

## Electronic Supplementary Information

# Magnetic Self-Assembly of Gold Nanoparticle Chains Using Dipolar Core-Shell Colloids

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### 1. Experimental

**Materials and Characterization** Anhydrous 1,2-dichlorobenzene (DCB), toluene (99.5%), 1,2,3,4-tetrahydronaphthalene (tetralin, 99%), oleylamine (70%), and gold(III) chloride trihydrate (HAuCl<sub>4</sub>·3H<sub>2</sub>O 99.9%) were purchased from Aldrich. Platinum(II) acetylacetonate (Pt(acac)<sub>2</sub> 98%, Acros), dicobalt octacarbonyl (Co<sub>2</sub>(CO)<sub>8</sub>, Strem), and absolute ethanol (Pharmco-Aaper) were commercially available. All commercially obtained reagents were used as received without further purification. An Omega temperature controller CSC32K with a K-type utility thermocouple and a Glas-Col fabric heating mantle were used for thermolysis reactions. Calcinations of the polymer coated cobalt and the polymer coated gold-cobalt nanoparticles were performed in the Barnstead/Thermolyne small bench-top muffled furnace at 400 °C in air. Tin-doped indium oxide-coated glass (ITO, sheet resistance = 9-15 Ω/cm<sup>2</sup>) was obtained from Colorado Concept Coatings LLC (Longmont, CO). A model 342 UVO-CLEANER (Jelight Company, Inc., lamp power 28 mW/cm<sup>2</sup> at 254 nm) was used for cleaning the ITO substrates. The instrument lamp was stabilized for at least 10 minutes prior to use. TEM images were obtained on a Phillips CM12 transmission electron microscope (CM12) at 80 kV, using in house prepared carbon coated copper grids (Cu, hexagon, 300 meshes). Image analysis was performed using ImageJ software (Rasband, W.S., National Institutes of Health, <http://rsb.info.nih.gov/ij/>, 1997-2007). Relative uncertainty of particle size determinations using ImageJ was found to be 1 % of diameter average (e.g., 20 ± 0.2 nm). SEM images were taken on a Hitachi 4800 FE-SEM on

the as-prepared samples (i.e., no metallic over coating). XPS characterization was performed on a KRATOS 165 Ultra photoelectron spectrometer, using a monochromatic Al K $\alpha$  radiation source (20 eV pass energy) at 1486.6 eV. VSM measurements were conducted using a Waker HF 9H electromagnet with a Lakeshore 7300 controller and a Lakeshore 668 power supply. Magnetic measurements were carried out at room temperature (27 °C or 300 K) and low temperature (-213 °C or 50 K) with a maximum S-2 applied field of 1190 kA/m, a ramp rate of 2630 Am<sup>-1</sup>s<sup>-1</sup> and a time constant of 0.1. XRD measurements were performed using the X'pert x-ray diffractometer (Phillips PW1827) at room temperature with a CuK $\alpha$  radiation source at 40 kV and 30 mA. UV-Vis spectra were obtained using Agilent UV-vis spectrometer (no. 8453A, Foster City, CA).

**Preparation of gold nanoparticles (AuNPs)** Gold nanoparticles were synthesized by method reported in elsewhere.<sup>1</sup> HAuCl<sub>4</sub>·3H<sub>2</sub>O (0.500 g, 1.25 mmol) was added to 50 mL of tetralin, followed by an addition of oleylamine (5.00 ml, 15.0 mmol) to form an orange solution. The solution was heated at 65 °C and the solution changed to dark red color. After 5 hrs at 65 °C, the reaction cooled down to room temperature. Gold nanoparticles were precipitated by adding ethanol and isolated via centrifugation (yield = 0.237 g). Sample for TEM analysis was prepared by dispersing the isolated AuNPs powder in toluene (1 mg/2 mL) via sonication for 15 minutes, followed by drop casting onto a carbon coated Cu grid. The particle size of resulting Au nanoparticles measured by TEM was 13 ± 3 nm.

