evaluate performances of the different structures of $ZnFe_2O_4$ catalysts, the degradation efficiency of gaseous *o*-DCB was conducted in a home-built quartz reaction cell (about 130 mL). First, 0.01 g of photocatalyst was mixed with ethanol under ultra-sonication for about 5 minutes, and the dissolved solution was then coated onto a piece of glass drop by drop. The piece was dried naturally and then placed at the bottom of the reactor. Now, the micro-reactor was immediately sealed up in ambient air and then the liquid *o*-DCB (5 μL) was injected into the cell by micro syringe. After about an hour volatilization, the adsorption mode between catalyst and gaseous *o*-DCB would reach equilibrium. At that moment, the concentration of *o*-DCB was designated as the initial value, and the light equipping with a UV-cut off filter ($\lambda > 400$ nm) (A 500 W Xenon lamp) was turned on. During the photocatalytic reaction, the pollutant concentration was detected at regular intervals through injecting the gas mixture (1 μL) from the quartz reactor into the gas chromatograph (GC, Agilent 7890A, USA) equipped with a FID.

***In situ FTIR Experiment*:** The adsorption process was conducted in a home-built *in situ* quartz cell with about 130 mL volume. The catalysts (0.02 g) pressed into the circular pieces were fixed to the holder and then the cell was sealed up. At that time, the reaction conditions were under a dry air atmosphere and the temperature was about 30 °C. Then the pollutant was brought into the reaction cell by injecting liquid *o*-DCB (5 μL) into a rubber hose with a micro syringe. After about an hour in the dark, the *o*-DCB completely evaporated to steam and could reach adsorption equilibrium.

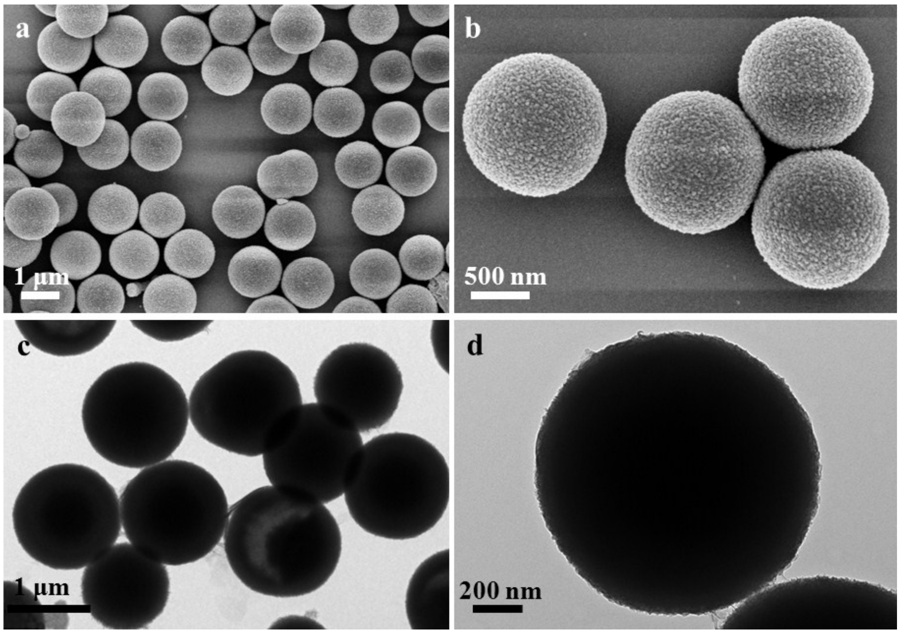

Fig. S1 a, b) FESEM images and c, d) TEM images of the as-prepared ZnFe-glycerate precursors.

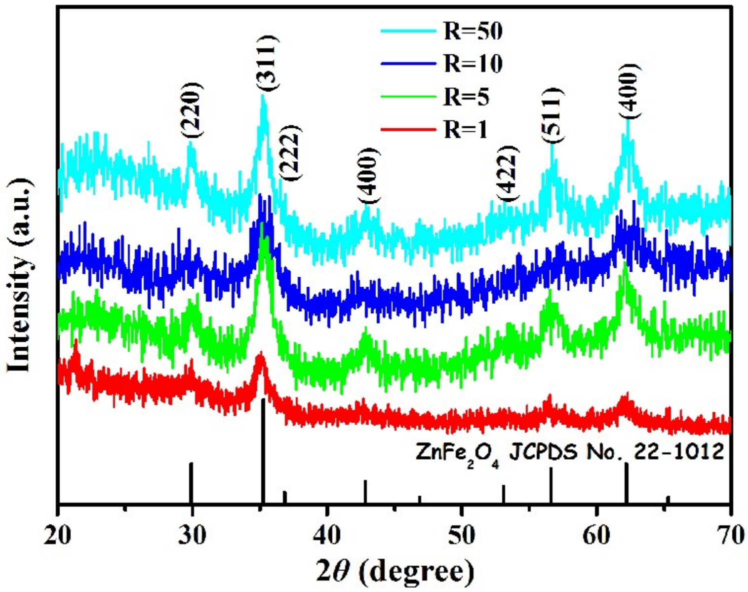

Fig. S2 XRD patterns of the as-prepared $ZnFe_2O_4$ microspheres with different interior structures.

