Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Supplementary Materials

1. Composition analysis of $CuInS_2$ nanocrystals with various copper deficiency

Table S1. Composition of $CuInS_2$ nanocrystals with various copper deficiency

$Cu_{1-x}InS_2$			
x(starting composition)	ICP-MS		
	[Cu] (at%)	[In] (at%)	x (nanocrystal)
0	49.8	50.2	0.01
0.2	44.6	55.4	0.19
0.5	34.1	65.9	0.48
0.8	15.5	84.5	0.81

The comparison of the copper deficiency (x) in the apparent composition of starting precursors and in the nanocrystals measured with ICP-MS was performed. As shown in table1, the copper deficiency in $Cu_{1-x}InS_2$ nanocrystals is consistent to the composition of starting precursors.

2. Composition analysis of the surface modified $Cu_{0.2}InS_2$ nanocrystals

Table S2. Composition of the $Cu_{0.2}InS_2$/MS (M=Zn, Cd) nanocrystals after surface modification

Nanocrystals	ICP-MS				
	[Cu] (at%)	[In] (at%)	[Zn] (at%)	[Cd] (at%)	[Cu]/[In]
$Cu_{0.2}InS_2$/ZnS	6.1	31.2	62.7	-	0.19
$Cu_{0.2}InS_2$/CdS	7.7	46.3	-	46.0	0.17

The compositional analysis by ICP-MS for core/shell CIS nanocrystals were presented in table S2. The incorporation of shell materials was confirmed with this data. In addition, the copper deficiency in $Cu_{1-x}InS_2$ nanocrystals is consistent to the composition of starting precursors.

3. Transmission electron microscopy of CdS-capped $Cu_{0.2}InS_2$ nanocrystals

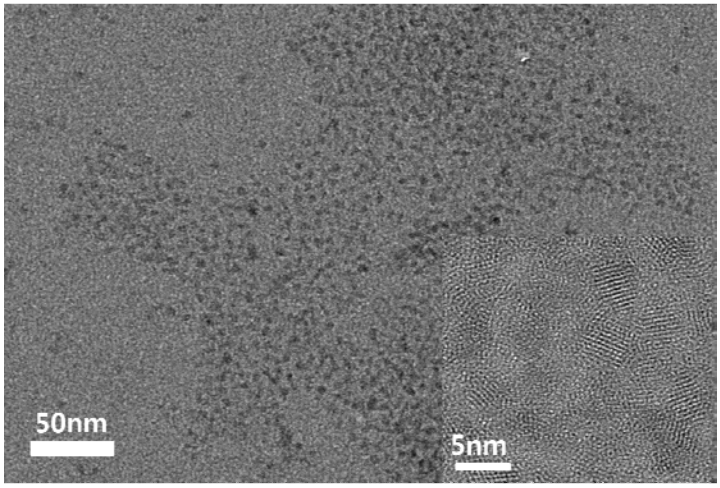

Figure S1. TEM image of $Cu_{0.2}InS_2$/CdS nanocrystals

The size/shape distribution of $Cu_{0.2}InS_2$/CdS nanocrystals was shown by a TEM image. Inset image shows their lattice image.

4. Controlled etching of nanocrystals

Nanocrystals for etching were prepared by the procedure described by Battaglia *et al*.[D. Battaglia, B. Blackman, X. Peng. *J. Am. Chem. Soc*.2005, 127, 10889.] The surface ligands of nanocrystals were exchanged with benzyl amine by mixing 0.5ml of nanocrystals solution with 1ml of benzyl amine (BA, 99%, Sigma-Aldrich) and sonicating for 10 minutes. Subsequently, 0.2ml of ligand-exchanged nanocrystal solution was added to 3ml of 1:2 methanol/toluene solution. 0.2M solution of benzoyl peroxide (BPO, 97%, Alfa aesar) was prepared by dissolving BPO to 1:2 methanol/toluene solvent. To start etching process, 0.2ml of 0.2M solution of BPO was added to the BA-capped nanocrystal solution.

The change in absorbance during etching process was measured with kinetics program using Cary5000 UV/VIS/NIR spectrometer at 450nm. Photoluminescence of nanocrystals were checked with Horiba Jovin-Yvon HR LabRam Raman/PL spectrometer excited with green laser (λ=514.5nm). Photoluminescence of nanocrystals during etching process was checked every 1 minutes

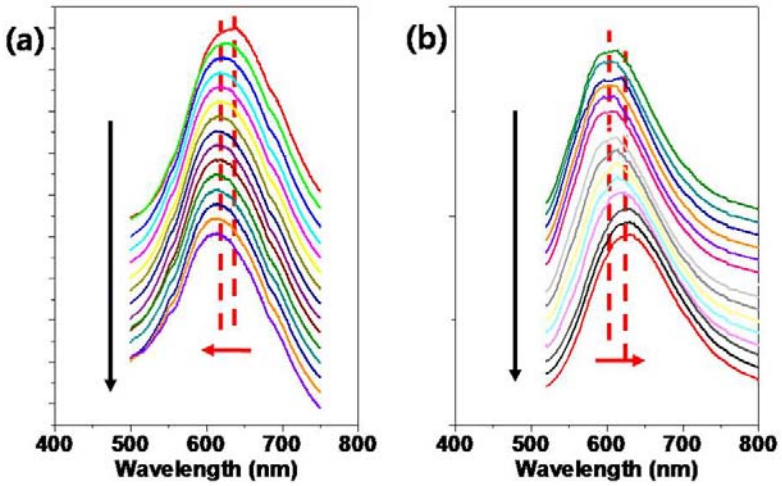

Figure S2. Change in photoluminescence spectra of nanocrystals during the first 15 minutes in the etching process: (a) $Cu_{0.2}InS_2$ (b) $Cu_{0.2}InS_2$/ZnS. The black arrows indicate time evolution.