**Preparation of amine end-functionalized polystyrene surfactants (PS-NH<sub>2</sub>)** PS-NH<sub>2</sub> was synthesized according to our previous report.<sup>2</sup>

**Preparation of polystyrene coated gold-cobalt core-shell nanoparticles (PS-AuCoNPs) with size ~25 nm (AuNPs : Co<sub>2</sub>(CO)<sub>8</sub> = 1:4 wt/wt)** PS-NH<sub>2</sub> (0.100 g; 1.42 x 10<sup>-2</sup> mmol; M<sub>n</sub> = 7000 g/mol; M<sub>w</sub>/M<sub>n</sub> = 1.07) and AuNPs (0.100 g) were dissolved in 10 mL and 5 mL of DCB, respectively. These two solutions were transferred into a three-neck-round bottom flask containing DCB (5 mL) and the resulting mixture was heated to reflux at 175 °C. Separately, Co<sub>2</sub>(CO)<sub>8</sub> (0.400 g; 1.16 x 10<sup>-3</sup> mol) was dissolved in DCB (4 mL) at room temperature in air and was rapidly injected into the hot AuNPs and polymer solution. Upon the injection, the reaction temperature dropped to around 155 °C and maintained at 160 °C for 60 minutes, followed by cooling to room temperature. PS-AuCoNPs were isolated by precipitation into hexanes (1000 mL), yielding a black powder (yield = 0.317 g) soluble in a wide range of non-polar solvents (e.g., methylene chloride, THF, and toluene). Sample for TEM analysis was prepared by dispersing the isolated powder in toluene (1 mg/2 mL) via sonication for 15 minutes, followed by drop casting onto a carbon coated Cu grid. The particle size of the PS-AuCoNPs was determined to be 25 ± 3 nm via TEM. Magnetic properties of PS-AuCoNPs were measured using VSM at room temperature: M<sub>s</sub> = 45.6 emu/g; H<sub>c</sub> = 213 Oe and at 50 K: M<sub>s</sub> = 47.2 emu/g; H<sub>c</sub> = 1520 Oe. TGA analysis showed 25.4% of organics by mass.

**Preparation of PS-AuCoNPs with size ~20nm (AuNPs : Co<sub>2</sub>(CO)<sub>8</sub> = 1:2 wt/wt)** PS-NH<sub>2</sub> (0.100 g; 1.42 x 10<sup>-2</sup> mmol; M<sub>n</sub> = 7,000 g/mol; M<sub>w</sub>/M<sub>n</sub> = 1.07) and AuNPs (0.100 g) were dissolved in 5 mL and 5 mL of DCB, respectively. These two solutions were transferred into a three-neck-round bottom flask containing DCB (3 mL) and the resulting mixture was heated to reflux at 175 °C. Separately, Co<sub>2</sub>(CO)<sub>8</sub> (0.200 g; 1.16 x 10<sup>-3</sup> mol) was dissolved in DCB (2 mL)

at room temperature in air. Following procedure was same as the procedure described previously. PS-AuCoNPs were isolated by precipitation into hexanes (500 mL), yielding a black powder (yield = 0.153 g). The particle size of the PS-AuCoNPs was determined to be  $20 \pm 3$  nm via TEM. Magnetic properties of PS-AuCoNPs were measured using VSM at room temperature:  $M_s = 22.3$  emu/g;  $H_c = 140$  Oe and at 50 K:  $M_s = 23.2$  emu/g;  $H_c = 1101$  Oe. TGA analysis showed 18.5% of organics by mass.

**Preparation of polystyrene ligand capped AuCo nanoparticles decorated with PtNP crystallites (PS-AuCoPt NPs)** PS-AuCoNPs ( $D = 25$  nm; 50.0 mg) was redispersed in 30 mL DCB via sonication. Separately, Pt(acac)<sub>2</sub> (50.0 mg; 0.126 mmol) was dissolved in 20 mL DCB. The homogeneous precursor solutions were mixed into a 250 mL three-neck-round bottom flask equipped with a reflux condenser and a stir bar. The precursor mixture was diluted with 50 mL DCB. DCB was bubbled with argon for 30 minutes to remove residual oxygen prior to use. The reaction mixture was heated at 175 °C under argon for 10 hours. After 10 hours reaction, the reaction cooled to room temperature and precipitated into hexane and acetone mixture (4:1). After centrifugation at 3000 rpm for 5 minutes, black powder was isolated (yield = 27.3 mg). Sample for TEM analysis was prepared by dispersing the isolated powder in toluene (1 mg/2 mL) via sonication for 15 minutes, followed by drop casting onto a carbon coated Cu grid.

