Electronic supplementary information (ESI)

Shape-Controlled Synthesis of Mn_2O_3 Hollow Structures and their Catalytic Properties

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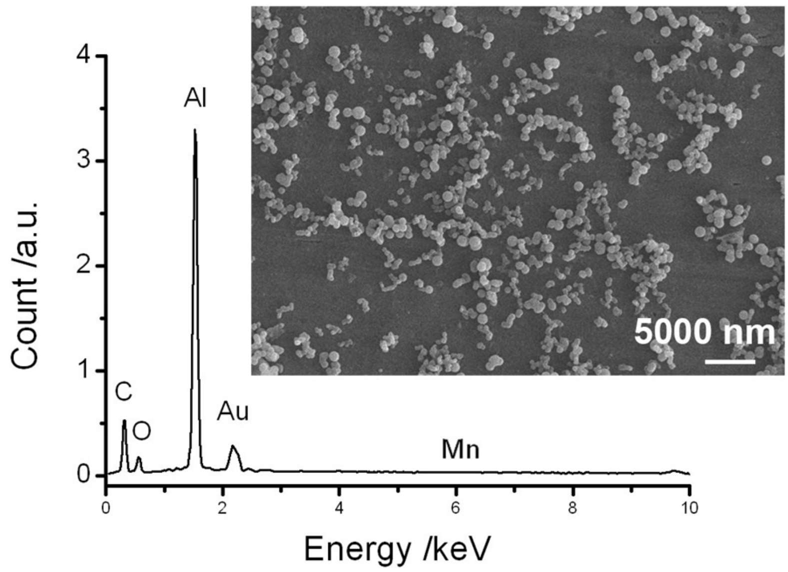

Fig. S1 SEM image and EDX pattern of rough carbon spheres obtained by the treating sample S3 with dilute HCl solution for 8 h.

After treating sample S3 with dilute HCl solution for 8 h, black precipitates composed many round sphere and dumbbell particles were obtained. The average size of these particles was about 1μm. The element composition of these particles was identified by EDS. Al signal was originated from the Al substrate. The result revealed that the particle mainly consists of carbon element, and contains an insignificant amount of Mn.

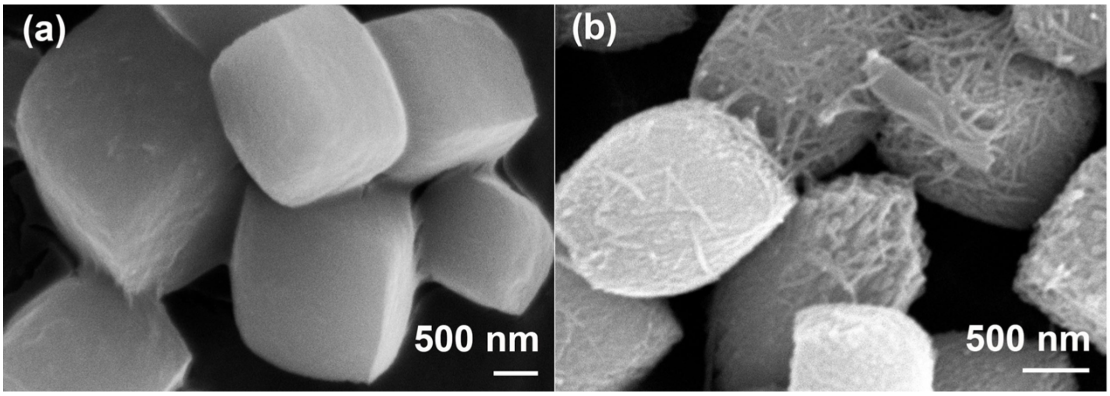

Fig. S2 SEM images of rhombic and ellipsoid particles obtained after hydrothermal growth for 4h.

To understand the growth process, some particles were sampled for SEM observation without washing. For rhombic particles, there are some soft materials connecting neighbor particles, indicating the present of oligosaccharide. However, for the ellipsoid particles, there are many nanorods collected at the ending of the particles, suggesting an ending-growth mode.

