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Supporting Information

Self-Assembled Synthesis of Hierarchical Zn_2GeO_4 Core-Shell Microspheres with Enhanced Photocatalytic Activity

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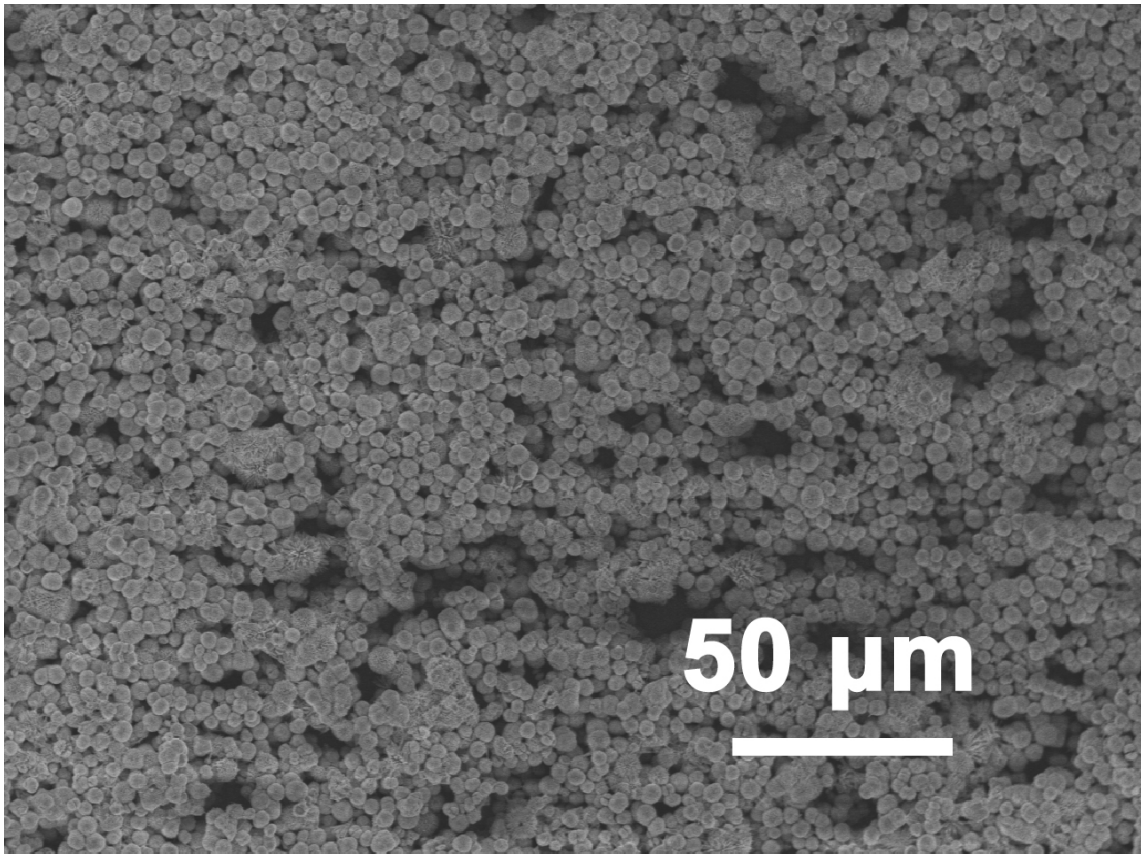

Fig. S1 Low-magnified SEM image of hierarchical Zn_2GeO_4 core-shell microspheres synthesized through a facile hydrothermal method, demonstrating that the Zn_2GeO_4 microspheres are successfully synthesized in large quantities and with a size distribution about 5-6 μm.

