

Supplementary Information

S1. The prepared products were also studied by transmission electron microscopy (TEM) and the results were shown in Fig. S1. Fig. S1a was the typical TEM image of single α -MnO₂ core-shell structure with a larger core (occupying *ca.* 90% volume), and Fig. S1b was that with a smaller core (occupying *ca.* 40% volume). The magnified TEM images of α -MnO₂ nanorods on the shell of the core-shell structure were shown in Fig. S1c and S1d, which indicated that the lengths of the nanorods were *ca.* 200~300 nm, and the diameters were *ca.* 30~40 nm. High-resolution transmission electron microscopy (HRTEM) image of these nanorods was shown in Fig. S1e, indicating their well crystallinity. The distance between two stripes was measured to be 0.49 nm, which could be indexed to the (002) plane of α -MnO₂ crystal. The HRTEM image showed that the α -MnO₂ nanorods in the core-shell structure had a preferential growth direction along [001].

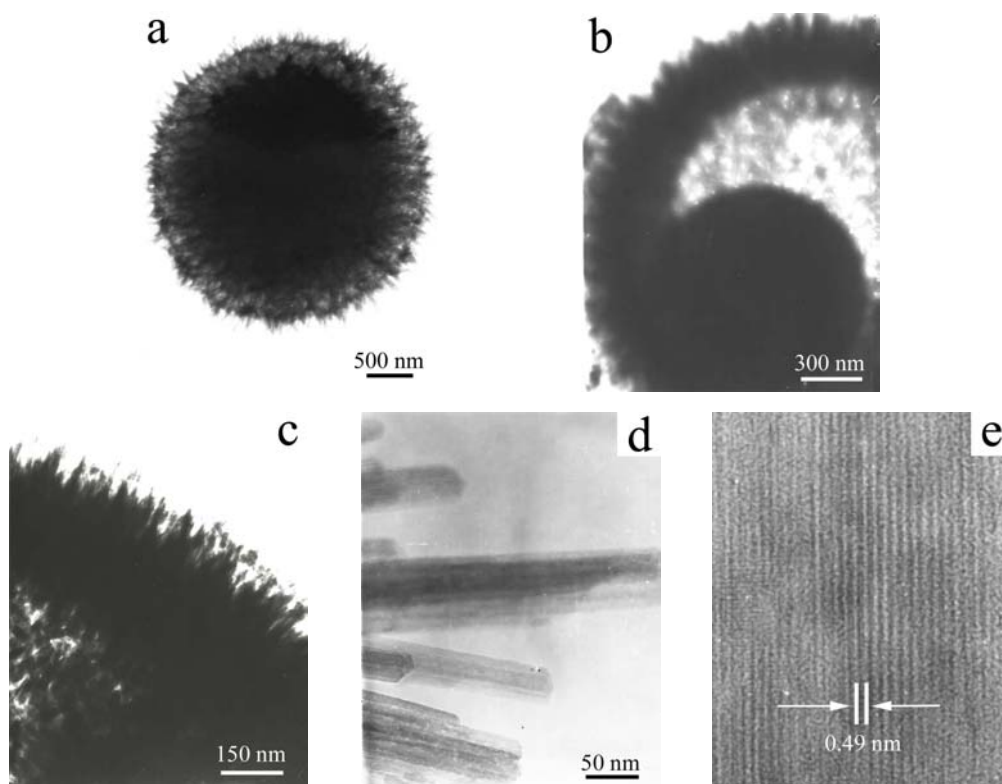


Fig. S1 (a) TEM image of single core-shell structure with a larger core; (b) TEM image of single core-shell structure with a smaller core; (c) Magnified TEM image of the shell; (d) Magnified TEM image of the nanorods on the shell; (e) HRTEM image of single α -MnO₂ nanorods on the shell.

S2. The X-ray photoelectron spectra (XPS) of the prepared sample were shown in Fig. S2. The binding energies in the XPS analysis were corrected for specimen charging by referencing the C 1s to 284.60 eV. The peak at 642.3 eV in Fig. S2a was attributed to Mn 2p_{3/2}, and the peak at 529.4 eV in Fig. S2b can be indexed to the O 1s in α -MnO₂. Two peaks at *ca.* 367 eV and 374 eV in Fig. S2c came from Ag 3d_{5/2} and Ag 3d_{7/2} of Ag⁺, respectively. But these two peaks were extremely weak, and the content of element Ag in the product was calculated to be no more than 1%. When the product was filtrated off from the solution, the content of Ag⁺ in the filtrate was examined by chemical titration. It was found that more than 95% Ag⁺ was still left in the solution, which confirmed the XPS analysis. Such trace Ag component could not be detected by XRD. It might was confined Ag⁺ in the 2×2 tunnels of α -MnO₂ produced in the catalytic reaction.