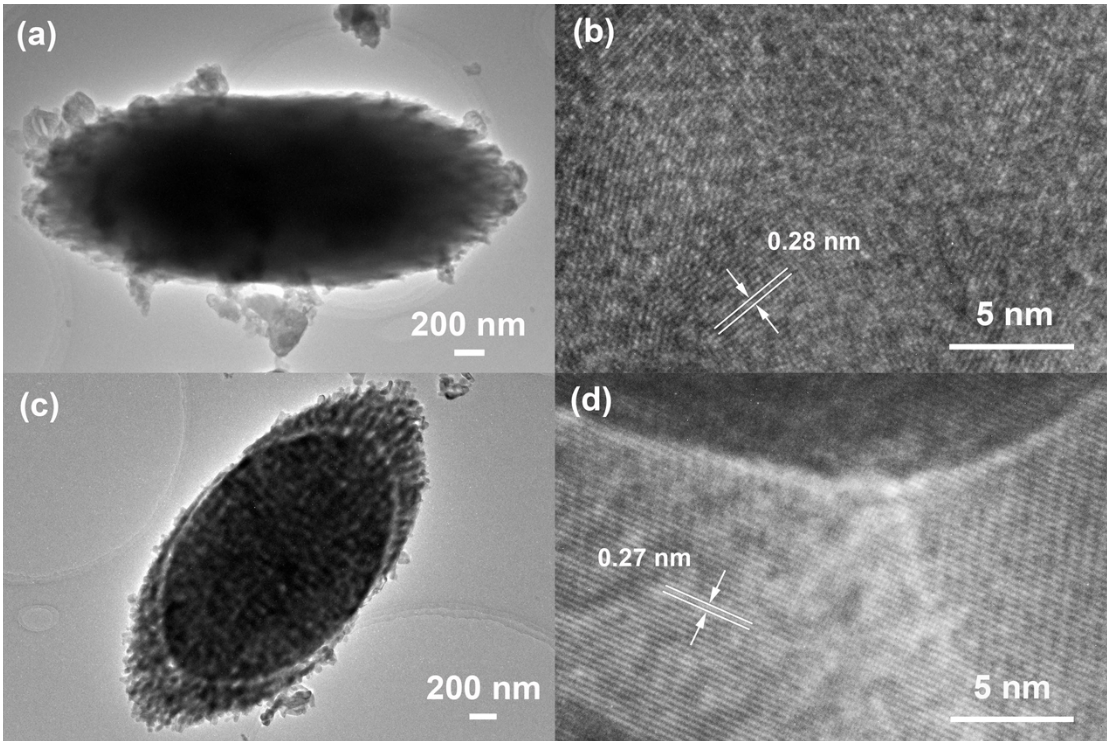

Fig. S3 TEM and HRTEM images of ellipsoid particles before and after annealing.

One can see the different between the ellipsoid particles before and after annealing. After annealing, the porous and hollow ellipsoid was obtained. A circular and closed stripe was formed internally, which is less mentioned in the literatures. However, due to the resolution, the nature of the stripe is still unclear. Visible lattice fringes are observed in the HRTEM images with interplanar spacings of ca. 0.28 nm, which corresponds to the (104) lattice plane of $MnCO_3$. The lattice spacing of the hollow particle is 0.27 nm, ascribed to the (222) plane of Mn_2O_3.