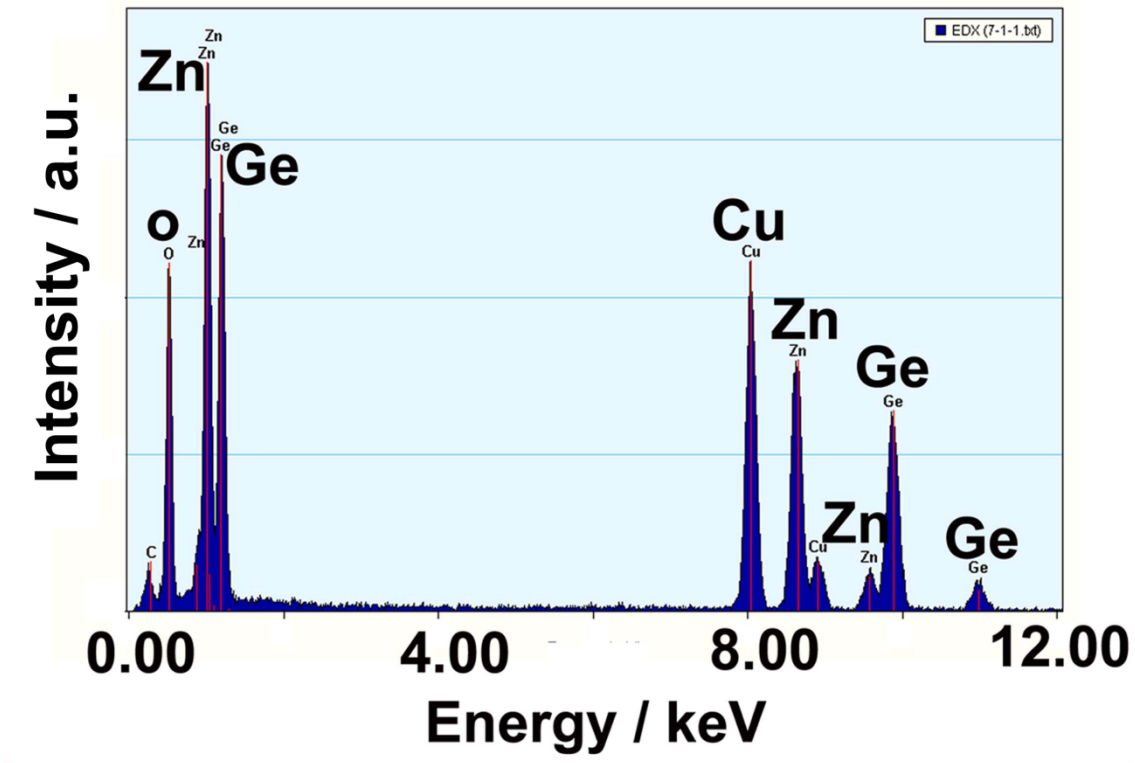

Fig. S2 Energy dispersive X-ray spectroscopy (EDS) spectrum of the as-prepared hierarchical Zn_2GeO_4 core-shell microspheres obtained under a mild hydrothermal condition. The result determines that the atomic ratio of Zn, Ge and O is around 2:1:4, which well matches the crystalline phase Zn_2GeO_4. The Cu signal comes from the copper grid.

