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Controlled Synthesis of Upconverting Nanoparticles/CuS Yolk-Shell Nanoparticles for in Vitro Synergistic Photothermal and Photodynamic Therapy of Cancer Cells

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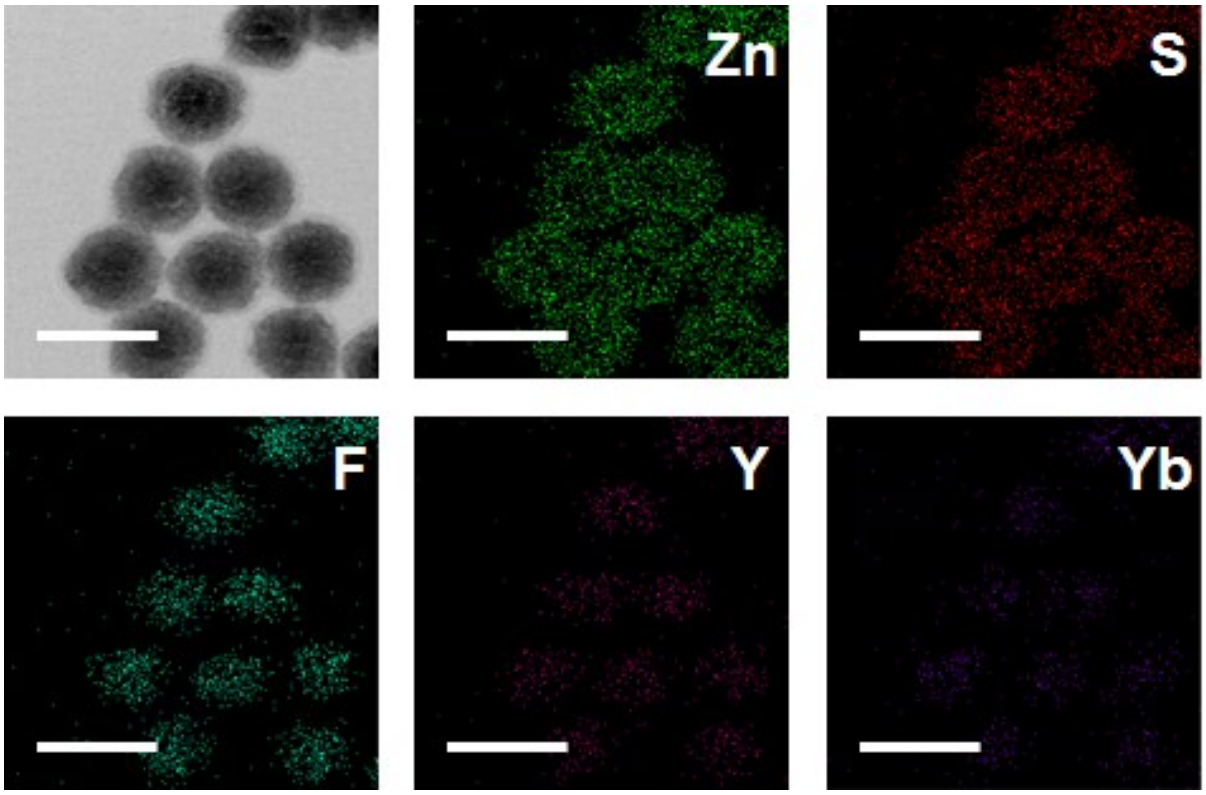


Fig. S1. STEM image and elemental mapping images of UCNPs@ZnS core-shell nanoparticles.