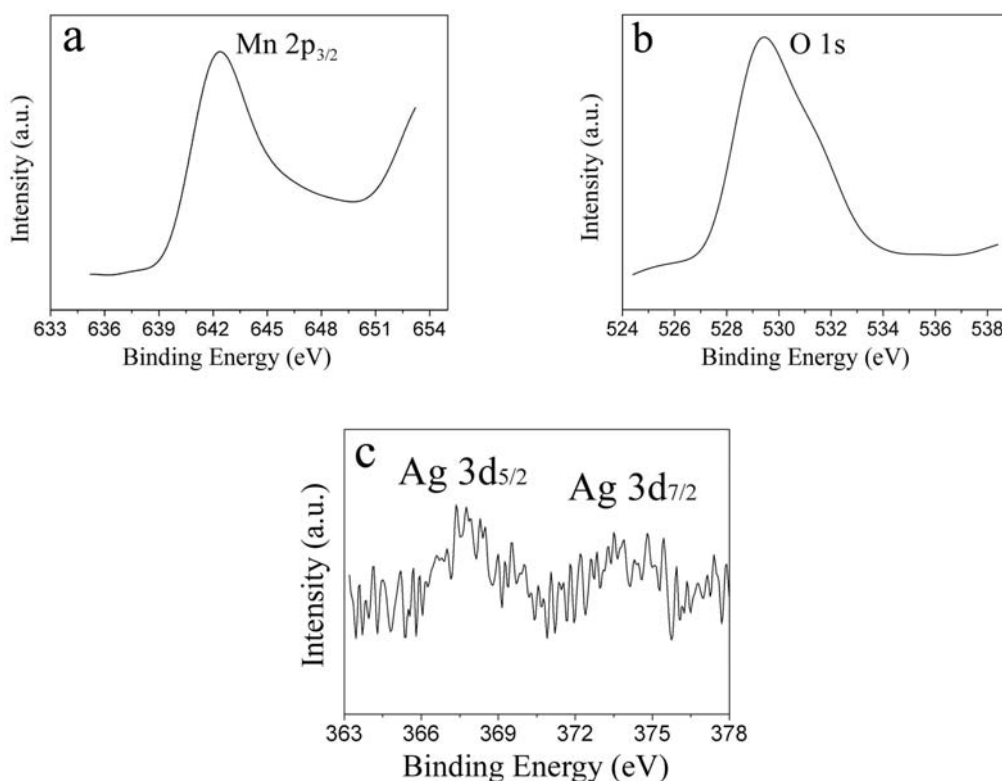


Fig. S2 XPS spectra of the prepared α -MnO₂ sample. (a) Mn 2p_{3/2} core-level spectrum; (b) O 1s core-level spectrum; (c) Ag 3d core-level spectrum.

S3. Longer ultrasonic treatment of the prepared products was also employed to show more information of the novel core-shell structures. Fig. S3 showed the FESEM images of the products after 30 minutes' ultrasonic treatment. From Fig. S3a, one could see that more spheres were broken than the product after 10 minutes ultrasonic treatment, indicating these spheres were not solid. Fig. S3b was the typical magnified FESEM image of a broken sphere, showing that the spheres had an obvious core-shell structure. The core-shell structure with a broken shell was shown in Fig. S3c, providing the inner morphological information of the core. From this image one could see the inner of the core was also constitutive of tightly aggregate nanoparticles, confirming the statement in the main text that the core was constructed by nanoparticles.