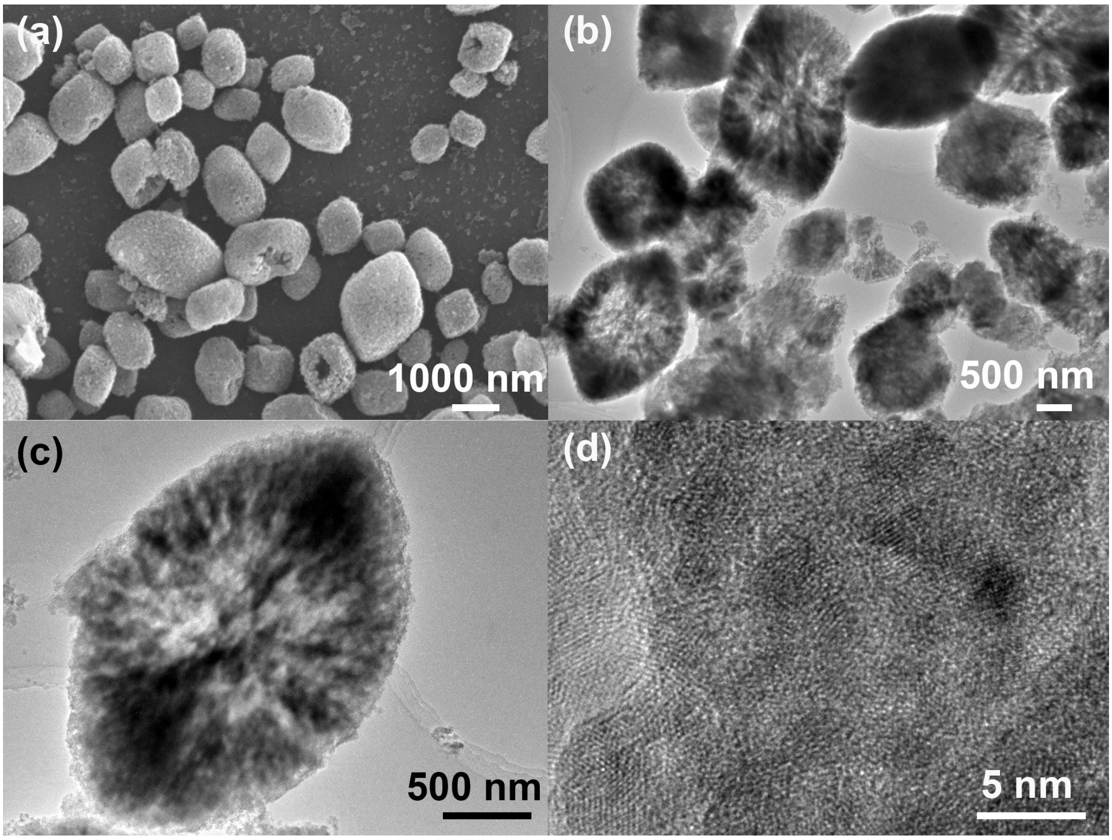

Fig. S4 SEM and TEM images of hollow ellipsoid particles of Mn oxide.

Carbon spheres can be oxidized and removed in ammonium persulfate and $AgNO_3$ solution at room temperature. Fig. S4d reveals a polycrystalline nature of Mn oxide shell after oxidation.

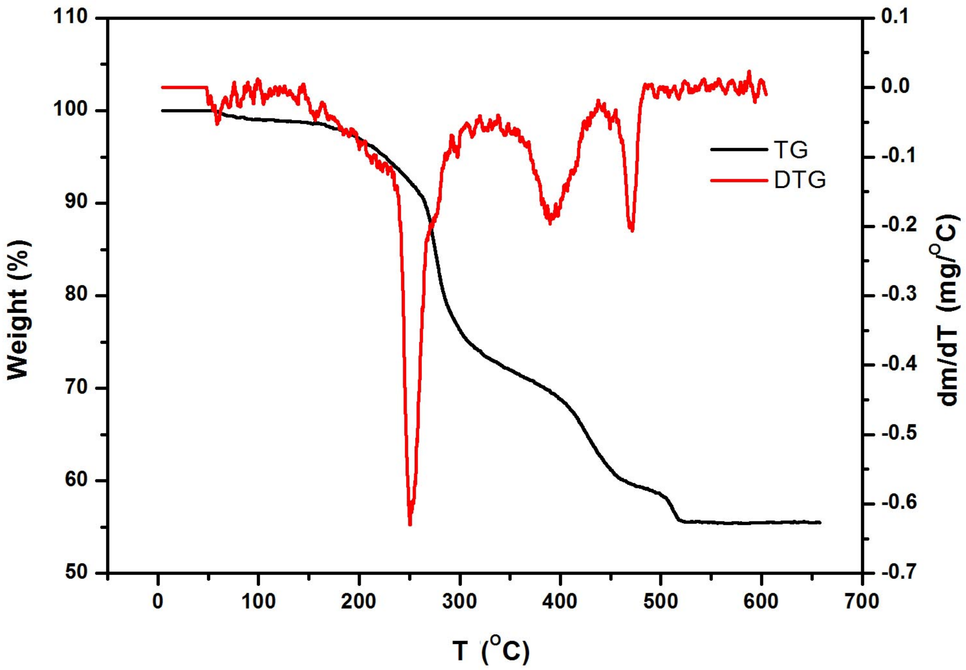

Fig. S5 TG and DTG curves of carbon@$MnCO_3$/MnC_2O_4 core/shell particles.

