

Supporting Information

Effect of shell structure on photocatalytic activity of UCNPs/NMC: comparison of inert and active shells

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1. Materials

$\text{Y}(\text{CH}_3\text{COOH})_3 \cdot 4\text{H}_2\text{O}$, $\text{Yb}(\text{CH}_3\text{COOH})_3 \cdot 4\text{H}_2\text{O}$, $\text{Tm}(\text{CH}_3\text{COOH})_3 \cdot 4\text{H}_2\text{O}$,
 $\text{Ce}(\text{CH}_3\text{COOH})_3 \cdot 4\text{H}_2\text{O}$, $\text{Ho}(\text{CH}_3\text{COOH})_3 \cdot 4\text{H}_2\text{O}$, Oleic acid (OA), Octadecene (ODE)
and polyvinylpyrrolidone (PVP, $M_w = 40,000$) were purchased from Sigma-Aldrich.
NaOH, NH_4F , 2-aminoterephthalic acid ($\text{NH}_2\text{-BDC}$) and Chromium nitrate
nonahydrate were purchased from Greagent. Rhodamine B (RhB), 1,4-benzoquinone
(BQ) and ethylenediaminetetraacetate (EDTA) were also purchased from Adamas. All
the chemical reagents were used without further purification.

2. Synthesis of **Tm@Yb** nanoparticles

The 1 mmol of $\text{RE}(\text{CH}_3\text{COO})_3$ ($\text{RE}=78\%\text{Y}+20\%\text{Yb}$) were dissolved in 6 mL OA
and 15 mL ODE in a three-necked round-bottom flask. The core-shell **Tm@Yb**

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nanoparticles were dispersed in 10 mL of cyclohexane for the next step. Then, the next steps are the same as the synthetic method of the **Tm@Y** except that the 300 °C was kept for 100 mins under Ar flow atmosphere. The core-shell **Tm@Yb** nanoparticles were dispersed in 10 mL of cyclohexane for the next step.

*3. Synthesis of **Tm@Ce** nanoparticles*

The 1 mmol of RE(CH₃COO)₃ (RE=50%Y+20%Yb+30%Ce) were dissolved in 6 mL OA and 15 mL ODE in a three-necked round-bottom flask. Then, the next steps are the same as the synthetic method of the **Tm@Y** except that the 300 °C was kept for 90 mins under Ar flow atmosphere. The core-shell **Tm@Ce** nanoparticles were dispersed in 10 mL of cyclohexane for the next step.

*4. Synthesis of **Tm@Ho** nanoparticles*

The 1 mmol of RE(CH₃COO)₃ (RE=50%Y+20%Yb+30%Ho) were dissolved in 6 mL OA and 15 mL ODE in a three-necked round-bottom flask. Then, the next steps are the same as the synthetic method of the **Tm@Ho** except that the 300 °C was kept for 120 mins under Ar flow atmosphere. The core-shell **Tm@Ho** nanoparticles were dispersed in 10 mL of cyclohexane for the next step.

*5. Surface modification of **Tm@Y***

The 10 mL solution including 1 mmol **Tm@Y** was dispersed in 20 mL PVP solution (12.5 mg mL⁻¹). The mixture was magnetically stirred at room temperature for 24 h. Then, the product was separated by centrifugation and washed with ethanol by 3 times. The products were dispersed in ethanol solution for the next step.

6. Stability tests.

After every 60 minutes of photocatalytic operation under simulated solar

radiation, the photocatalyst was collected by centrifugation, washed three times with deionized water and ethanol, and dried at 60 °C. The regenerated photocatalyst is then reused for the next cycle under the same reaction conditions. The concentration of the solution was measured by ultraviolet visible spectrophotometer.