**Preparation of Polystyrene-coated Nanoparticle films on the substrate** ITO, silicon wafer and glass substrates were cut and cleaned with 10 % aqueous Triton X-100 solution, followed by rinsing and sonicating in nano-pure water (18 MΩ/cm) for 10 minutes. Substrates were then sonicated in the absolute ethanol for 10 minutes. Once removed from ethanol, the slides were dried under a stream of Ar and cleaned in UV-ozone cleaner for 30 minutes. The colloidal dispersion was drop casted on the substrates and used for acid etching. For aligned PS-AuCoNPs ( $D = 25 \pm 3$  nm) samples, colloidal dispersion was drop casted on the substrate under external fields. Bracelet-type assembled sample was prepared by drop casting of PS-AuCoNPs ( $D = 20 \pm 3$  nm) solution on the substrate without fields.

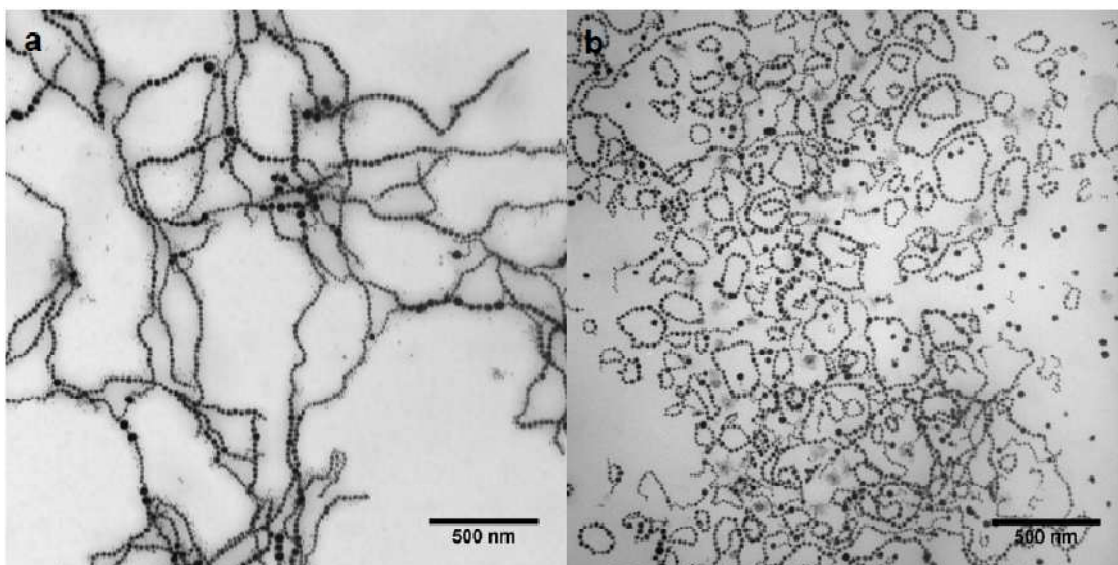
**Acid etching of PS-CoNPs and PS-AuCoNPs solutions for UV measurement** The sample was prepared by dispersing the isolated powder in toluene (2.0 mg/1.0 mL) via sonication for 15 minutes, followed by adding 1.0 M aqueous solution of HCl (0.1 mL). The solution was shaken for various time and quenched by adding toluene (2.0 mL) and H<sub>2</sub>O (2.0 mL). Organic phase was separated and sonicated for 20 minutes then used for UV measurement.

