

Supplementary Material

Hierarchically-Structured TiO₂/MnO₂ Hollow Spheres Exhibiting the Complete Mineralization of Phenol

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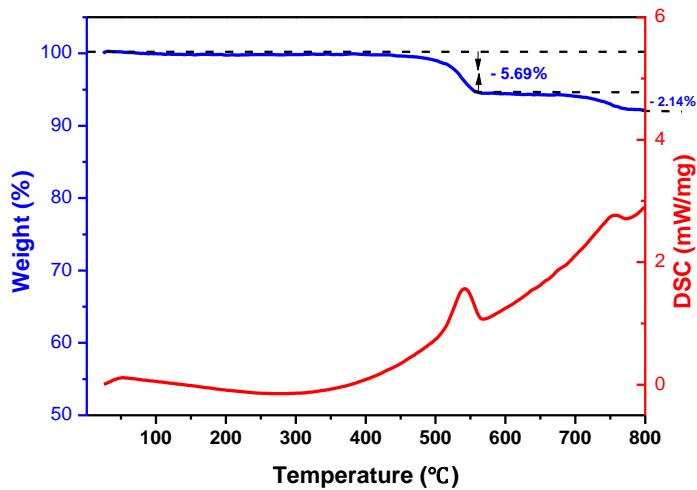


Figure S1. TGA and DSC curves of as-synthesized HTM spheres.

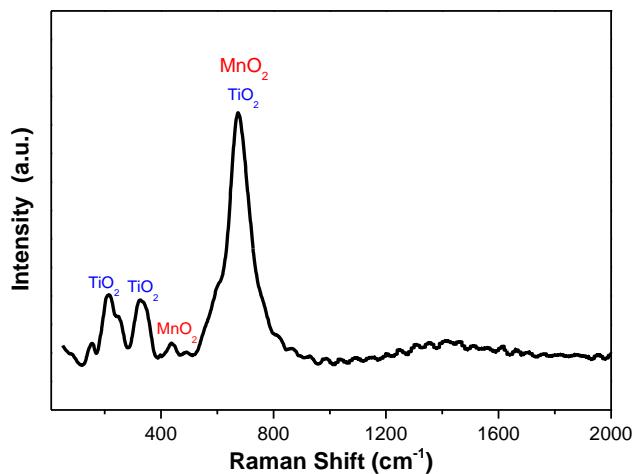


Figure S2. Raman spectra of as-synthesized HTM spheres.

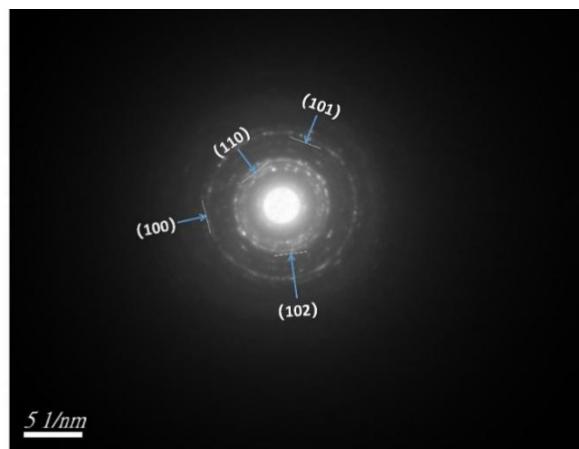


Figure S3. Selected electron area diffraction of the as-synthesized HTM spheres.

Table S1. the parameters of Ti and Mn in XPS spectrum for HTM sample.

| | Ti2p _{3/2} Ti ³⁺ | Ti2p _{3/2} Ti ⁴⁺ | Ti2p _{1/2} Ti ³⁺ | Ti2p _{1/2} Ti ⁴⁺ | Mn2p _{3/2} Mn ³⁺ | Mn2p _{3/2} Mn ⁴⁺ |
|----------------|---|--------------------------------------|--------------------------------------|--------------------------------------|---|---|
| peak positions | 458.05eV | 459.05eV | 463.62eV | 464.84eV | 641.75eV | 643.26eV |
| FWHM | 1.5 | 1.6 | 1.9 | 2.12 | 2.13 | 2.69 |
| area | 3274.46 | 4501.371 | 1637.23 | 2250.686 | 17309.46 | 17710.5 |