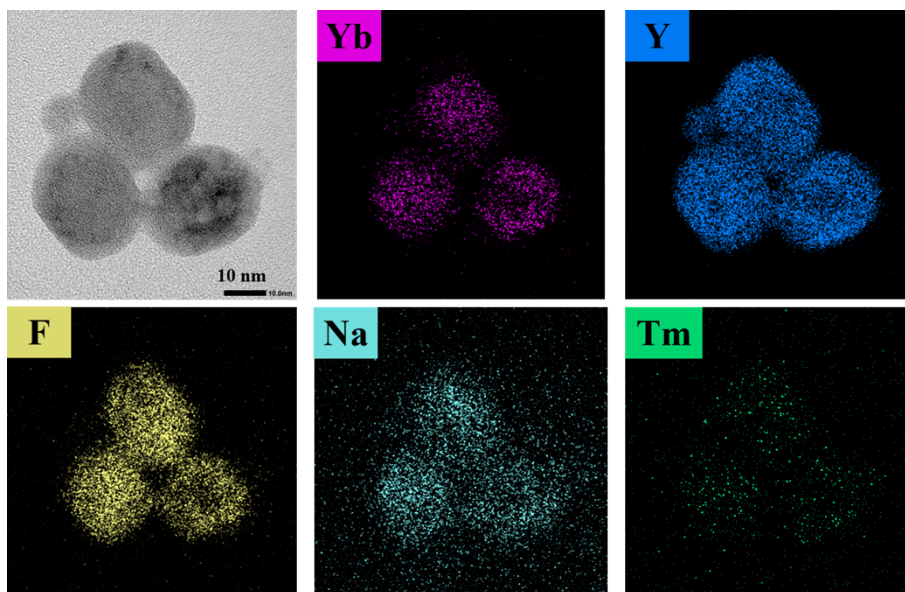


Fig. S1. Elemental mapping images of Tm@Y/NMC.

Fig. S2. XPS spectrum of **Tm@Ho/NMC**: (a) full-scan spectrum, (b) Na 1s, (c) F 1s, (d) Y 3d, (e) Ho 4d, (f) Yb 4d, and (g) Cr 2p.

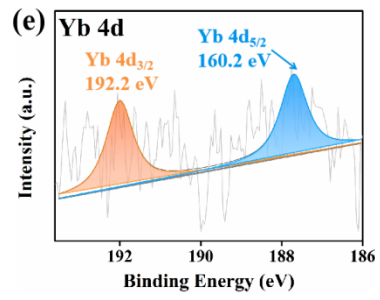


Fig. S3. XPS spectrum of **Tm@Yb/NMC**: (a) full-scan spectrum, (b) Na 1s, (c) F 1s, (d) Y 3d, (e) Yb4d, and (f) Cr 2p.

Fig. S4. XPS spectrum of **Tm@Ce/NMC**: (a) full-scan spectrum, (b) Na 1s, (c) F 1s, (d) Y 3d, (e) Ce 3d, (f) Yb 4d, and (g) Cr 2p.

Fig. S5. The UV-Vis-NIR diffuserefectance spectra of **Tm@Y/NMC**.

Fig. S6. The dark adsorption time curve of **Tm@Y/NMC**.

Fig. S7. Photodegradation of RhB solution by different photocatalysts under simulated solar light irradiation.

Fig. S8. Photocatalytic degradation of BPA over **Tm@Y/NMC** and **Tm@Yb/NMC** under simulated solar light irradiation.

Fig. S9. XRD patterns of **Tm@Y/NMC** photocatalyst before and after photocatalytic reaction.

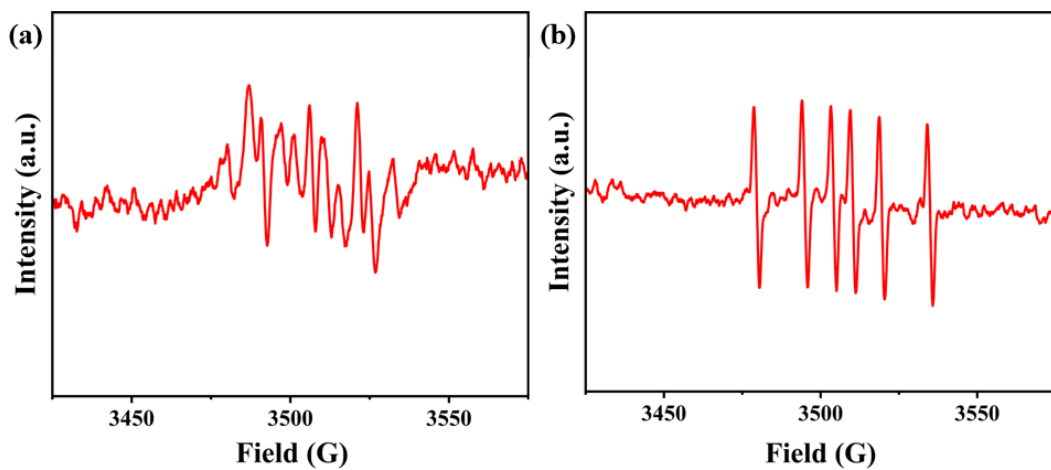


Fig. S10. EPR spectra for (a) $\text{DMPO}\cdot\text{OH}$ and (b) $\text{DMPO}\cdot\text{O}_2\cdot$ radicals of Tm@Y/NMC under light irradiation.

Fig. S11. Zeta potentials of **Tm@Yb/NMC**, **Tm@Ce/NMC**, **Tm@Ho/NMC**, and **Tm@Y/NMC**

Sample	k/ (min ⁻¹)
RhB	0.000
Tm/NMC	0.017
Tm@Yb/NMC	0.020
Tm@Y/NMC	0.029
Tm@Ho/NMC	0.023
Tm@Ce/NMC	0.026

Table. S1. Kinetic fitting results of RhB concentration evolution with irradiation time in the presence of different photocatalysts under simulated solar light irradiation.