Supporting Information

X-ray diffraction patterns

The X-ray diffraction patterns of the precursor (bottom) and the resultant hierarchical hollow α -Fe₂O₃ nanospheres (top) are shown in Fig. S1. The peaks seen in the precursor pattern indicate the formation of two-phase structures, coinciding with previously reported data on γ -Fe₂O₃ (JCPDS card No. 39-1346) and Fe_{1.833}O_{2.5}(OH)_{0.5} (JCPDS card No. 76-0182). Iron hydroxide oxide Fe_{1.833}O_{2.5}(OH)_{0.5} is known to be formed from γ -Fe₂O₃ when the O²⁻ of γ -Fe₂O₃ is replaced by the OH⁻ of water.³¹ In contrast, the product is composed of single-phase α -Fe₂O₃ as indicated by the peaks in the diffraction pattern of the hierarchical hollow α -Fe₂O₃ nanostructure (JCPDS card No. 33-0644). Furthermore, the sharp diffraction peaks indicate the good crystallinity of the hierarchical hollow nanostructure.



Fig. S1 X-ray diffraction patterns. The peaks of the precursor pattern (bottom) indicate twophase structures of γ -Fe₂O₃ and Fe_{1.833}O_{2.5}(OH)_{0.5}. The peaks of the product (top) indicate single-phase α -Fe₂O₃.

Adsorption-desorption isotherm and pore size distribution

The nitrogen adsorption–desorption isotherms of hierarchical hollow-structured α -Fe₂O₃ nanospheres formed by nanotubes and porous α -Fe₂O₃ nanospheres formed by nanorods are shown in Fig. S2. The hierarchical hollow-structured α -Fe₂O₃ nanospheres have a fairly large BET surface area of 133.6 m² g⁻¹ primarily because of the micro-scale hollow structure and the

unique secondary nanotube (Fig. S2a). The surface area is much larger compared to most of the previous studies as is stated in introduction section. The Barrett–Joyner–Halenda method and the branch desorption of hierarchical hollow-structured α -Fe₂O₃ nanospheres (the inset in Fig. 3d) indicate that the bimodal pores in the mesoporous regions have mean diameters of 3 and 40 nm. However, the BET surface area of porous α -Fe₂O₃ nanospheres is only 58 m² g⁻¹ (Fig. S2b), which is much lower than that of hierarchical hollow-structured α -Fe₂O₃ nanospheres.



Fig. S2 Typical nitrogen adsorption–desorption isotherms and Barrett-Joyner-Halenda pore size distribution plots. a, The hierarchical hollow-structured α -Fe₂O₃ nanospheres with the main pore size distribution of 3 and 40 nm have a BET surface area of 133.6 m² g⁻¹. b, The porous α -Fe₂O₃ nanospheres with the main pore size distribution of 7 nm have a BET surface area of 58 m² g⁻¹.