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An unusual temperature gradient crystallization process: Facile synthesis of hierarchical ZnO porous hollow spheres with controllable shell numbers

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Supporting information

The crushed carbon microspheres after soaking in zinc sulphate solution (namely, the zinc precursor-carbon composites) were characterized by FE-SEM and FE-SEM-EDX mapping**.** The results show that the metal ions were distributed evenly into the carbon spheres by one step process (Figure S1 in the Supporting Information). From the images, it could demonstrate that carbon particles can absorb a significant amount of metal ions within the interior of the particle. Such distribution could be achieved directly during the formation process of carbon spheres.

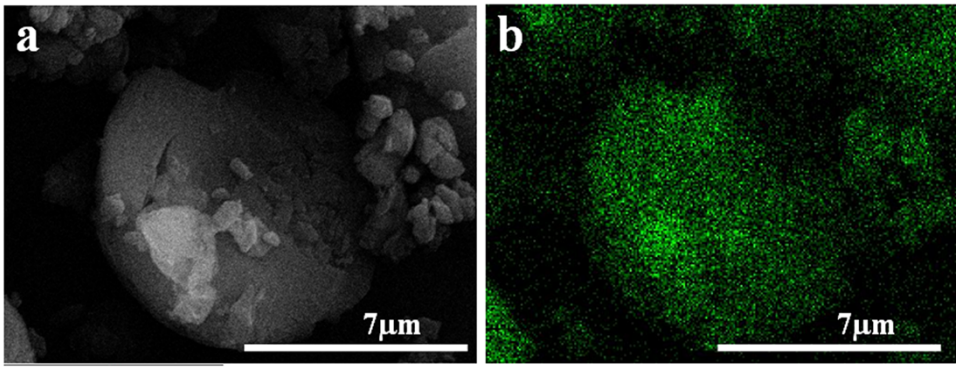

Fig.S1 FE-SEM (a) and FE-SEM-EDX mapping (b) of the carbon microspheres after soaking in zinc sulphate solution (green indicates Zn). Note: FE-SEM and FE-SEM-EDX mapping images are at the same magnification.

The zinc precursor-carbon microspheres composites obtained were porous spheres with a

diameter of about 9 μm (see the SEM images in Fig. S2a). The inset was the particles size distribution. Fig. S2b was the XRD pattern of the composite spheres. The only peak was attributed to the amorphous carbon.

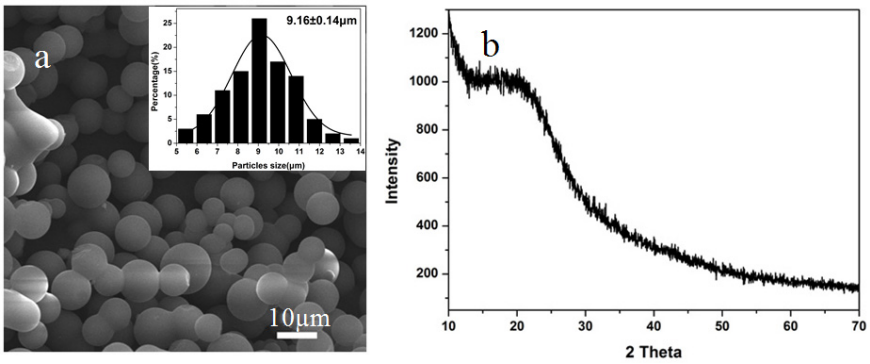

Fig.S2 SEM (a) and XRD pattern (b) of the zinc precursor-carbon microspheres composites

The crystalline structures of the as-prepared hierarchical multi-shelled ZnO porous hollow spheres were investigated by X-ray diffraction (XRD) along with the structure of commercial ZnO powder for comparison (Figure S3). All reflection peaks are exactly indexed to a pure hexagonal wurtzite ZnO structure (JCPDS card no. 36-1451, space group: P63mc, a = b=3.2499Å, c=5.2066Å), with no additional peaks detected, suggesting that the as-synthesized samples are of high phase purity.