For the transformation of $MnCO_3$ or $MnC_2O_4 \cdot 2H_2O$ to Mn_2O_3, the theoretical weight loss is 31.3% or 55.9 %, respectively. For carbon@$MnCO_3$/MnC_2O_4 core/shell particles, the weight loss is 44.5 wt%, suggesting the coexistence of $MnCO_3$ and $MnC_2O_4 \cdot 2H_2O$.

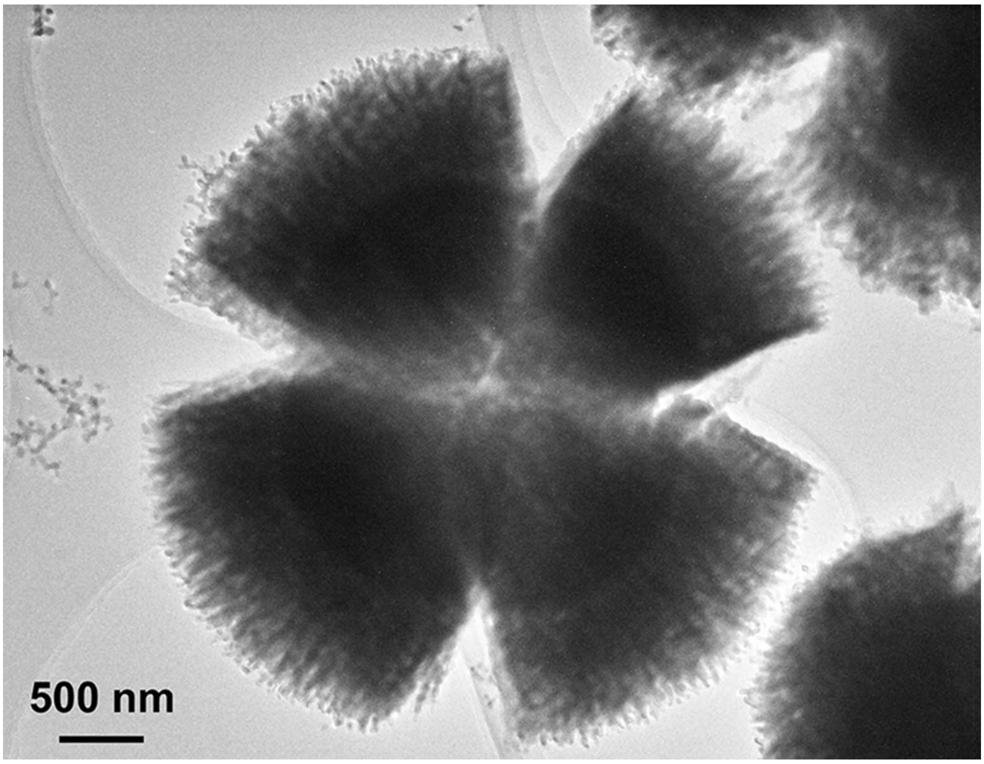