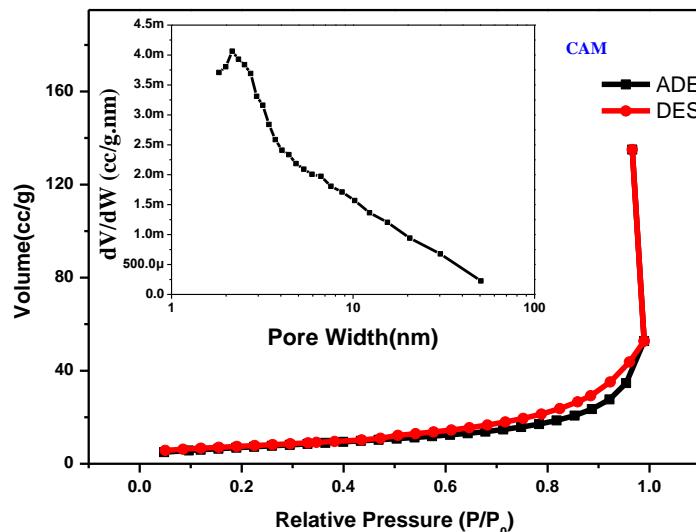


Figure S4. N₂ adsorption-desorption isotherms and pore size distribution (insert) of CAM.

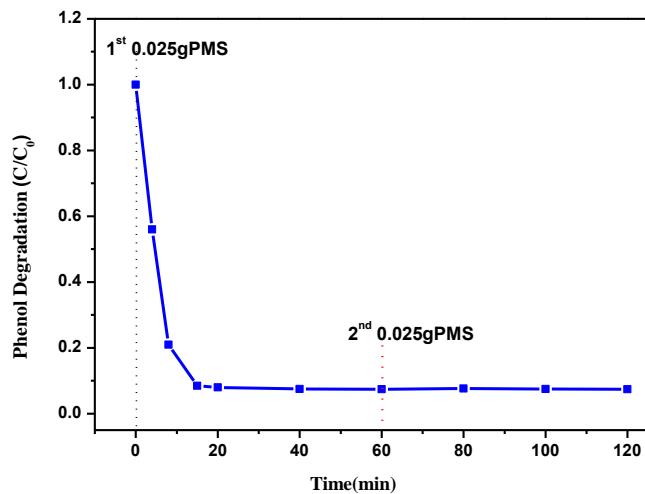


Figure S5. Effect of oxidant on the degradation of Phenol for HTM.

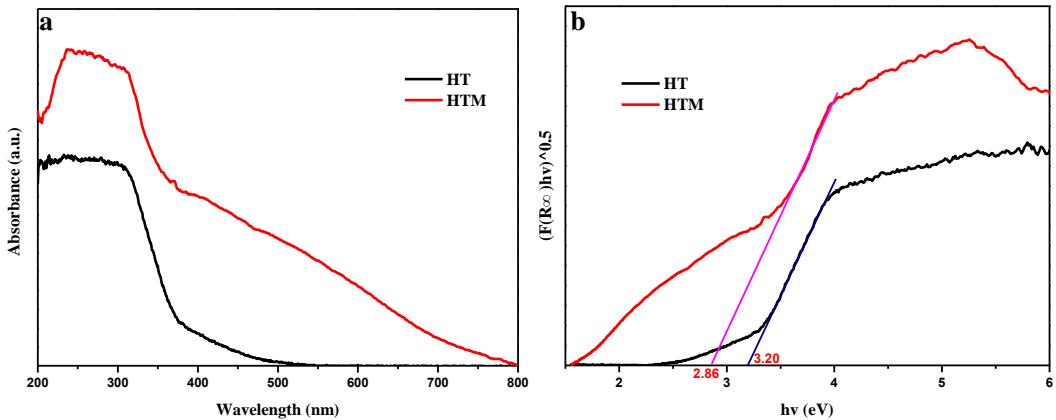


Figure S6. (a) UV-vis absorption spectra of HTM and hollow TiO_2 spheres; (b) Band gap energy (E_g) of HTM and hollow TiO_2 spheres.

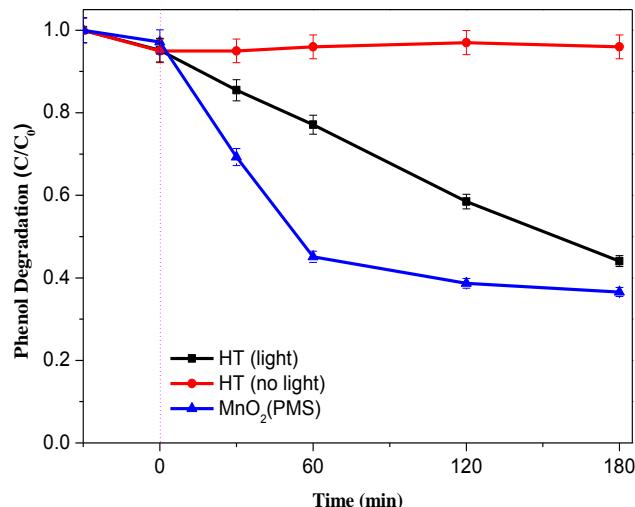


Figure S7. Degradation of phenol for hollow TiO_2 photocatalyst and MnO_2 under simulated solar light irradiation.

