Supporting Information

Shape Tunability of Copper Nanocrystals Deposited on Nanorods

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(a)



Figure S1. (a) illustration of the synthesis of SR. (b) TEM image of primary CdSe seeds with a diameter of about 2.3 nm. (c, d) TEM images of SR under different magnifications.



Figure S2. (a, b) TEM images of SR-c-Cu heterojunctions synthesized by adding different amount of SR.

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Figure S3. TEM images of SR-e-Cu (a), SR-s-Cu (b), SR-c-Cu (c) and SR-Cu multipedes (d-f) taken after 15 months of synthesis.

Crystallite size was determined utilizing the Scherrer equation (Eq. 1) from the (200) diffraction peak which was deemed as the most suitable due to its high intensity and absence of overlap with other peaks.

$$D = k\lambda/\beta \cos\theta \tag{1}$$

In Eq. 1, D represents the crystallite size in nm, k is the shape factor which is 0.89 or 0.94 for roughly spherical and cubic crystallites, λ is the CuK α radiation wavelength (0.15405 nm), β is the peak full width at half maximum (FWHM), and θ is the Bragg angle of the (200) diffraction peak at 50.5° (2 θ).



Figure S4. (a) XRD patterns of SR-Cu multipods zoomed in on Y axis. (b) XPS survey of the sample.



Figure S5. Control experiments: (a) TEM image of the products obtained when OLA is used as a reducing regent without TBAB during reaction. Cu nanocrystals are generated separately from the NRs (homogenous nucleation) (b-d) TEM images of the products obtained by replacing CuOAc with CuBr, CuI or CuCl, respectively.



Figure S6. (a) Illustration of the photodeposition pathway. (b-d) TEM images of the products by photodoposition (via 455 nm excitation with an LED operating at 200 mW). (e-h) the HAADF image and its STEM-EDX mapping of the resulting products.



Figure S7. (a) illustration of the cation exchange pathway. (b) TEM image of the products obtained by cation exchange (without TOP). (c-f) the HAADF image and its STEM-EDX mapping of the resulting products.



Figure S8. (a) Experimental (upper) and calculated (bottom) isotopic distribution at 803 m/z in MS (calculated formula $C_{48}H_{102}P_2Cu$). (b) ³¹P {¹H} NMR spectra of TOP and TOP₂–Cu complexes synthesized by adding different amount of Cu precursor.

τ_1 (ns)	τ_2 (ns)	τ ₃ (ns)	$\tau_{ave}(ns)$
1.64	14.88	47.16	22.71
(5.05%)	(68.61%)	(26.34%)	
0.99	8.65	30.40	17.16
(7.05%)	(51.34%)	(41.61%)	
3.40	13.90	20.16	15.02
(7.51%)	(62.04%)	(30.45%)	
1.20	6.17	18.37	10.35
(12.49%)	(48.18%)	(39.33%)	
0.49	3.70	17.57	8.41
(20.54%)	(40.77%)	(38.68%)	
	$\begin{array}{c} \tau_{1} (ns) \\ \hline 1.64 \\ (5.05\%) \\ \hline 0.99 \\ (7.05\%) \\ \hline 3.40 \\ (7.51\%) \\ \hline 1.20 \\ (12.49\%) \\ \hline 0.49 \\ (20.54\%) \end{array}$	τ_1 (ns) τ_2 (ns)1.6414.88(5.05%)(68.61%)0.998.65(7.05%)(51.34%)3.4013.90(7.51%)(62.04%)1.206.17(12.49%)(48.18%)0.493.70(20.54%)(40.77%)	τ_1 (ns) τ_2 (ns) τ_3 (ns)1.6414.8847.16(5.05%)(68.61%)(26.34%)0.998.6530.40(7.05%)(51.34%)(41.61%)3.4013.9020.16(7.51%)(62.04%)(30.45%)1.206.1718.37(12.49%)(48.18%)(39.33%)0.493.7017.57(20.54%)(40.77%)(38.68%)

Table S1. Excitons lifetime of SR-Cu heterojunctions