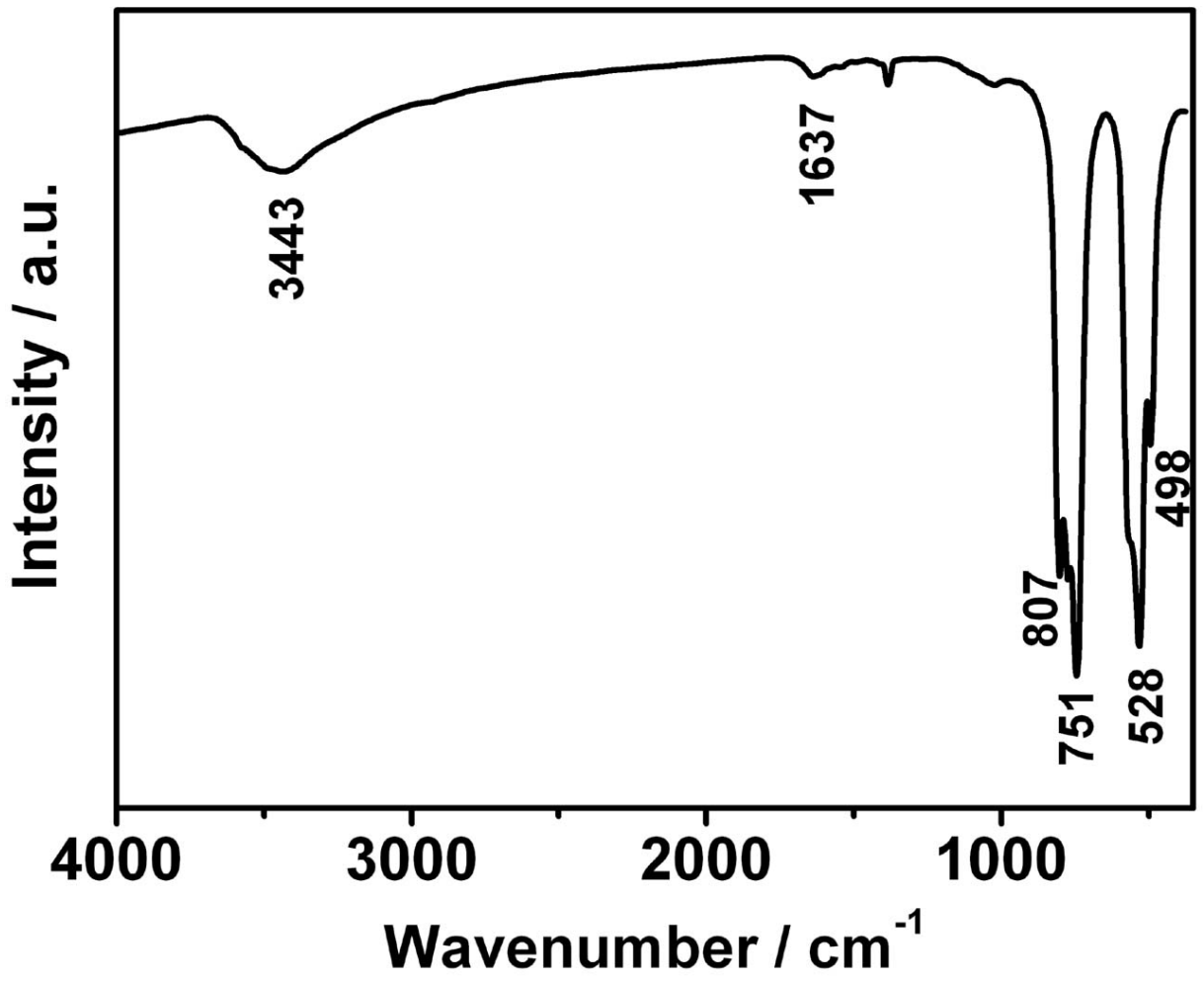

Fig. S3 FTIR spectrum of hierarchical Zn_2GeO_4 core-shell microspheres. Strong absorptions at *ca.* 498, 528, 751 and 807 cm^{-1} are observed for the as-prepared Zn_2GeO_4 sample. The bands can be attributed to the vibration modes of ZnO_4 and GeO_4 tetrahedral units in Zn_2GeO_4. A small absorption band at 1637 cm^{-1} and a broad absorption band at 3443 cm^{-1} are derived from water molecules on the surface. The result further demonstrates the purity of the resulting Zn_2GeO_4 samples (*Chem. Commun.*, 2011, **47**, 10719-10721; *CrystEngComm*, 2013, **15**, 382-389; *Solid State Commun.*, 2011, **151**, 1036-1041.).

