

SUPPORTING INFORMATION

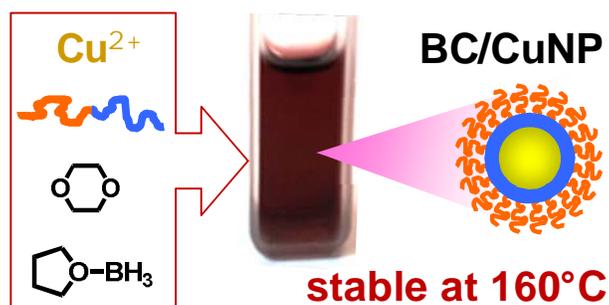
High thermal stability of block copolymer-capped Au and Cu nanoparticles

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EXPERIMENTAL INFORMATION

Synthesis of gold and copper nanoparticles:

1.5–3.0 mg PS-P4VP (Polymer Source Inc., Canada; Table SI-3) was dissolved in 10 mL anhydrous and oxygen-free THF or 1,4-dioxane. 6–25 mg (17–70 μmol) copper (II) 2-ethylhexanoate (Sigma-Aldrich), 14 mg (22 μmol) copper (II) stearate (95%, Pfaltz & Bauer Inc.), or 3–6 mg (8–15 μmol) gold (III) chloride trihydrate ($\text{HAuCl}_4 \times 3\text{H}_2\text{O}$, $\geq 99.9\%$, Sigma-Aldrich) was dissolved in the above solution (ratio metal to VP unit varied between 0.6:1 to 10:1) and left stirring overnight in a glove box under inert atmosphere. 0.3–1 mL borane tetrahydrofuran complex solution ($\text{BH}_3\text{-THF}$, 1.0 M in THF; Sigma-Aldrich) or borane dimethyl sulfide complex solution ($\text{BH}_3\text{-SMe}_2$, 2.0 M in THF; Sigma-Aldrich) was added slowly (over period of ca. 5 min.) to the block copolymer / metal salt solution resulting in gradual change of colour to dark brown or dark red indicating the formation of CuNPs or AuNPs, respectively.

Table SI-1. Characteristics of PS-P4VP diblock copolymers.

Nomenclature	Molecular weight, g/mol		M_w/M_n	mol % P4VP
	$M_n(\text{PS})$	$M_n(\text{P4VP})$		
PS ₃₈₄ -P4VP ₅₃	40,000	5,600	1.09	12 %
PS ₃₉₈ -P4VP ₁₆₆	41,500	17,500	1.07	30 %
PS ₁₉₂ -P4VP ₁₆₂	20,000	17,000	1.08	46 %
PS ₁₉₁ -P4VP ₂₈₀	19,900	29,400	1.15	60 %

Thermal stability studies:

Solutions of CuNP and AuNP were heated in high pressure vessels (ChemGlass) equipped with a stir bar at 110°C (THF solutions) or 105–160°C (1,4-dioxane solutions) for 14–48 h. [*Note: the reaction mass is under high pressure! Use protecting shield; do not manipulate the vessel until complete cooling to room temperature. Loading: 1 mL of solution in 15 mL vessel, 3 mL of solution in 48 mL vessel*].

Characterization techniques:

- **UV-Vis spectra** were obtained on a Varian Cary 5000 spectrometer. Solutions were measured in 1 cm quartz cuvettes, using pure solvent as a reference.
- **TEM (transmission electron microscopy)** imaging was done on Philips CV200 TEM. In a glove box, solutions were deposited on copper grids coated with carbon (SPI Supplies) and left to evaporate slowly under a Petri dish.
- **XPS (X-ray photoelectron spectra)** were obtained on a ThermoFisher Scientific K-alpha instrument equipped with a monochromatic Al K α X-ray source (1486.6 eV). Spectral energies were calibrated by setting the binding energy of C 1s to 285 eV. Peak-fitting procedure was performed using the Thermo Avantage software (version 4.60).

Table SI-2. Thermal stability of AuNP with various ligand–solvent combinations.
Temperature is given in °C, time in hours.