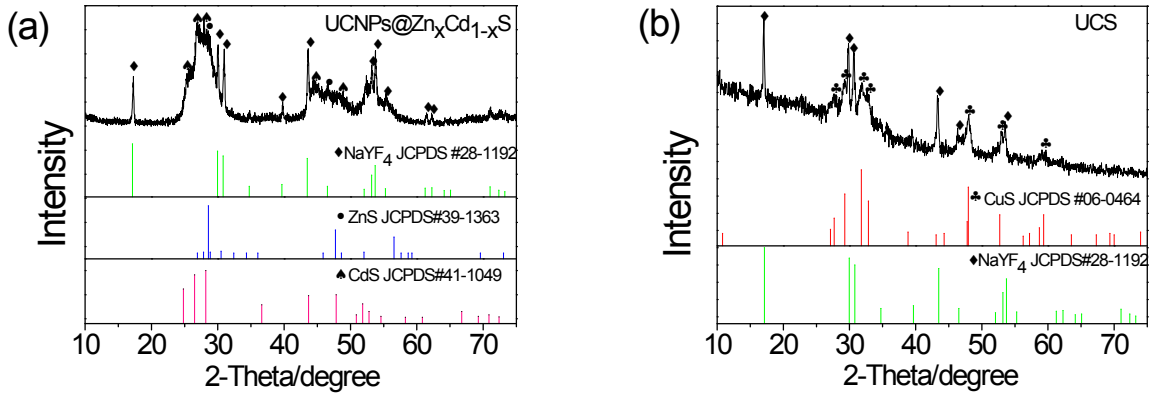
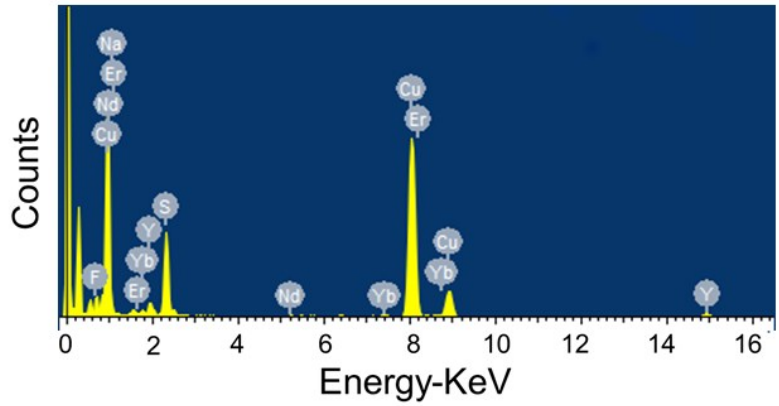


Fig. S2. X-ray diffraction patterns of the as-prepared (a) UCNPs@ZnxCd1-xS, and (b) UCS nanoparticles.

(a)



(b)

Element	Weight %	Atomic %
F	4.77	12.94
Na	0.52	1.17
S	14.56	23.42
Cu	72.13	58.56
Y	5.17	3.00
Er	0	0
Nd	1.01	0.36
Yb	1.85	0.55
Totals	100	

Fig. S3. (a) The energy dispersive X-ray (EDX) spectra and (b) the chemical composition of the UCNPs@CuS yolk-shell nanoparticles.

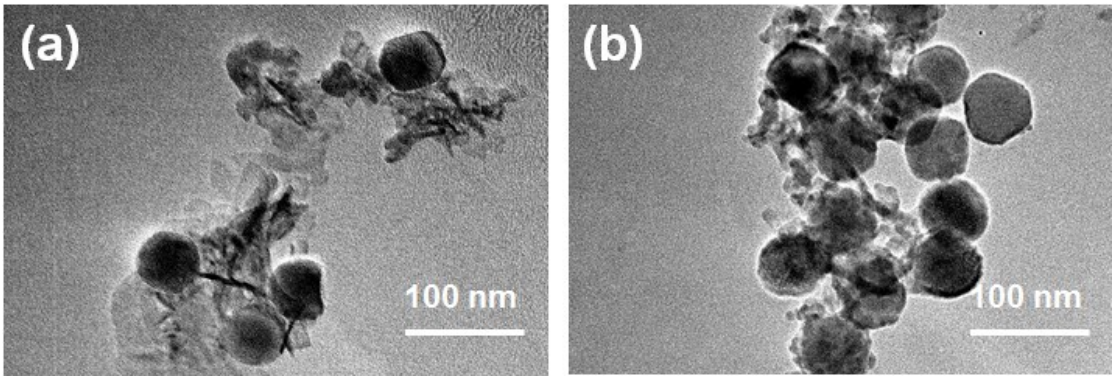


Fig. S4. TEM images of the as-prepared samples were obtained from UC@ZnS and Cu^{2+} in different reaction media: (a) aqueous solution; and (b) ethanol.