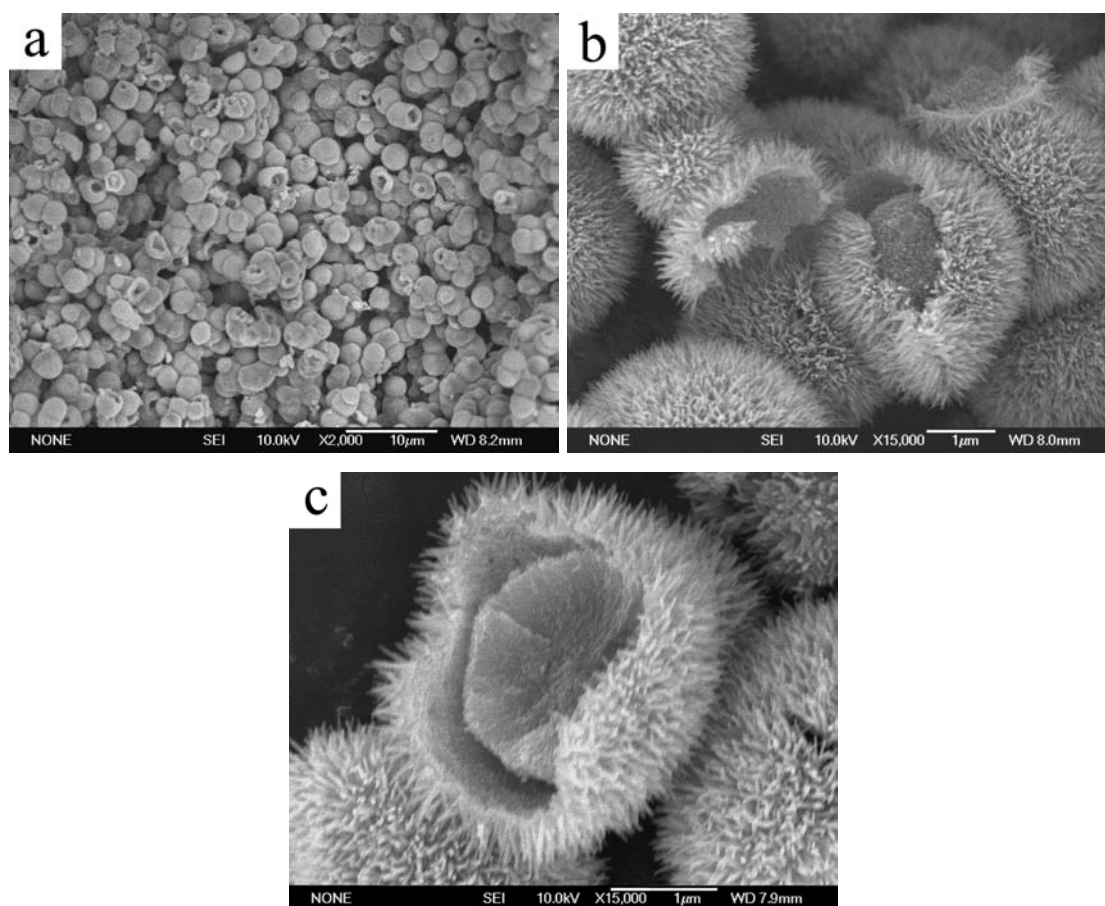


Fig. S3 FESEM image of prepared product after 30 minutes ultrasonic treatment. (a) Panoramic morphology; (b) Typical broken core-shell structure; (c) Core-shell structure with both broken core and broken shell.

S4. The X-ray powder diffraction (XRD) patterns of the intermediate products prepared with 6 h and 12 h were shown in Fig. S4a and S4b, respectively. The corresponding TEM images of these two samples have been shown in Fig. 3a and 3b in the main text. From these two XRD patterns, one could see that the initial stages of product contained many amorphous components. While, the XRD pattern of the final product was shown in Fig. S4c, namely Fig. 1 in the main text, in which no amorphous components were be detected. Comparing the XRD patterns in Fig. S4a and S4b, one could see that some new small peaks appeared in the 12 h product. They might come from the newly formed well-crystallized α -MnO₂ nanorods. However, many amorphous colloids still existed. When the crystallization of amorphous colloids was completed, the peaks in the range of 10~30 degree were clearly displayed (Fig. S4c). Meanwhile, the loosely adhered colloids aggregated tightly to form the core, which was induced by the crystallization process.

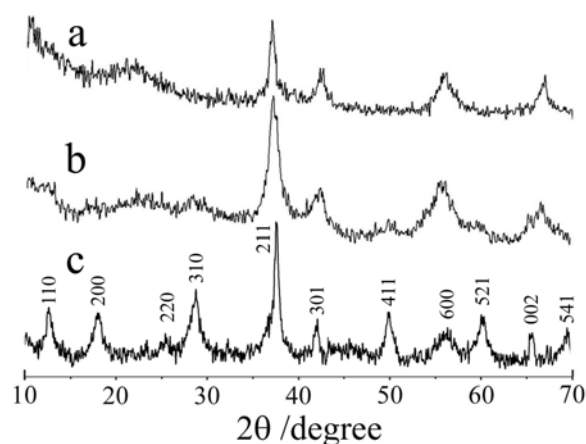


Fig. S4 XRD patterns of the intermediate products prepared with different time. (a) 6 h; (b) 12 h; (c) XRD patterns of the prepared product.