<i>AuNP</i>	<i>H₂O</i> (<i>b.p.</i> =100°C)	<i>toluene</i> (<i>b.p.</i> =111°C)	<i>THF</i> (<i>b.p.</i> =66°C)	<i>1,4-dioxane</i> (<i>b.p.</i> =101°C)	<i>pyridine</i> (<i>b.p.</i> =115°C)	<i>2,6-lutidine</i> (<i>b.p.</i> =144°C)
Au-CTAB	20° > months 100° < 12 h	-	-	20° < 5 min	-	-
Au-S-(PEO) ₆	90° > 3 h 100° < 3 h	105° < 2 h	-	20° >> 24 h 100° < 2 h	-	105° < 2 h
Au-S-(PEO) ₄₅	100° < 6 h	-	-	20° >> 24 h 100° < 2 h	100° > 4 h 150° < 15 h	-
Au-S-(PS) ₁₆	-	20° >> 24 h 105° < 12 h	65° > 24 h	20° >> 24 h 100° < 2 h	100° > 4 h 150° < 15 h	20° >> 24 h 100° < 2 h
Au / PS-P4VP	-	-	65° > 60 h	100° > 24 h	-	-

Table SI-3. Absorbance maxima (λ_{max}) of NP solutions in 1,4-dioxane.

	<i>BC / metal NPs prepared using:</i>		λ_{max} (nm)	
	<i>stabilizing agent</i>	<i>metal precursor</i>	<i>before heating</i>	<i>after heating at 100–160°C</i>
CuNPs	PS ₃₈₄ -P4VP ₅₃	Cu(II) n-octadecanoate	568	565
	PS ₃₉₈ -P4VP ₁₆₆	Cu(II) n-octadecanoate	567	566
		Cu(II) 2-ethylhexanoate	571	567
	PS ₁₉₂ -P4VP ₁₆₂	Cu(II) n-octadecanoate	560	563
Cu(II) 2-ethylhexanoate		558	572	
AuNPs	PS ₁₉₁ -P4VP ₂₈₀	HAuCl ₄ ×3H ₂ O	526	534

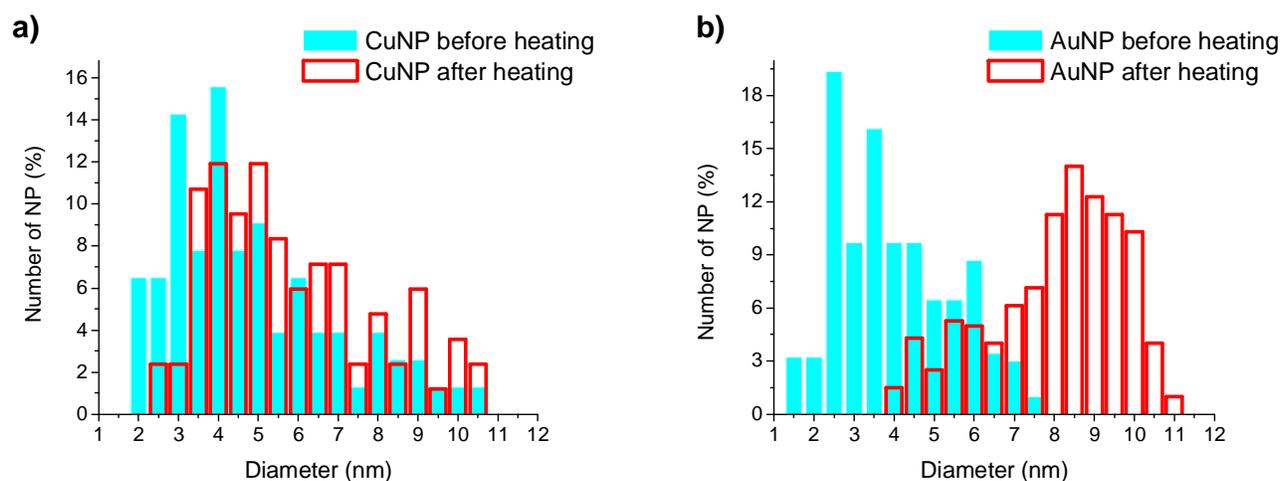


Figure SI-1. Average size of (a) PS-P4VP/CuNP and (b) PS-P4VP/AuNP before and after heating in 1,4-dioxane at 105°C for 20–48 h (determined by TEM).

