Electronic Supplementary Information

Template-free Solvothermal Synthesis of $WO_3/WO_3 \cdot H_2O$ Hollow Spheres and Their Enhanced Photocatalytic Activity from The Mixture Phase Effect

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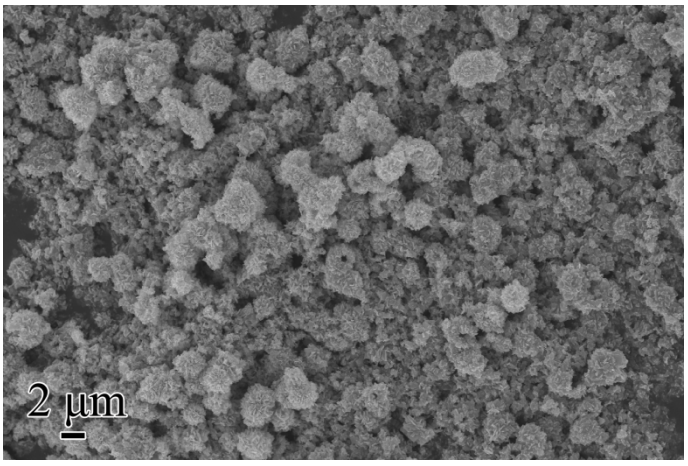
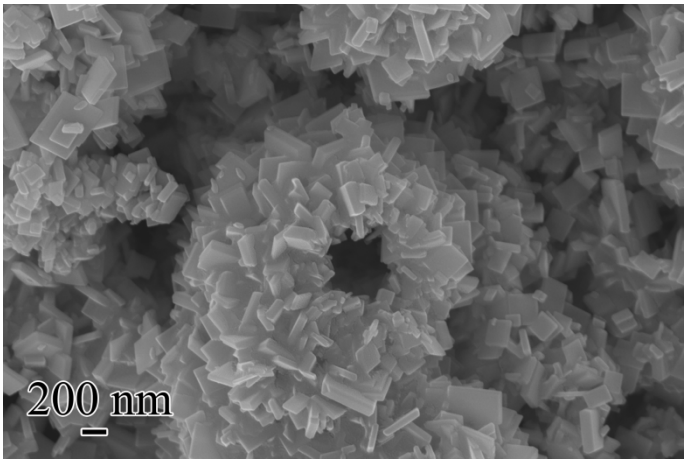
The morphology of the sample synthesized with DI H_2O as the solvent

Fig. S1 shows the SEM images of the sample synthesized with DI H_2O as the solvent. The obtained product was composed of both individual nanoflakes and hollow spherical aggregates from nanoflakes with different sizes and shapes.



(a)

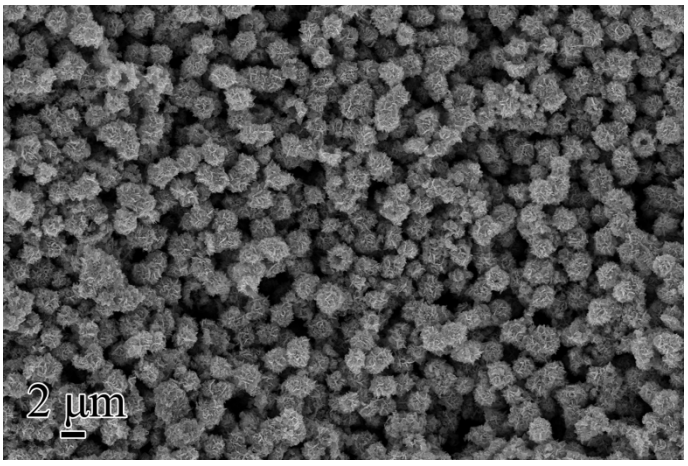


(a)

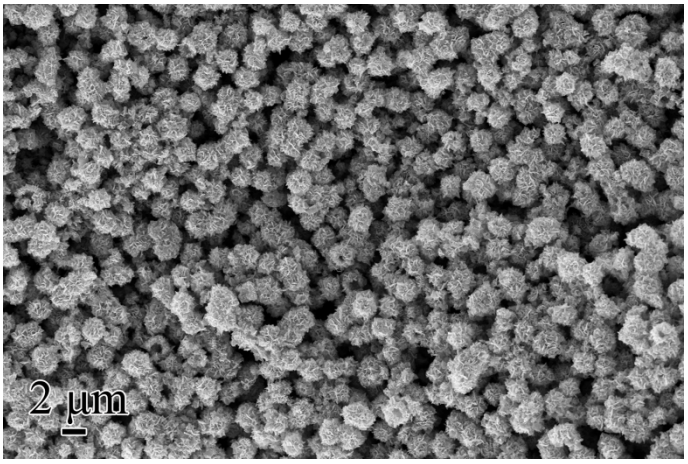
Fig. S1 SEM images of the sample synthesized with DI H_2O as the solvent: (a) with a lower magnification, and (b) with a higher magnification on the center part of (a), respectively.

The morphology of samples calcinated at 350 °C and 500 °C, respectively

Fig. S2 (a) and (b) show the SEM images of samples calcined at 350 °C and 500 °C, respectively. It could be found that samples after calcination kept their hollow sphere morphology.



(a)



(b)

Fig. S2 SEM images of the samples calcinated at (a) 350 °C and (b) 500 °C.

Estimation of the CB and VB edges of WO_3 and $WO_3 \cdot H_2O$

The conduction band (CB) bottom values and valence band (VB) top values of the two semiconductors could be estimated by Eq. (S1) and Eq. (S2):[1]

$$E_{CB} \approx X_{comp} - E^e - 1/2E_g \qquad \text{(S1)}$$

$$E_{VB} = E_{CB} + E_g \qquad \text{(S2)}$$

where E^e equals 4.5 eV and X_{comp} is the the electronegativity of a compound.

X_{comp} could be calculated from Eq. (S3):[2]

$$X_{comp} = (X_1^r X_2^s \cdots X_{n-1}^p X_n^q)^{1/N} \qquad \text{(S3)}$$

where X_n, n and N are the electronegativity of the constituent atom, the number of species, and the total number of atoms in the compound, respectively. The superscripts *r, s, p* and *q* refer to the numbers of the atoms 1, 2, n-1, and n, respectively, in the molecule. Thus, $r + s + \cdots + p + q = N$.

The values of X_n could be found from in literature[3] that X_O = 7.54 eV, X_W = 4.4 eV, and X_H = 7.18 eV, respectively.

Thus, for WO_3:

$X_{WO3} = (4.4*7.54^3)^{1/4} = 6.59$ eV

$E_{CB} = 6.59 - 4.5 - 0.5*2.72 = 0.73$ eV

$E_{VB} = 0.73 + 2.72 = 3.45$ eV

For $WO_3 \cdot H_2O$:

$X_{WO3 \cdot H2O} = (4.4*7.54^4*7.18^2)^{1/7} = 6.885$ eV

$E_{CB} = 6.885 - 4.5 - 0.5*2.35 = 1.21$ eV

$E_{VB} = 1.21 + 2.35 = 3.56$ eV

References:

1. P. Wang, B. Huang, X. Zhang, X. Qin, Y. Dai, H. Jin, J. Wei, M.H. Whangbo, *Chem. Eur. J.*, 2008, **14**, 10543.
2. R. T. Sanderson, Chemical Periodicity, Reinhold, New York, 1960.
3. R. G. Pearson, *Inorg. Chem.*, 1988, **27**, 734.