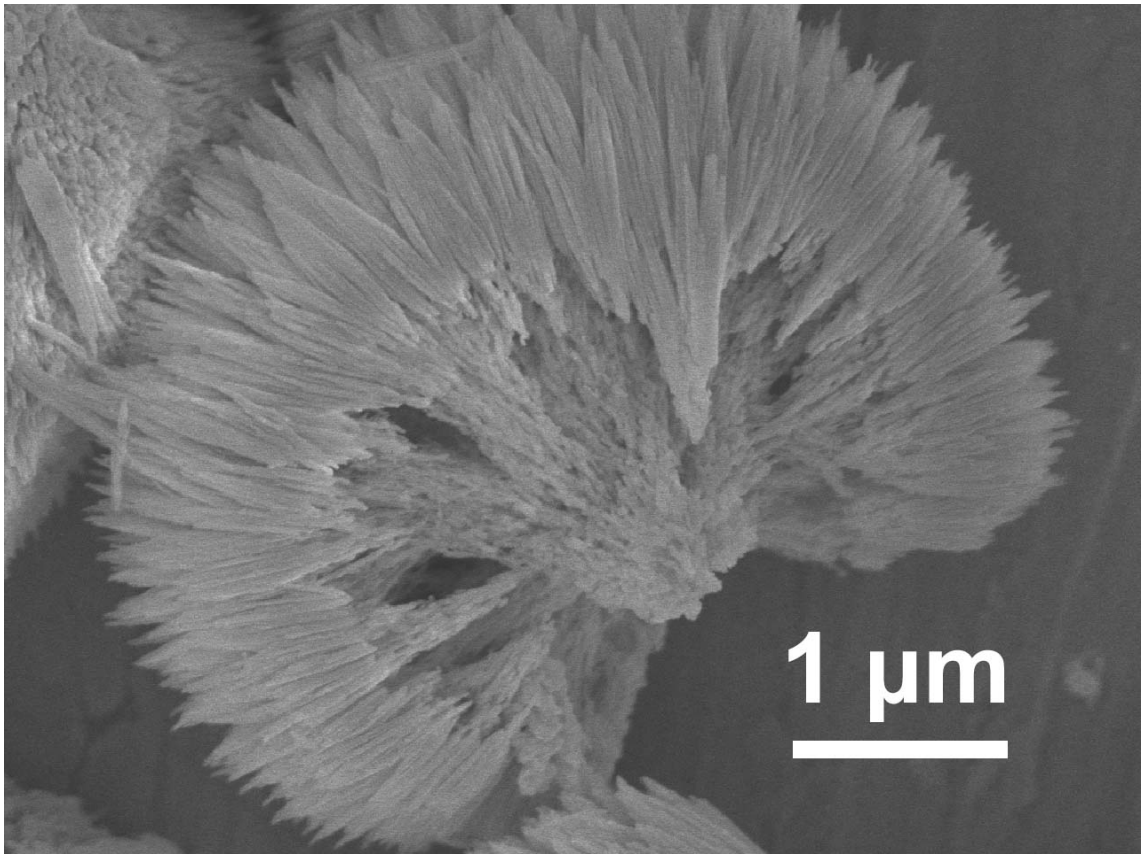

Fig. S4 SEM image of a cracked Zn_2GeO_4 microsphere, showing that the as-obtained Zn_2GeO_4 microspheres are composed of two parts. The interior region has a core consisting of stacked nanoparticles. External shell is built from ordered parallel and overlapped rod-like microcrystals with a diameter *ca.* 50-100 nm and length *ca.* 1-2 μm. The results demonstrate that the Zn_2GeO_4 microspheres possess a typical hierarchical core-shell structure.