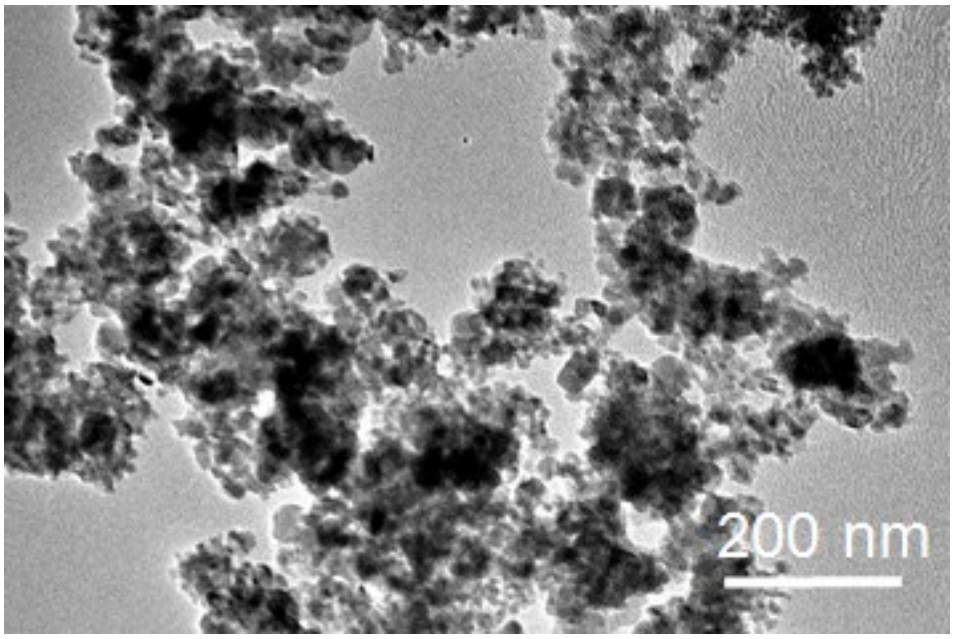


Fig. S5. TEM image of the sample obtained from UCNPs@$Zn_xCd_{1-x}S$ and Cu^{2+} in aqueous solution via the ions exchanging reaction.