**Acid etching of PS-AuCoNPs and PS-AuCoPtNPs films on the substrates** Prepared film on the substrate was slowly immersed into 6.0 M aqueous solution of HCl for a minute, followed by soak in nanopure water for a minute. Film color was changed from black to red. All of acid etched films on the substrate were treated by O<sub>2</sub> plasma with 500 mtorr O<sub>2</sub> flow at 18W for 30 minutes to remove residual organics and used for UV-vis measurement and SEM imaging.

## 2. Preparation of PS-AuCoNPs

Preparation of PS-AuCoNPs was performed with varied ratios of AuNP seeds to Co<sub>2</sub>(CO)<sub>8</sub> precursors. When the feed ratio of AuNP seeds to Co<sub>2</sub>(CO)<sub>8</sub> precursors was lower than 1 : 2 (wt/wt), the encapsulation yield was low resulting in a mixture of superparamagnetic core-

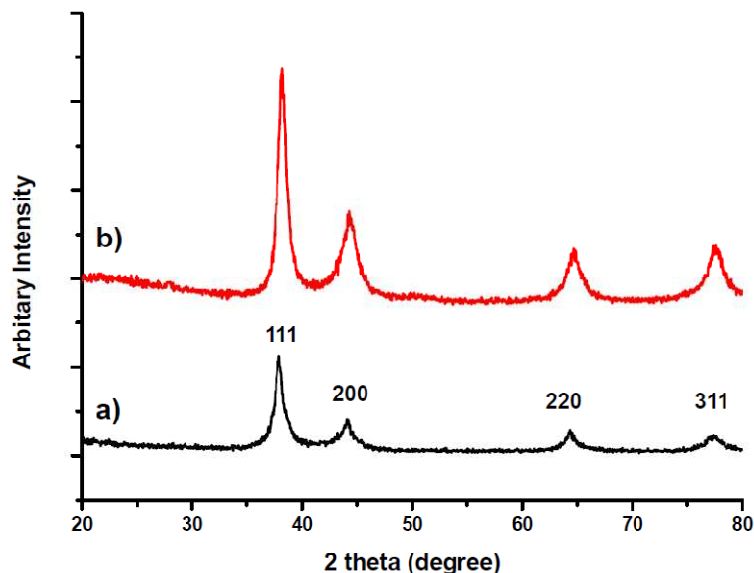
shell PS-AuCoNPs and AuNPs without Co shells. As feed ratio of the  $\text{Co}_2(\text{CO})_8$  precursor increased, the yield of core-shell nanoparticles increased as well. With 100 mg of AuNP seeds and 400 mg of  $\text{Co}_2(\text{CO})_8$  precursors, a high encapsulation yield along with the ferromagnetic behavior in PS-AuCoNPs ( $D = 25 \pm 3$  nm) were observed. At the 1:2 (by wt) ratio of AuNP seeds (100 mg) to  $\text{Co}_2(\text{CO})_8$  precursors (200 mg), most of all AuNP seeds were encapsulated but the size of PS-AuCoNPs ( $D = 20 \pm 3$  nm) became smaller because of thinner cobalt shells. Despite PS-AuCoNPs had smaller size ( $D = 20 \pm 3$  nm) and thinner Co shells, PS-AuCoNPs exhibited ferromagnetic properties. Larger PS-AuCoNPs ( $D = 25 \pm 3$  nm) with thicker Co shells exhibited the random chain assembly on the TEM grid spanning several microns in size (Fig. S1-a). Smaller PS-AuCoNPs ( $D = 20 \pm 3$  nm) were self-assembled into the flux-closure rings due to relatively weak dipolar interactions on the TEM grid (Fig. S1-b).