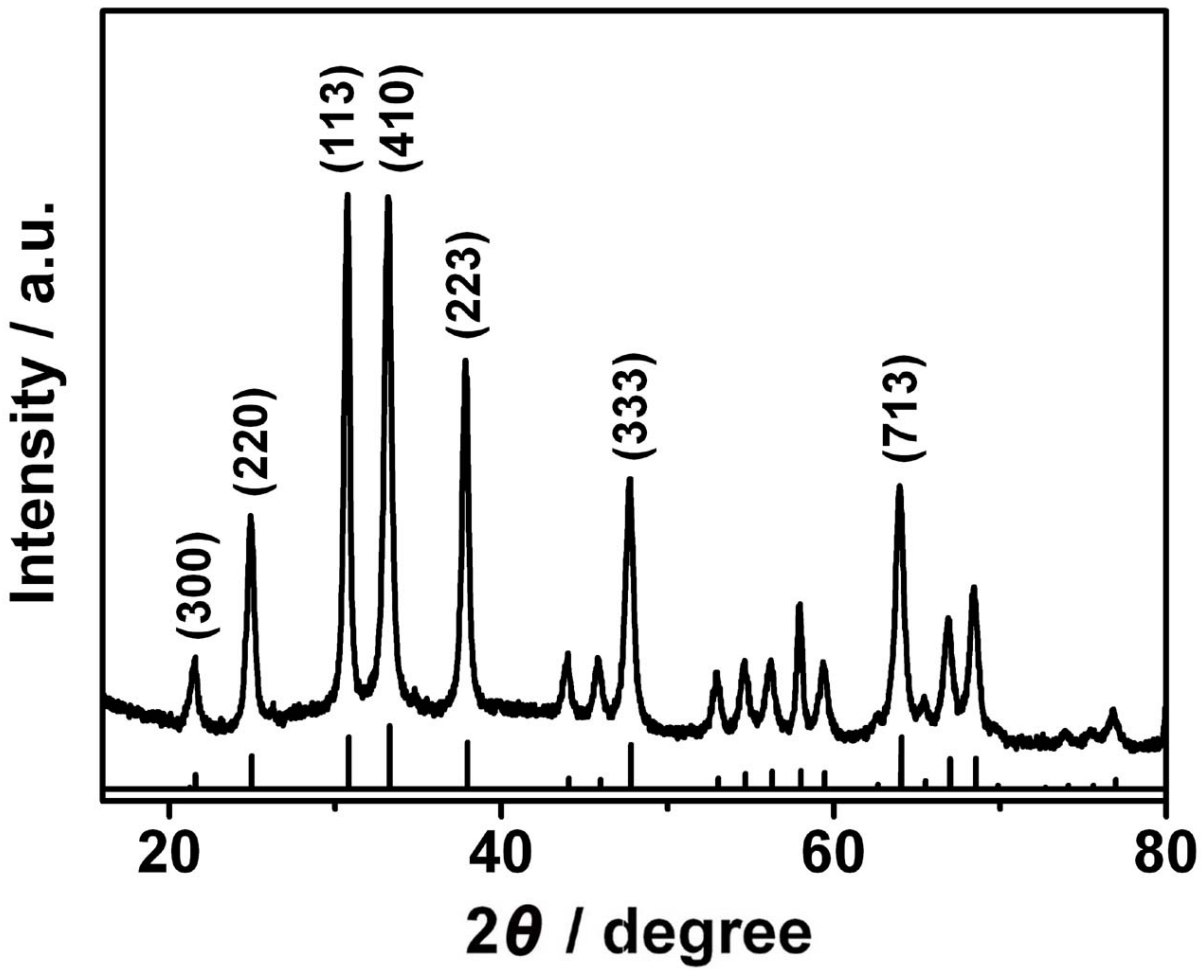

Fig. S5 XRD pattern of the intermediate collected at 1 h. It demonstrates that the intermediates have already been Zn_2GeO_4 phase (JCPDS No. 11-0687).