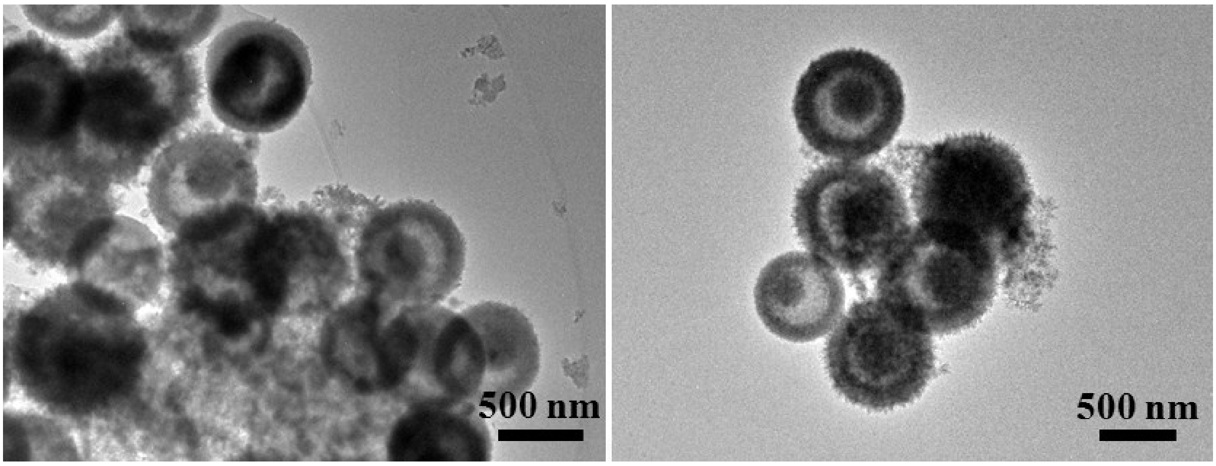

Fig. S3 Typical TEM images of $ZnFe_2O_4$ spheres annealed at 350 °C in air for 2 h with 50 °C min^{-1}

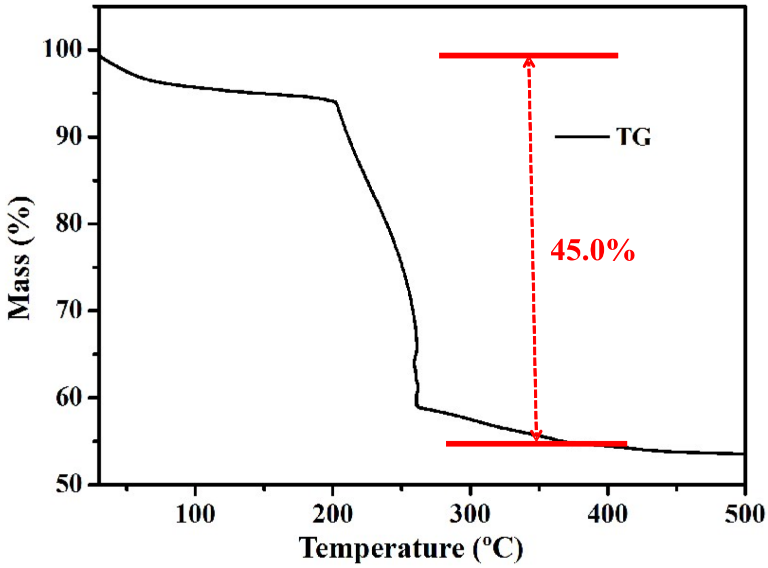

Fig. S4 Thermogravimetry (TG) curves of the ZnFe-glycerate precursors.