**Figure S1.** TEM images of a) PS-AuCoNPs ( $D = 25 \pm 3$  nm) with thicker Co shells and b) PS-AuCoNPs ( $D = 20 \pm 3$  nm) with thinner Co shells

### 3. XRD

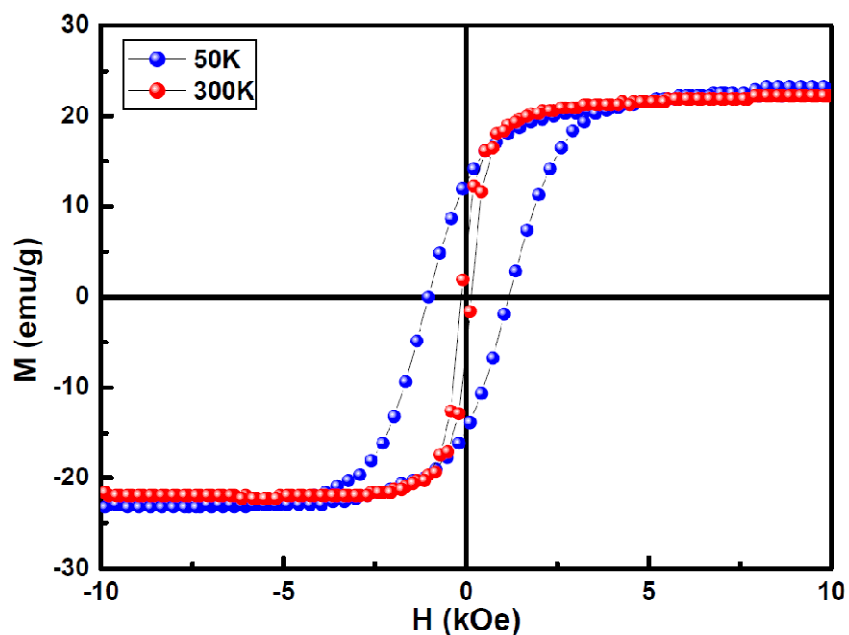
Powder X-ray diffraction (XRD) was used to characterize the solid-state structure of PS-AuCoNPs ( $D = 20 \pm 3$  nm) with thinner Co shells. XRD of larger PS-AuCoNPs ( $D = 25 \pm 3$  nm) with thicker Co shells has been reported in previous work.<sup>3</sup> The diffraction from AuNP cores (Fig. S2-a) dominates the pattern in PS-AuCoNPs (Fig. S2-b) due to both the higher Z of Au relative to Co atoms and the significant weight fraction of Au present in the material.