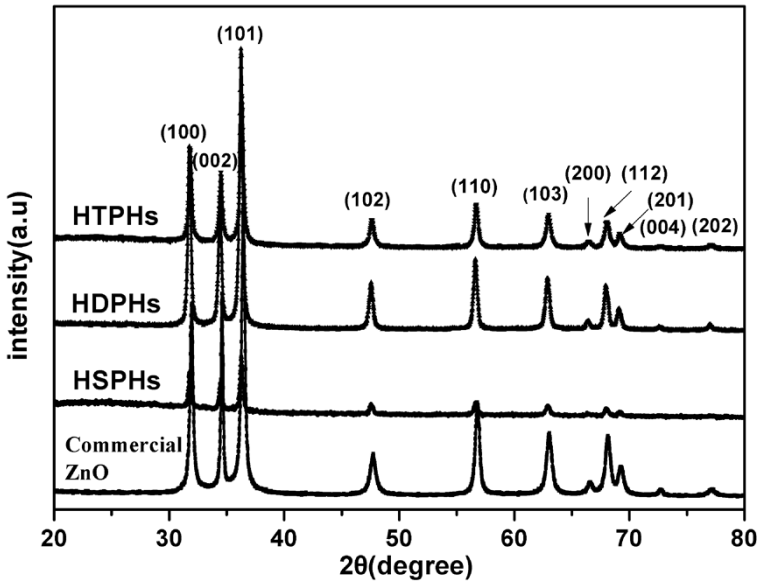

Fig.S3 XRD patterns of the as-prepared hierarchical multi-shelled ZnO porous hollow spheres and commercial ZnO.

Table S1: Specific surface area, pore volume and average pore size of the hierarchical multi-shelled ZnO porous hollow spheres.

Sample	BET Surface Area (m^2/g)	Pore Volume(cm^3/g)	Pore Size(nm)
HTPHs	25.13	0.09	23.2
HDPHs	19.03	0.07	25.5
HSPHs	10.41	0.04	19.0

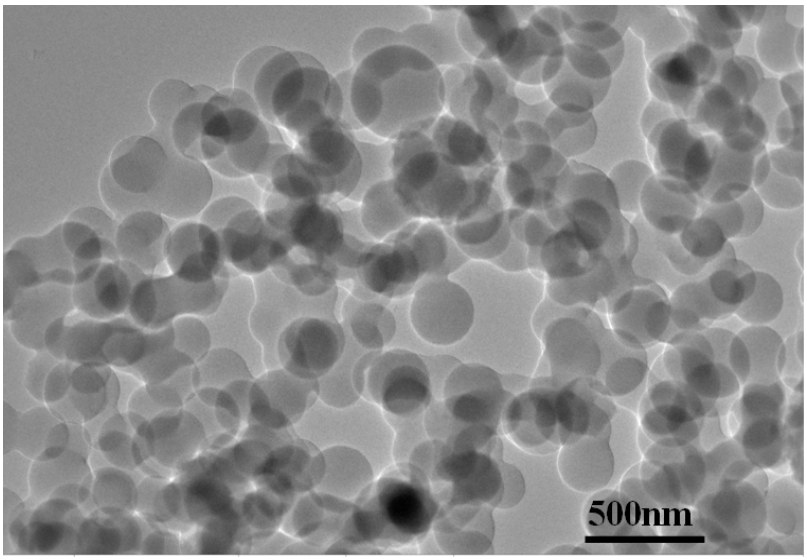

Fig. S4 TEM images of the carbon microspheres

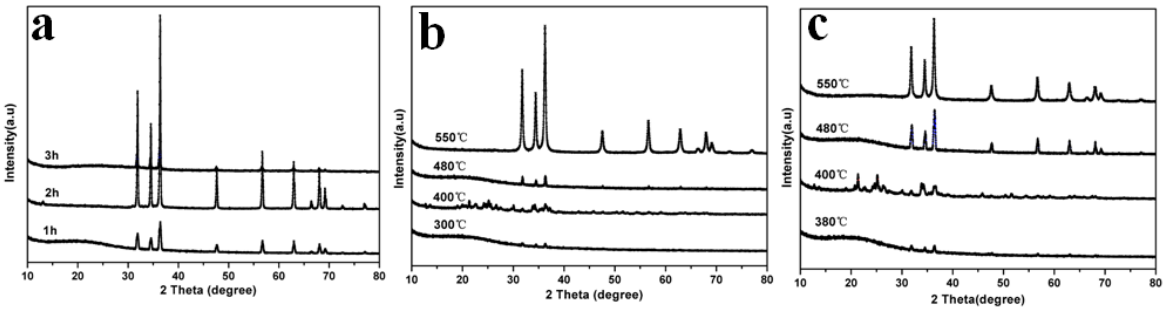

Fig. S5 XRD patterns of the zinc precursor-carbon microspheres (a) calcined directly at 550℃ for 1h, 2h and 3h, respectively, (b) calcined at a heating rate of 5℃/min to 300℃, 400℃, 480℃, and 550℃ for 3 hours, respectively. (c) The zinc precursor-carbon microspheres were calcined at a heating rate of 2℃/min to 300℃, 400℃, 480℃, and 550℃ for 3 hours, respectively.

