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Supporting Information

The pH responsive upconversion fluorescence and photothermal conversion properties of $NaYF_4:Yb^{3+}/Er^{3+}@NaYF_4@MnO_2@Au$

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Synthesis of $NaYF_4$: Yb^{3+}/Er^{3+} (core) nanocrystals.

In a typical synthesis method, $YbCl_3 \cdot 6H_2O$ (0.18 mmol), $YCl_3 \cdot 6H_2O$ (0.8 mmol), $ErCl_3 \cdot 6H_2O$ (0.02 mmol), oleic acid (6 mL) and 1-octadecene (15 mL) were added to a 100 mL three-mouth flask. Under the flow of nitrogen and the appropriate magnetic stirring, the mixture was heated to 100 ^oC by a temperatures-controlled electric heating sleeve, and the oxygen and residual water in the system were replaced by a vacuum system. Then the transparent yellow solution was obtained when the mixed system was heated to 160 ^oC and kept for 60 min under the flow of nitrogen. After the solution was cooled to room temperature, 8 mL methanol solution containing NH_4F (4 mmol) and NaOH (2.5 mmol) was evenly added into the transparent yellow solution under stirring. After 120 min, the solution was heated to 50 ^oC to remove the methanol from the reaction mixture. The oxygen, residual water and methanol in the system were secondly replaced by a vacuum system at 100 ^oC. Then the mixture was heated to 305 ^oC in the nitrogen atmosphere and kept for 90 min. When the reaction system was cooled to room temperature, excess ethanol was added to obtain the product through centrifugation. The product was washed with ethanol and cyclohexane for several times and then re-dispersed in cyclohexane for later use.

Synthesis of $NaYF_4$:Yb^{3+}/Er^{3+}@$NaYF_4$ (core@shell@OA) nanocrystals.

0.5 mmol $YCl_3 \cdot 6H_2O$、oleic acid (6 mL) and 1-octadecene (15 mL) were added to a 100 mL three-mouth flask. Under the flow of nitrogen and the appropriate magnetic stirring, the mixture was heated to 100 ^oC by a temperatures-controlled electric heating sleeve, and the oxygen and residual water in the system were replaced by a vacuum system. Then the transparent yellow solution was obtained when the mixed system was heated to 160 ^oC and kept for 60 min under the flow of nitrogen. After the solution was cooled to room temperature, the newly prepared $NaYF_4$:Yb^{3+}/Er^{3+} core nanoparticles (1 mmol) were added to the flask. Then 8 mL methanol solution containing NH_4F (2 mmol) and NaOH (1.25 mmol) was evenly added into the transparent yellow solution under stirring. 120 min later, the solution was heated to 50 ^oC to remove the methanol from the reaction mixture. The oxygen, residual water and methanol in the system were secondly replaced by a vacuum system at 100 ^oC. Then

the mixture was heated to 305 ^{o}C in the nitrogen atmosphere and kept for 90 min. When the reaction system was cooled to room temperature, excess ethanol was added to obtain the product through centrifugation. The product was washed with ethanol and cyclohexane for several times and then re-dispersed in chloroform for later use.

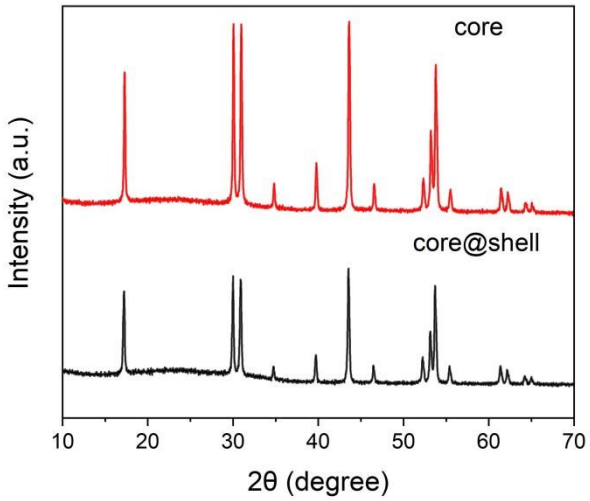

Fig. S1 XRD patterns of $NaYF_4$:Yb^{3+}/Er^{3+} (core) and $NaYF_4$:Yb^{3+}/Er^{3+}@$NaYF_4$ (core@shell).

