Alpha-calcium sulfate hemihydrate used as water-soluble template for synthesis of ZnO hollow microspheres

Jie Li^a, Luchao Wu^a, Caiyun Jia^a, Qiaoshan Chen^b, Zirong Song^a, and Baohong Guan^{a,c,*}

^aDepartment of Environmental Engineering, Zhejiang University, Hangzhou 310058, China.

^bDepartment of Environmental Science and Engineering, Fuzhou University, Minhou 350108, China.

^cKey Laboratory of Environment Remediation and Ecological Health, Ministry of Education, College of Environmental Resource Sciences, Zhejiang University, Hangzhou 310058, China.

*Corresponding Author E-mail addresses: guanbaohong@zju.edu.cn. (B. H. Guan)

Supporting information

Characterization. The fragments of ZnO seed layers after dissolving α -HH microspheres template in water was investigated by scanning electron microscopy (SEM, Hitachi SU-8010, Japan). The sliced α -HH/ZnO core-shell microspheres, the sliced α -HH/ZnO core-shell microspheres during water rinsing and the sliced ZnO hollow microspheres were characterized by transmission electron microscopy (TEM, HT-7700, Japan) and scanning electron microscopy (SEM, Hitachi SU-8010, Japan), accompany with the EDX-mapping. The infrared spectrum at range of 400-4000 cm⁻¹ with 2 cm⁻¹ resolution was determined by FTIR spectrometer (NicoLET iS50 , Thermo Scientific, USA) using KBr self-supported pressing technique to analyze the groups of α -HH microspheres. Zeta potential analyzer (Malvern Zetasizer Nano ZS90, Malvern Instrument, UK) was used to analyze the charge characteristics of samples. The optical properties of ZnO hollow microspheres and ZnO solid microspheres in comparison were evaluated with diffuse reflectance spectra (DRS) in UV-vis region. The BET surface area was measured by a nitrogen adsorption apparatus (JW-BK132F, Beijing JWGB Sci. & Tech., China).

Particle size distribution for α -HH, ZnO hollow microspheres and ZnO solid particles was measured by laser particle size analyzer (Malvern Zen 3600, Malvern, UK).



Fig. S1 Particle size distribution of (a) α -HH, (b) α -HH/ZnO seed layers, (c) α -HH/ZnO core-shell microspheres, (d) ZnO hollow microspheres and (e) ZnO solid particles.



Fig. S2 Fragments of ZnO seed layers after dissolving α -HH microspheres coated with seed layers of ZnO in water.



Fig. S3 SEM images of the α -HH microspheres (a), α -HH/ZnO seeds (b), α -HH/ZnO core-shell microspheres after 2nd deposition-precipitation for 0.5h(c), 1h(d), 2h(e), 3h(f), 4h(g), (h)ZnO hollow microspheres after α -HH microspheres template removal by water rinse.



Fig. S4 SEM (a1) and elemental line scanning (a2) and EDX-mapping (a3-a6) of the sliced α -HH/ZnO core-shell microspheres; SEM (b1) and elemental line scanning (b2) and EDX-mapping (b3-b6) of the sliced α -HH/ZnO core-shell during rinsing process, SEM (c1) and elemental line scanning (c2) and EDX-mapping (c3-c6) of the sliced ZnO hollow microspheres.



Fig. S5 TEM and EDX elemental mapping of the ZnO hollow microspheres.

FTIR spectra shows that the characteristic peaks emerging at 3609 cm⁻¹ and 3553 cm⁻¹ are attributed to vibration of O-H, while the peaks at 1412 cm⁻¹ and 1620 cm⁻¹ are assigned to COO- stretching vibrations of EDTA, indicating the incorporation of EDTA ions in α -HH microspheres.



Fig. S6 FTIR spectra of α -HH microspheres.



Fig. S7 Zeta (ζ) potentials of α -HH microspheres, ZnO nanoparticles and α -HH/ZnO seed layers.



Fig. S8 The UV-vis diffuse reflectance spectra (a,c) and Tauc's plot (b,d) for ZnO hollow microspheres and ZnO solid microspheres in the two parallel experiments.



Fig. S9 N_2 adsorption-desorption isotherm (BET) of the ZnO hollow microspheres and ZnO solid particles.