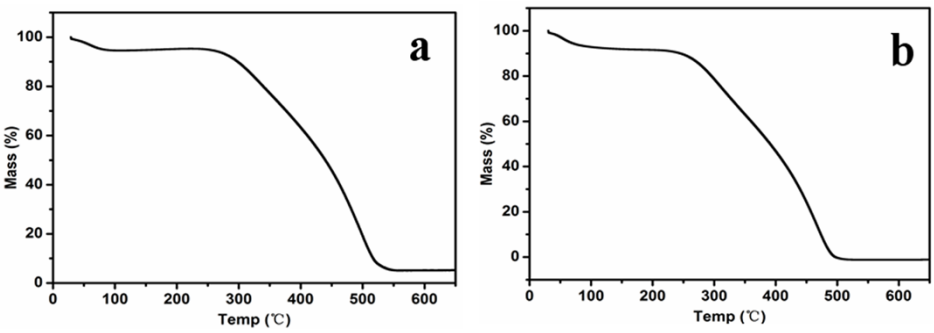

Fig. S6 TG curves of the zinc precursor-carbon microspheres composites obtained at different heating rates: (a) heating rate of 5℃/min and (b) heating rate of 2℃/min.

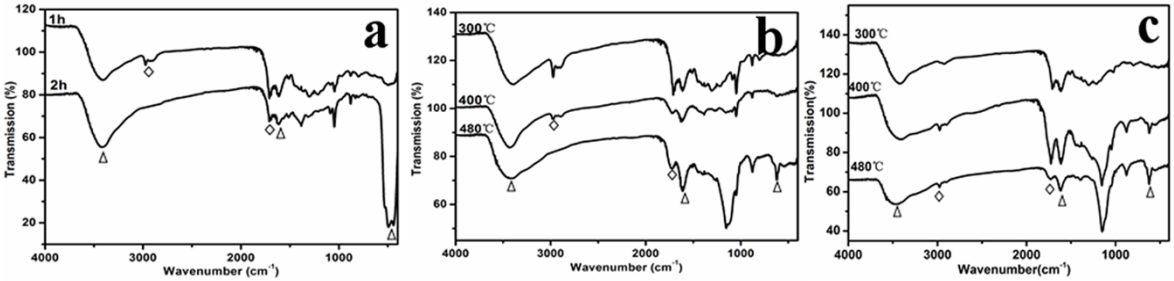

Fig. S7 FT-IR spectra of the zinc precursor-carbon microspheres composites obtained at different calcination stages with different heating rates: (a) products obtained when directly heating at 550℃ for 1h and 2h; (b) products obtained at 300℃, 400℃ and 480℃ with a heating rate of 5℃/min; (c) products obtained at 300℃, 400℃ and 480℃ with a heating rate of 2℃/min. (indicates the characteristic peaks of carbonaceous templates, and indicates the characteristic peaks of ZnO)

From the TG curves, these two procedures, the oxidation of carbonaceous microspheres and the decomposition of the zinc precursor (zinc sulphate), couldn't be distinguished clearly. Combined with the FT-IR spectra, it's obvious to see the degradative oxidation of carbonaceous templates is accompanied with the gradual formation of ZnO during the calcination procedures. These results were consistent with the XRD information in Fig. S5. And it's due to this that the sequential template processes could take place, which would be beneficial to the formation of multishelled ZnO porous hollow spheres.

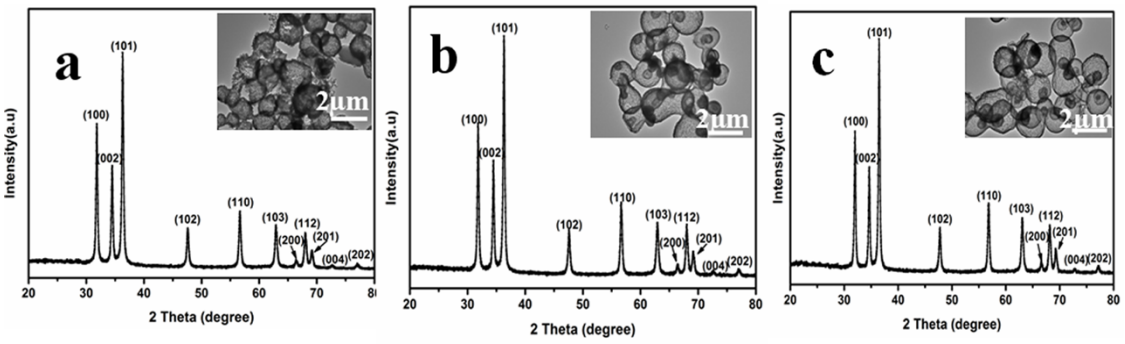

Fig. S8 XRD results (a, b, c) and TEM images (insets in Fig. a, b and c) of hierarchical single-, double- and triple-shelled ZnO porous hollow spheres after the fifth photocatalysis experiment, respectively.

From the XRD and TEM analysis, we could see that the crystal type and the morphologies are nearly the same as products before photocatalysis, which indicates the rigidity and photostability of the samples.