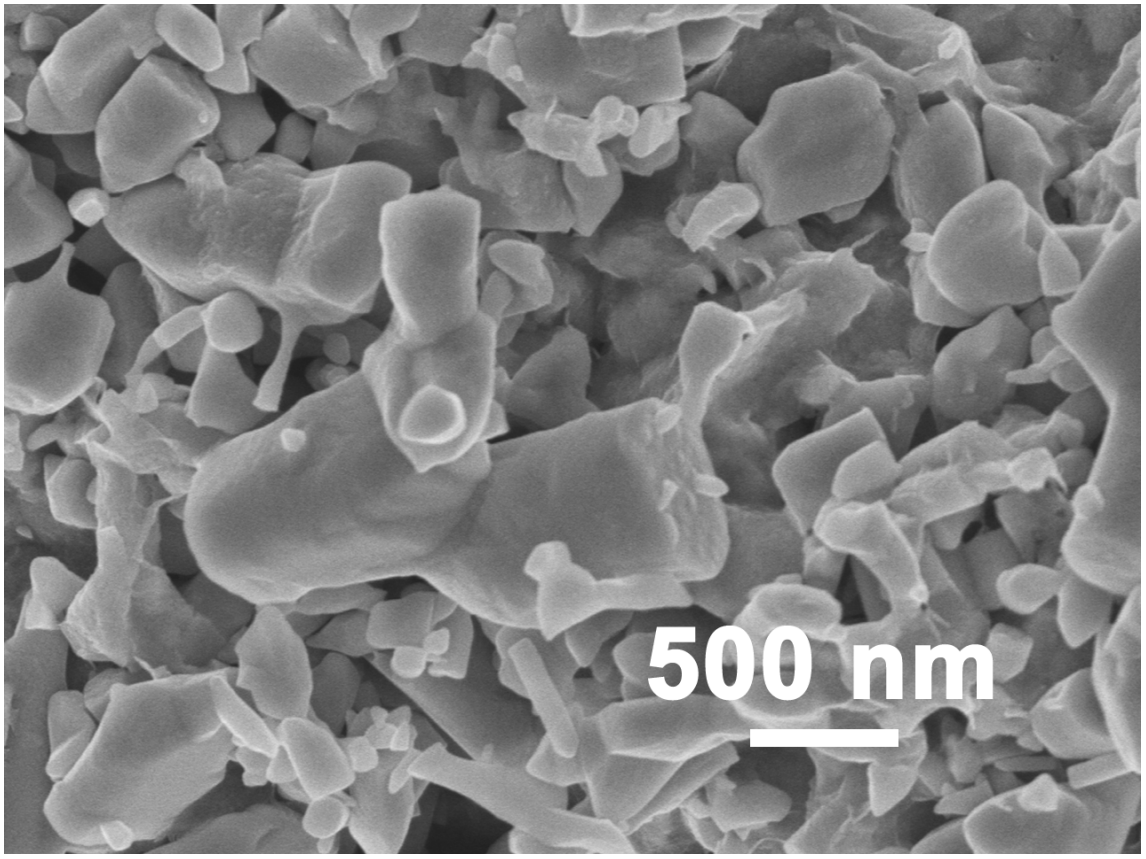

Fig. S6 SEM image of the bulk Zn_2GeO_4 synthesized in the pure solvent of TETA molecules. It demonstrates that only irregular bulk Zn_2GeO_4 structures are obtained.

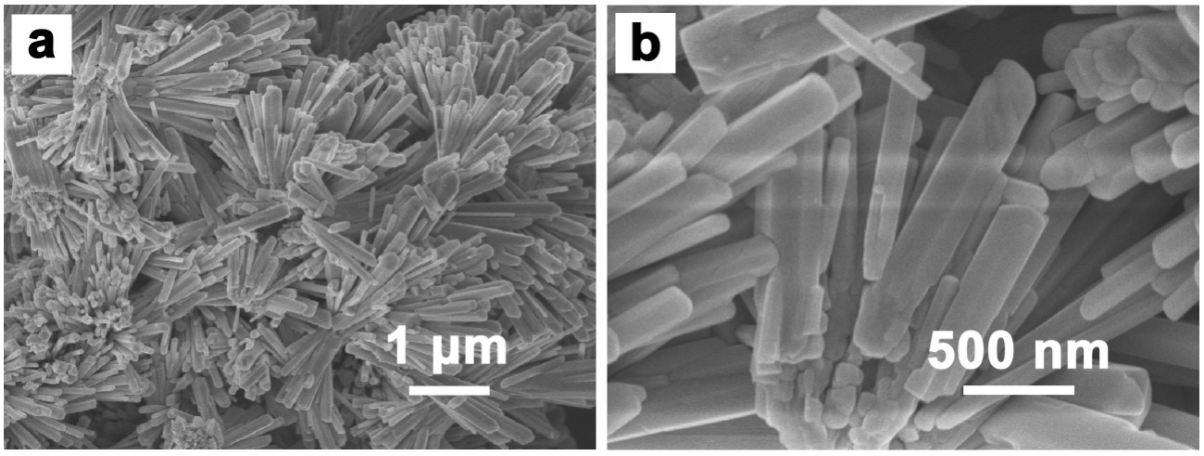

Fig. S7 SEM image of the Zn_2GeO_4 rods synthesized in the absence of TETA molecules. It displays that only prismatic rod-like structure is obtained.