Table S2. comparative degradation rate of various catalysts.

| Catalyst | First-order Rate Constant (min^{-1}) |
|-----------------------------|---|
| HT(oxidation) | 0.00123 ± 0.00013 |
| CAM(oxidation) | 0.00675 ± 0.00058 |
| HTM(oxidation) | 0.10887 ± 0.005 |
| HTM(photo-degradation) | 0.0623 ± 0.019 |
| Mn-100 [1] | 0.069 |
| 5wt% Co/ MnO_2 [2] | 0.0425 ± 0.0018 |

References

- [1] Y. Wang, H. Sun, H.M. Ang, M.O. Tadé, S. Wang, 3D-hierarchically structured MnO_2 for catalytic oxidation of phenol solutions by activation of peroxymonosulfate: Structure dependence and mechanism, *Appl. Catal. B-Environ.*, 164 (2015) 159-167.
- [2] H. Liang, H. Sun, A. Patel, P. Shukla, Z.H. Zhu, S. Wang, Excellent performance of mesoporous $\text{Co}_3\text{O}_4/\text{MnO}_2$ nanoparticles in heterogeneous activation of peroxymonosulfate for phenol degradation in aqueous solutions, *Appl. Catal. B-Environ.*, 127 (2012) 330-335.

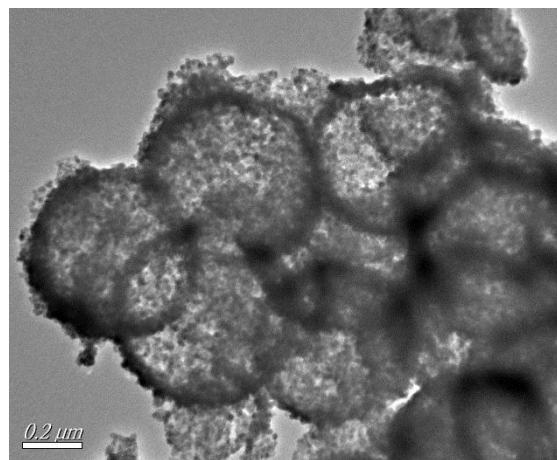


Figure S8. TEM image of HTM after cycles.

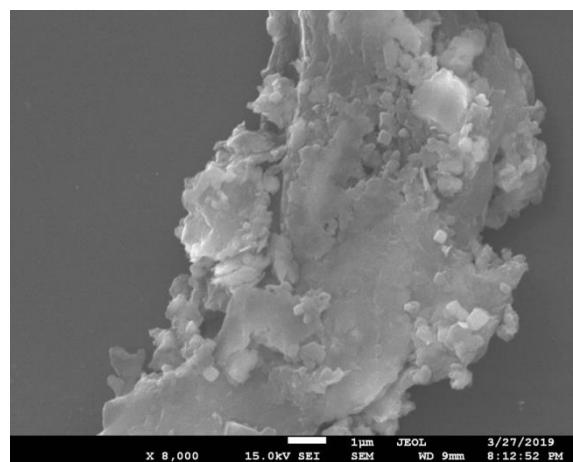


Figure S9. SEM of CAM.

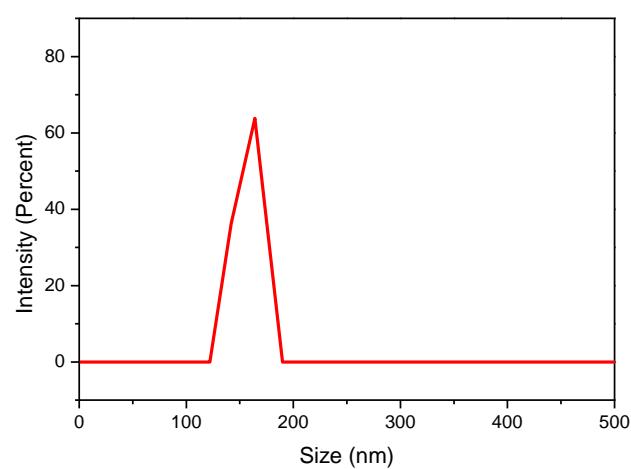


Figure S10. Particle distribution of as-synthesized MnO₂ nanoparticles.