**Figure S2.** Overlay XRD patterns of a) AuNPs and b) PS-AuCoNPs ( $D = 20 \pm 3$  nm) with thinner Co shells

#### 4. VSM

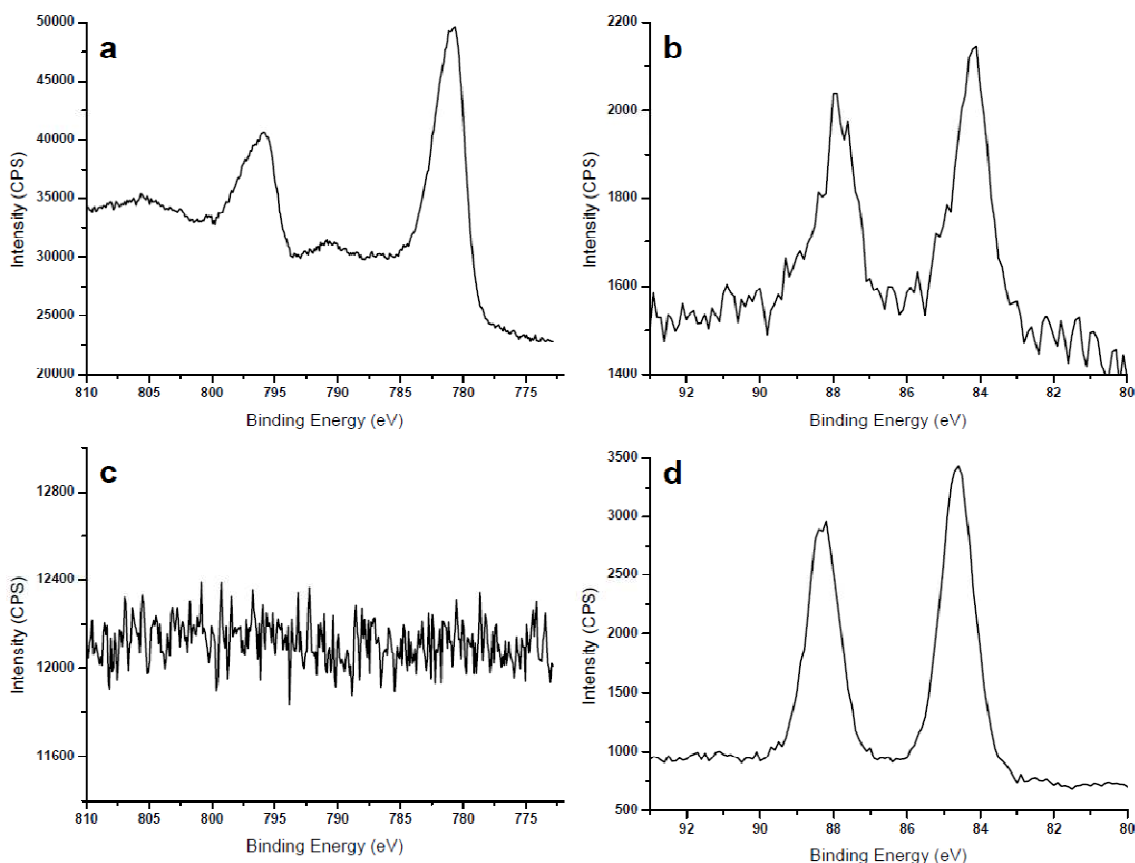
The magnetic properties of PS-AuCoNPs ( $D = 20 \pm 3$  nm) were measured using vibrating sample magnetometry (VSM) at room temperature (300K) and at 50 K (Fig. S3). PS-AuCoNPs exhibited weak ferromagnetic behavior at room temperature ( $M_s = 22.3$  emu/g;  $H_c = 140$  Oe) and at 50 K ( $M_s = 23.2$  emu/g;  $H_c = 1101$  Oe). The magnetometry of the smaller PS-AuCoNPs ( $D = 20 \pm 3$  nm) was weaker than larger PS-AuCoNPs ( $D = 25 \pm 3$  nm) ( $M_s = 45.6$  emu/g;  $H_c = 213$  Oe at RT and  $M_s = 47.2$  emu/g;  $H_c = 1520$  Oe at 50K)<sup>3</sup> in the saturation magnetization and coercivity at both temperatures.



**Figure S3.** Overlay hysteresis curves of applied magnetic field ( $H$ ) vs. magnetization ( $M_s$ ) of PS-AuCoNPs ( $D = 20 \pm 3$  nm) at 300K (red) and at 50K (blue)

## 5. XPS

X-ray photoelectron spectroscopy (XPS) was used to confirm disappearance of Co shells after the acid etching of PS-AuCoNPs. XPS was performed in regions of  $\text{Co}_{2p}$  and  $\text{Au}_{4f}$ . Before acid etching, XPS in the  $\text{Co}_{2p}$  region exhibited two major peaks at 795.8 eV and 780.6 eV, corresponding to  $\text{Co } 2p_{1/2}$  and  $\text{Co } 2p_{3/2}$  spin-orbit components, respectively (Fig. S4-a). Also XPS in the  $\text{Au}_{4f}$  region showed two peaks at 88.0 eV and 84.1 eV, corresponding to  $\text{Au } 4f_{5/2}$  and  $\text{Au } 4f_{7/2}$  spin-orbit components, respectively (Fig. S4-b). After the acid etching experiment, two peaks were disappeared in the  $\text{Co}_{2p}$  region as shown in Figure S4-c. Two peaks in the  $\text{Au}_{4f}$  region after acid etching exhibited enhanced signal to noise ratio (Fig. S4-d). XPS of acid etched PS-AuCoNPs indicated that Co shells in PS-AuCoNPs were etched completely by the acid treatment.