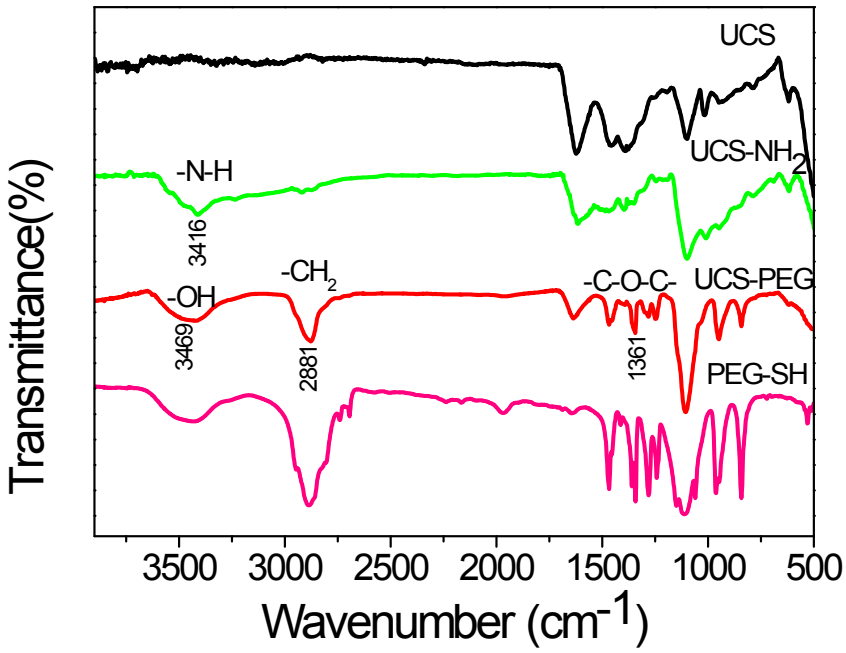


Fig. S6. FTIR spectra of UCS, UCS-NH_2, UCS-PEG and pure PEG-SH。

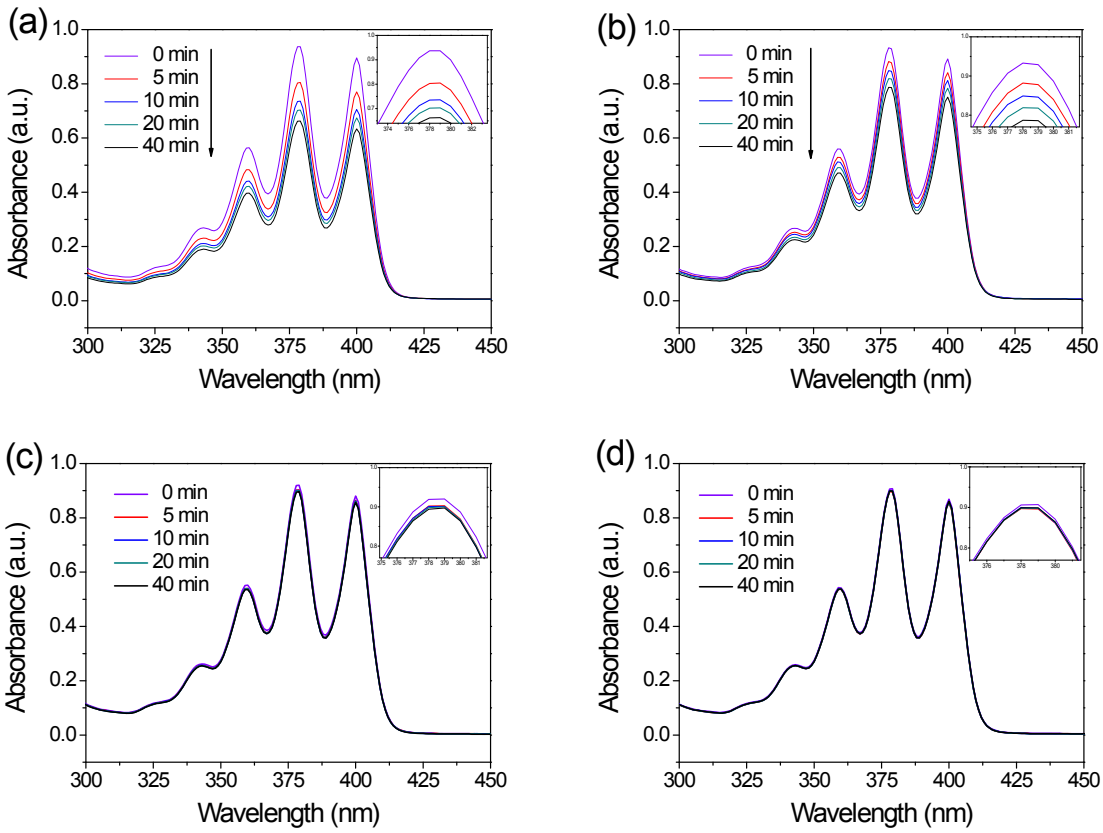


Fig. S7. UV-Vis absorption spectra of the solution of ABDA in presence of UCS (a) and CuS hollow nanospheres(b) exposed to 6W/cm^2 of 808 nm laser, indicating the production of $^1O_2$ species.(c, d) UV-Vis absorption spectra of the solution of ABDA in presence of UCS (c) and CuS hollow nanospheres (d) without irradiation of the laser.

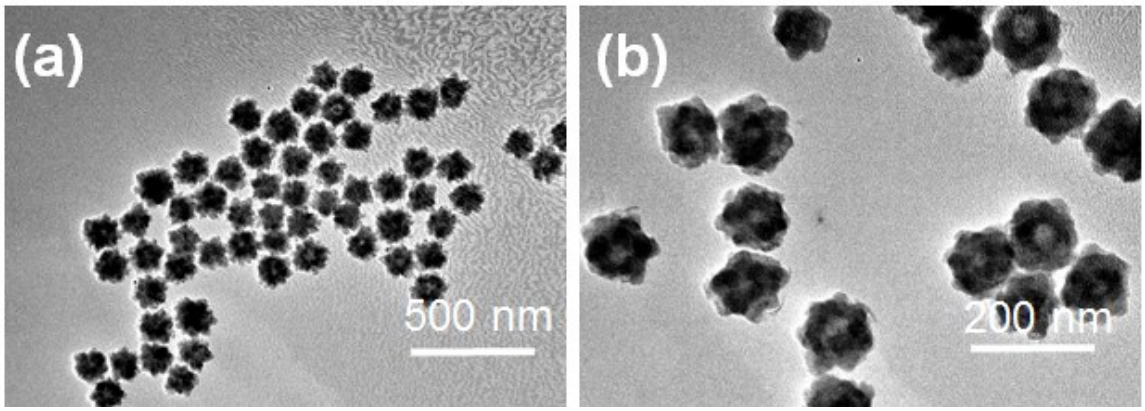


Fig. S8. TEM images of (a) $Zn_xCd_{1-x}S$ hollow nanospheres, and (b) CuS hollow nanospheres.