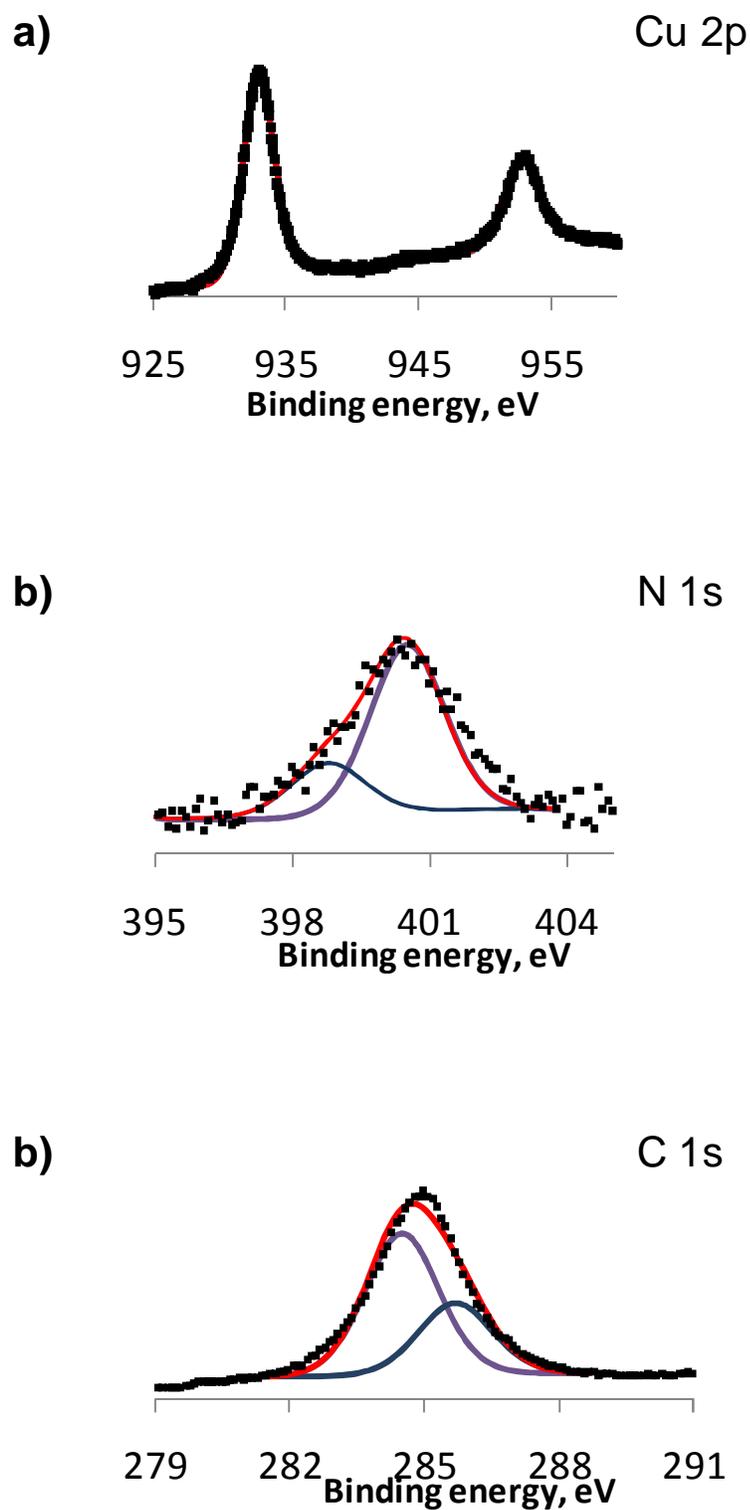


Figure SI-2. XPS spectra of (a) Cu 2p, (b) N 1s, and (c) C 1s core level binding energies for PS₁₉₂-P4VP₁₆₂/CuNPs before heating.