Fig. S6 TEM image of a Mn_2O_3 hollow particle with cross pattern

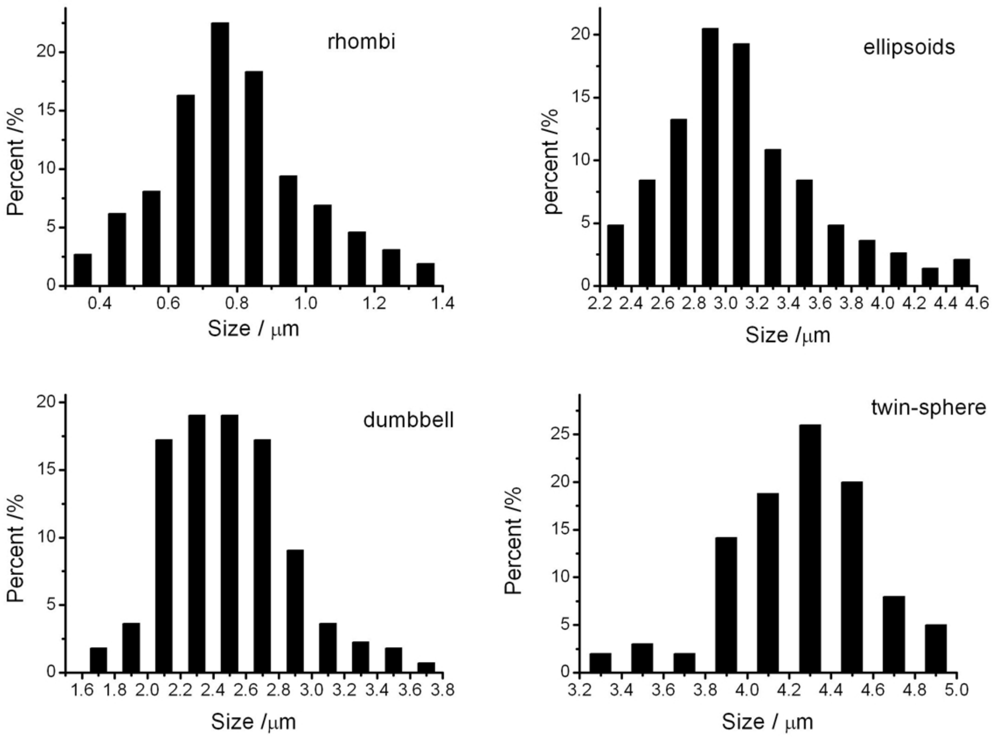

Fig. S7 Size distributions of the obtained Mn_2O_3 hollow particles.

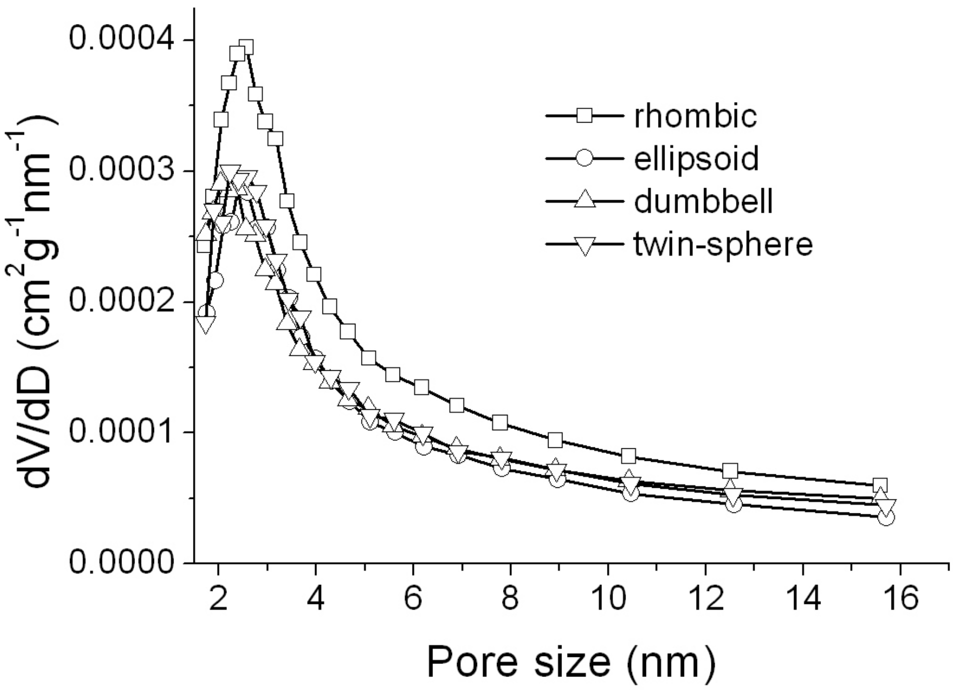

Fig. S8 The pore size distribution of the obtained annealing products.