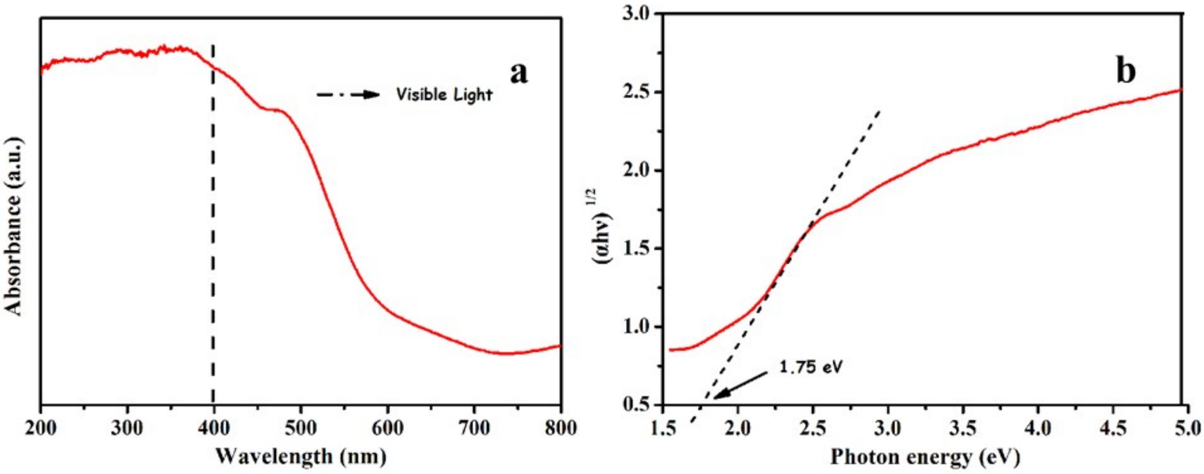

Fig. S5 UV-vis DRS of the $ZnFe_2O_4$ double-shelled hollow spheres (a), and the Tauc's plot for the band-gap (b)

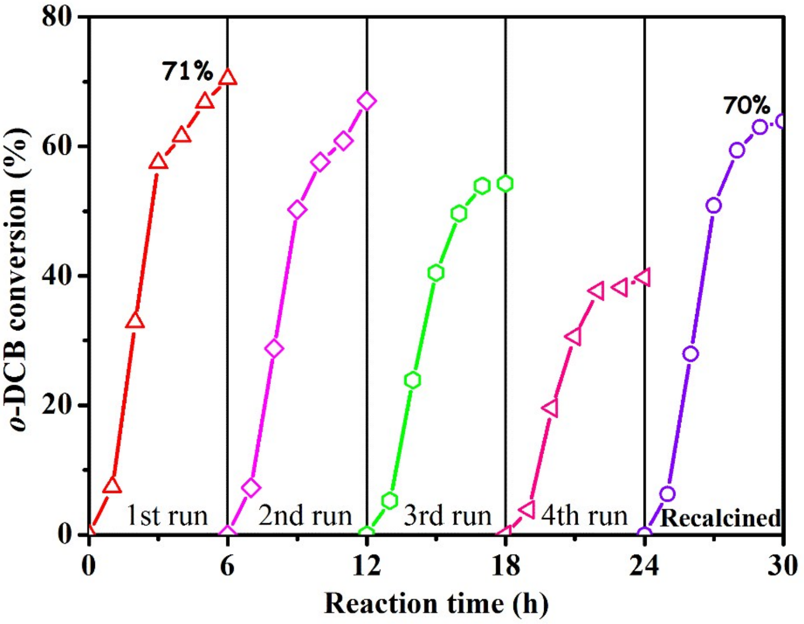

Fig. S6 Cyclic degradation of gaseous *o*-DCB over $ZnFe_2O_4$ double-shelled hollow spheres under visible light irradiation.

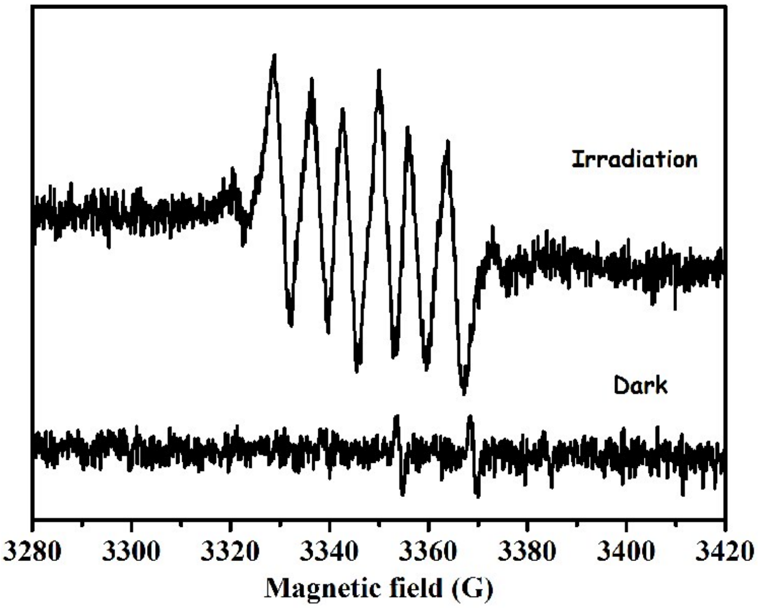

Fig. S7 EPR spectra of the double-shelled $ZnFe_2O_4$ in the methanol solution after 40 seconds under visible light irradiation.