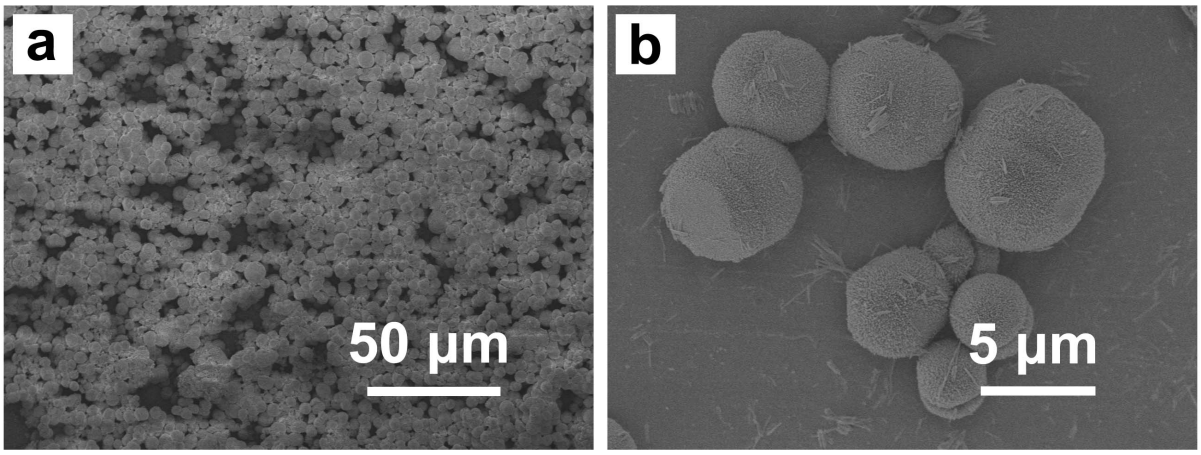

Fig. S8 SEM images of the hierarchical Zn_2GeO_4 core-shell microspheres after the catalytic reaction recycled for 4 times. It can be suggested the high morphology stability of hierarchical Zn_2GeO_4 core-shell microspheres towards photocatalytic degradation of methyl orange (MO).