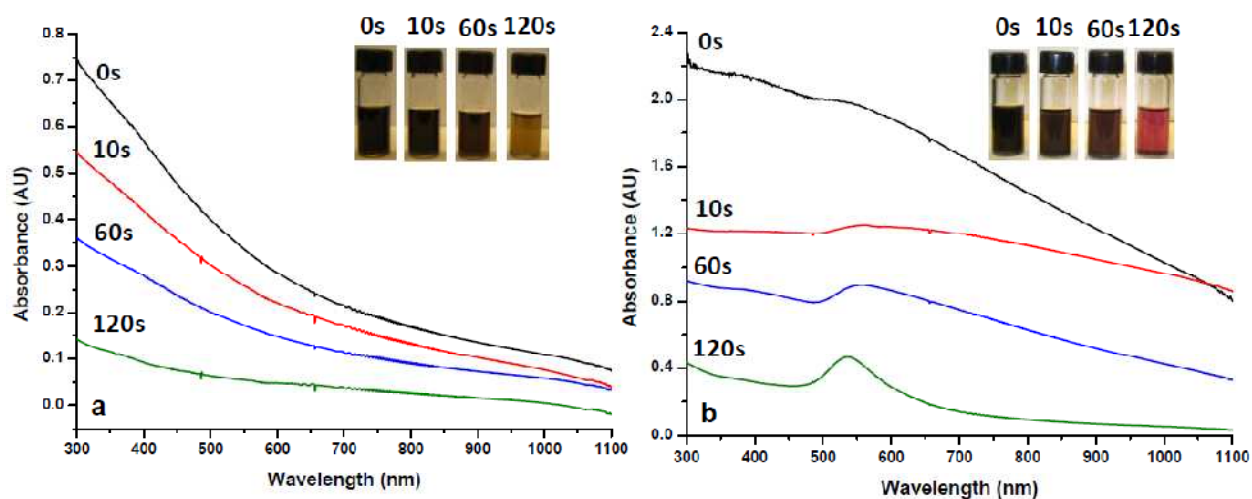


**Figure S4.** XPS spectroscopy of (a)  $\text{Co}_{2p}$  and (b)  $\text{Au}_{4f}$  of PS-AuCoNPs and (c)  $\text{Co}_{2p}$  and (d)  $\text{Au}_{4f}$  of acid etched PS-AuCoNPs

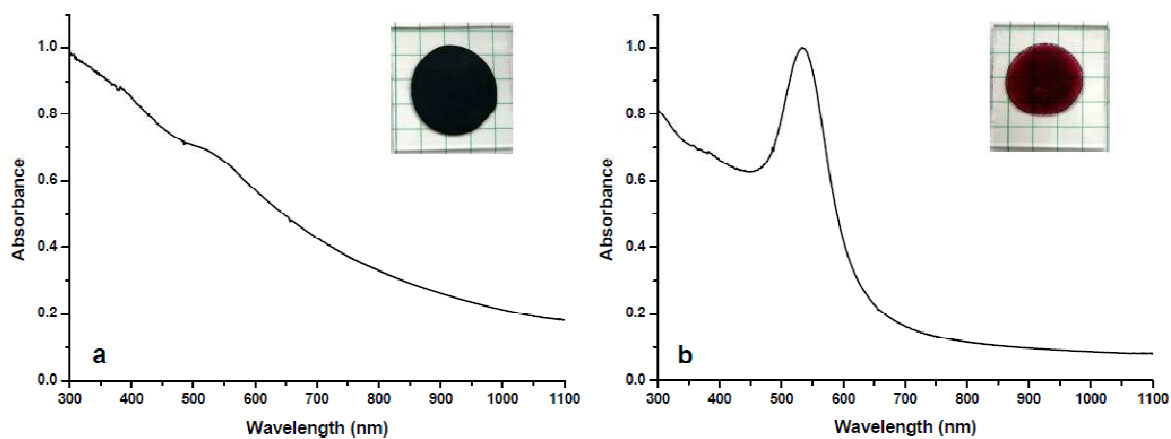
## 5. UV-visible spectroscopy

Selective etching of Co outer shells from PS-AuCoNPs by HCl dissolution was confirmed using optical absorption spectroscopy. The kinetics of the Co shell disappearance during acid etching was examined by using dispersion solutions via UV-visible spectroscopy. Acid etching kinetic of PS-CoNPs was also examined as a control experiment. Isolated powder of PS-AuCoNPs ( $D = 25 \pm 3$  nm) and PS-CoNPs ( $D = 23 \pm 4$  nm) were dispersed in toluene (2 mg/ml), followed by adding 1M aqueous solution of HCl (0.1 ml). The solutions were shaken for 10s, 60s, and 120s and quenched by adding toluene (2 ml) and  $\text{H}_2\text{O}$  (2 ml). The organic phase