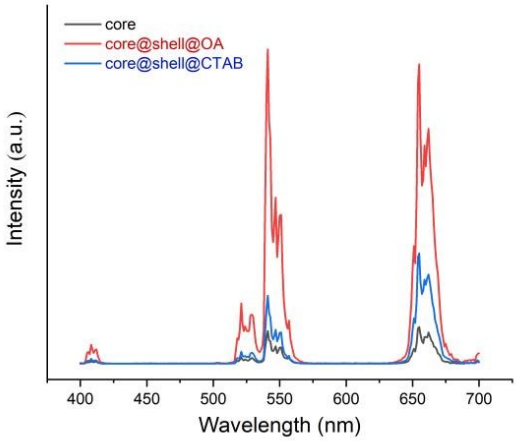

Fig. S2 Upconversion luminescence spectra of core, core@shell@OA and core@shell@CTAB, (0.334 W).

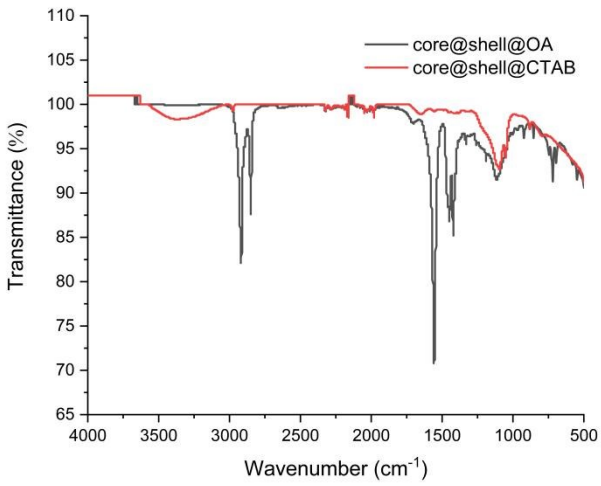

Fig. S3 FTIR-spectra of lipophilic core@shell@OA and hydrophilic core@shell@CTAB.

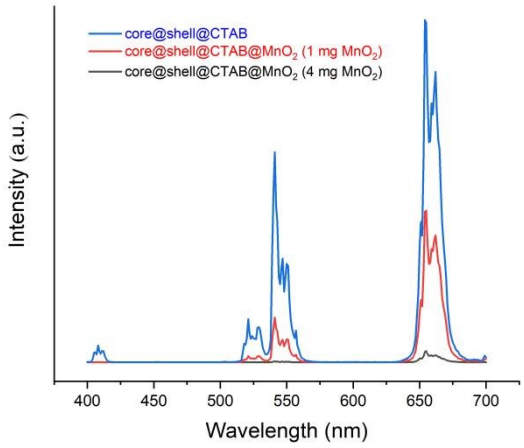

Fig. S4 Upconversion luminescence spectra of core@shell@CTAB and core@shell@MnO_2 with different amount of MnO_2 under 980 nm excitation (0.684 W).

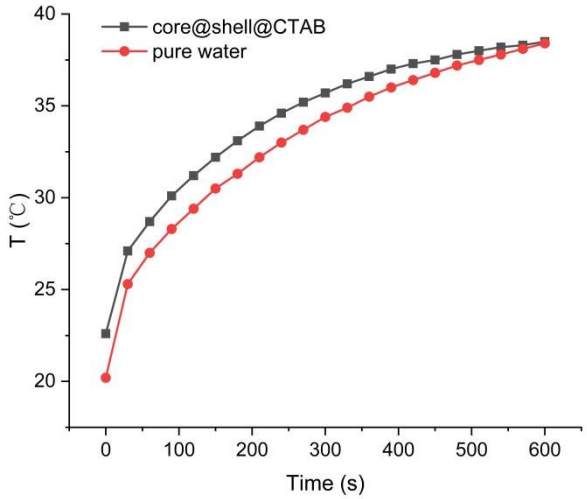

Fig. S5 Photothermal curves of pure water and hydrophilic core@shell@CTAB irradiated by 980 nm laser (0.8 W • cm^{-2}) for 10 min.