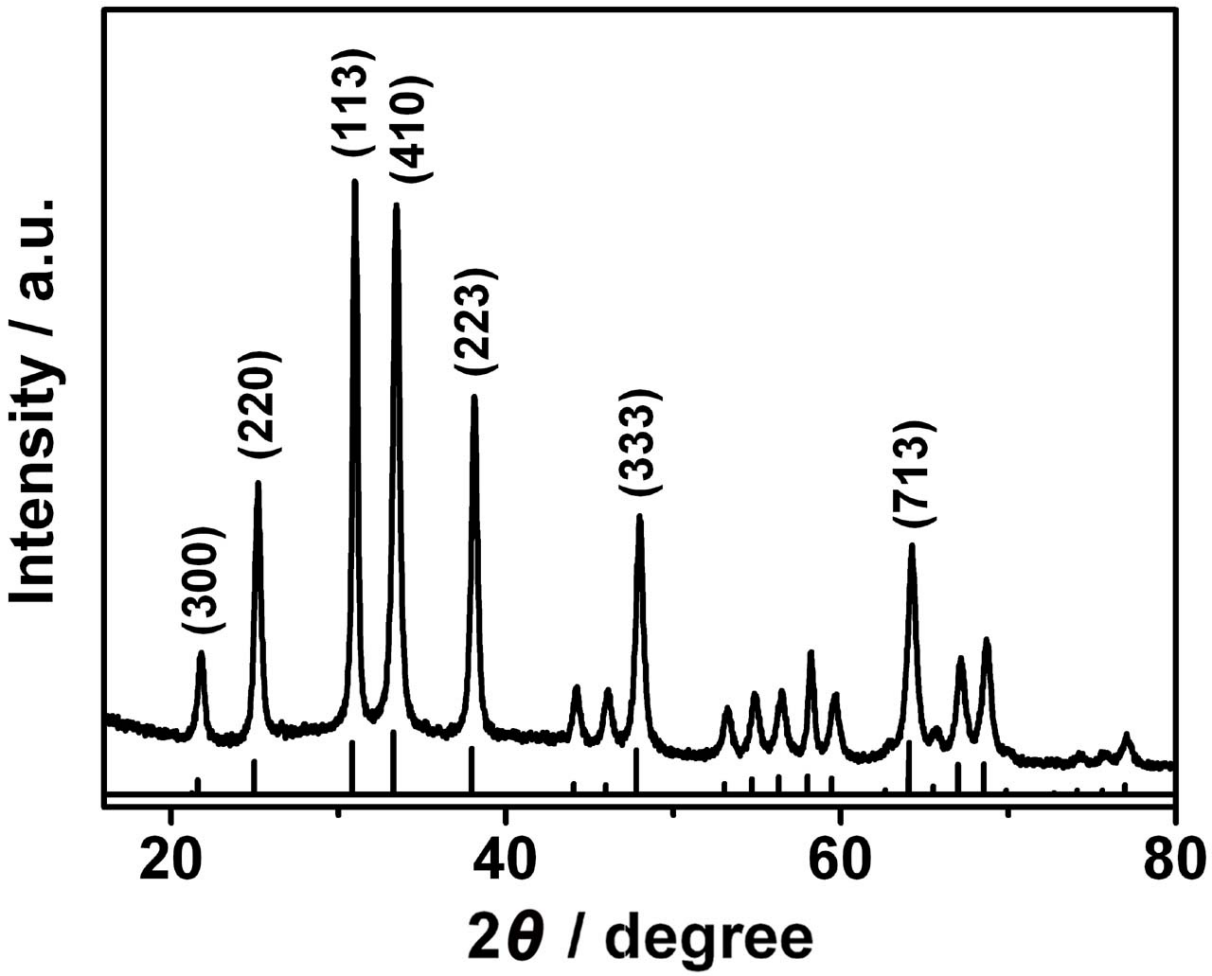

Fig. S9 XRD of the hierarchical Zn_2GeO_4 core-shell microspheres after the catalytic reaction is recycled for 4 times. It further confirms the high stability of phase structure of the hierarchical Zn_2GeO_4 core-shell microspheres towards photo-degradation of methyl orange (MO).

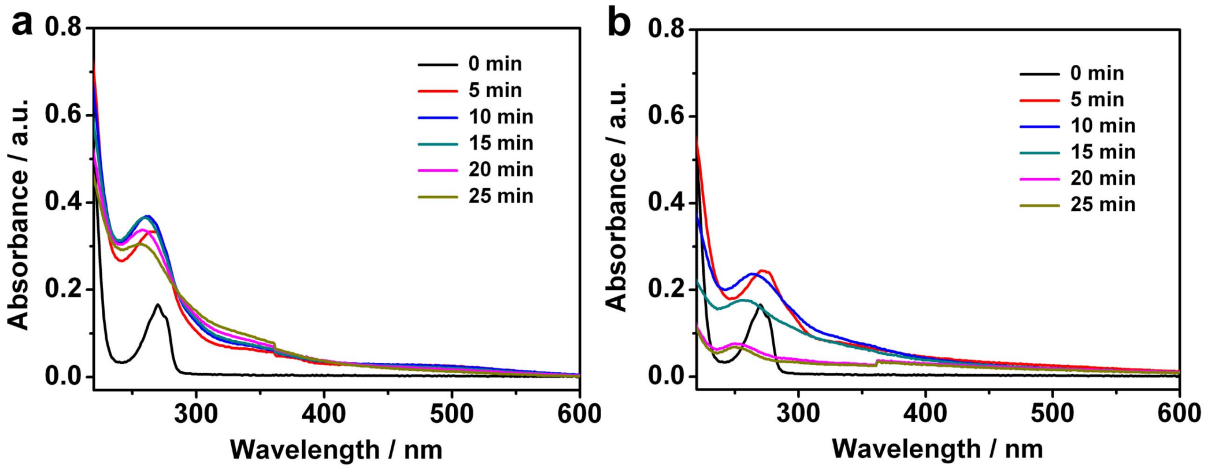

Fig. S10 (a-b) UV-Vis absorption spectra of phenol solution without (a) and with (b) hierarchical Zn_2GeO_4 core-shell microspheres catalysts after various times of UV exposure. Fig. S10a shows that the decomposition of phenol is negligible in a blank experiment (without catalyst), demonstrating that the highly stable of the phenol. Fig. S10b displays that the absorption maximum of phenol solution after catalyzed by hierarchical Zn_2GeO_4 core-shell microspheres gradually decreases during UV irradiation, indicating the as-prepared hierarchical Zn_2GeO_4 core-shell microspheres own efficient UV photocatalytic activity towards photocatalytic degradation of phenol. The increase of the absorption peak intensity may be attributed to the structure transformation of the phenol to the corresponding intermediates during decomposition (*Appl. Catal. B: Environmental*, 2011, **102**, 19-26; *Intermetallics*, 2014, **52**, 9-14; *Inorg. Chem.*, 2014, **53**, 4989-4993.).