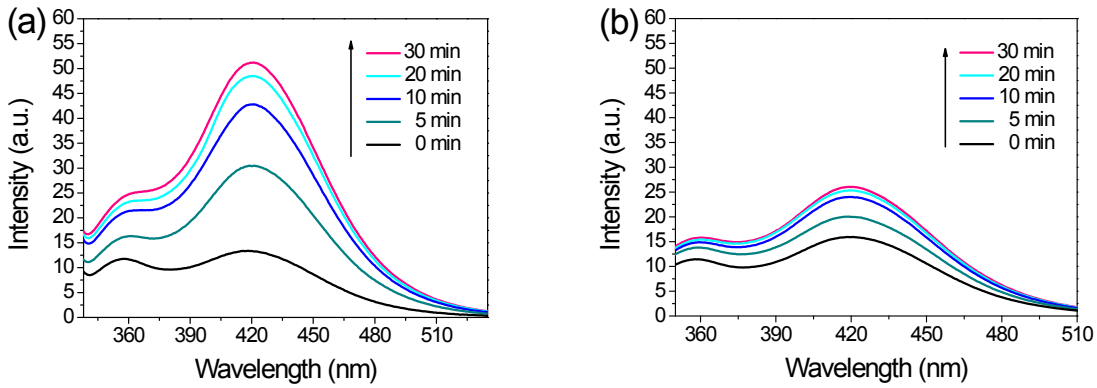


Fig. S9. (a) Fluorescence spectra of terephthalic acid (TAOH) with the addition of UCS (a), and CuS hollow nanospheres excited by an 808 nm CW laser.

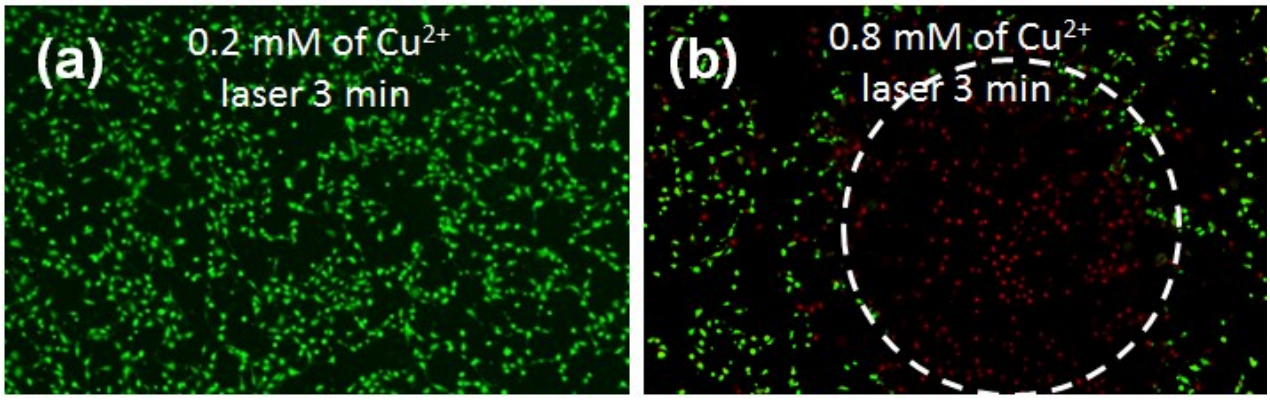


Fig. S10. The localized photothermal destruction of 4T1 cancer cells treated with different amount of UCS with various Cu^{2+} concentration exposed to laser for 3 min (808 nm, 6 W/cm^2): (a) 0.2 mM Cu^{2+}; (b) 0.8 mM Cu^{2+}.

Table S1. Cell apoptosis in presence of UCS under different condition.

Concentration / Apoptosis of cell / Experimental group	0.2 mM Cu^{2+}	0.4 mM Cu^{2+}
CuS+ laser	31.63%	46.87%
UCS+VC+laser	28.06%	46.16%
UCS+ laser	41.75%	60.65%