was separated and sonicated for the UV-visible spectroscopy. PS-CoNPs dispersion solution exhibited broad absorption over entire wavelength range (Fig S5-a). As acid etching proceeded, the overall intensity of absorption decreased as shown in Figure S4-a. The color of solution was also getting fade from black to light brown. PS-AuCoNPs dispersion solution exhibited broad absorption over entire wavelength range as same as PS-CoNPs, except small shoulder around 540 nm (Fig S5-b). The weak absorption peak around 540 nm is the surface plasmon peak from the AuNP core. The intensity of absorption over entire wavelength range decreased while the peak at 537nm showed up clearly as acid etching was proceeded (Fig. S5-b). As the AuNPs core was exposed by acid etching, the surface plasmon peak from AuNPs appeared and the solution color was changed from black to red. Acid etching of Co phases was also conducted on PS-AuCoNPs thin films cast onto a glass substrate (Fig. S6). Optical absorbance spectroscopy of acid etched PS-AuCoNPs films on glass afforded strong surface plasmon resonance peak of AuNPs at 535 nm and a corresponding change in film color from black to red (Fig. S6-b).



**Figure S5.** UV-vis spectrum of acid etched of (a) PS-CoNPs (2 mg/mL) and (b) PS-AuCoNPs (2 mg/mL) solution in toluene at various time (inset: digital image of solutions)

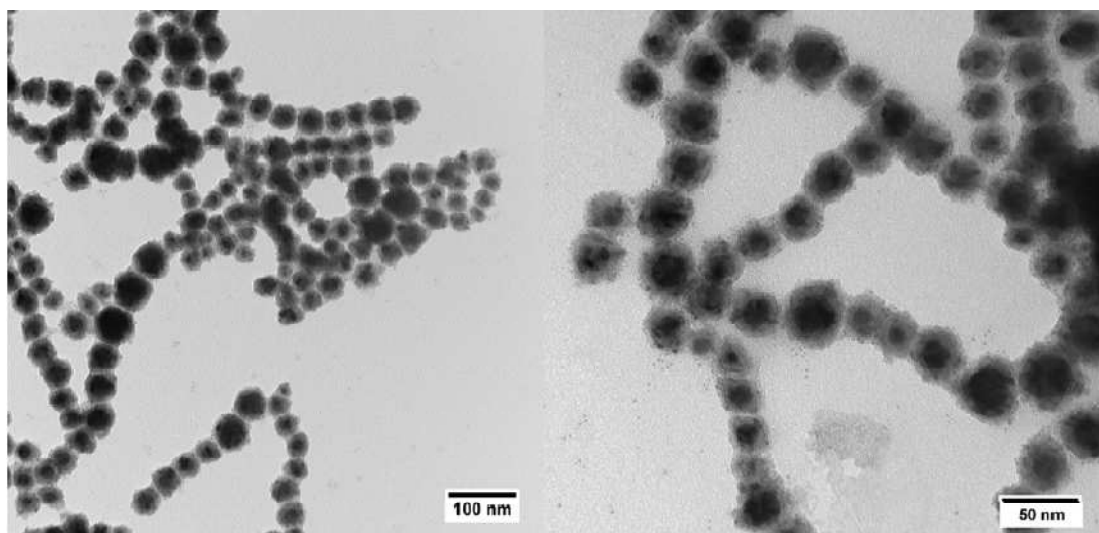


**Figure S6.** UV-vis spectrum of (a) PS-AuCoNPs and (b) acid etched PS-AuCoNPs film on the glass substrates (inset: digital image of films)



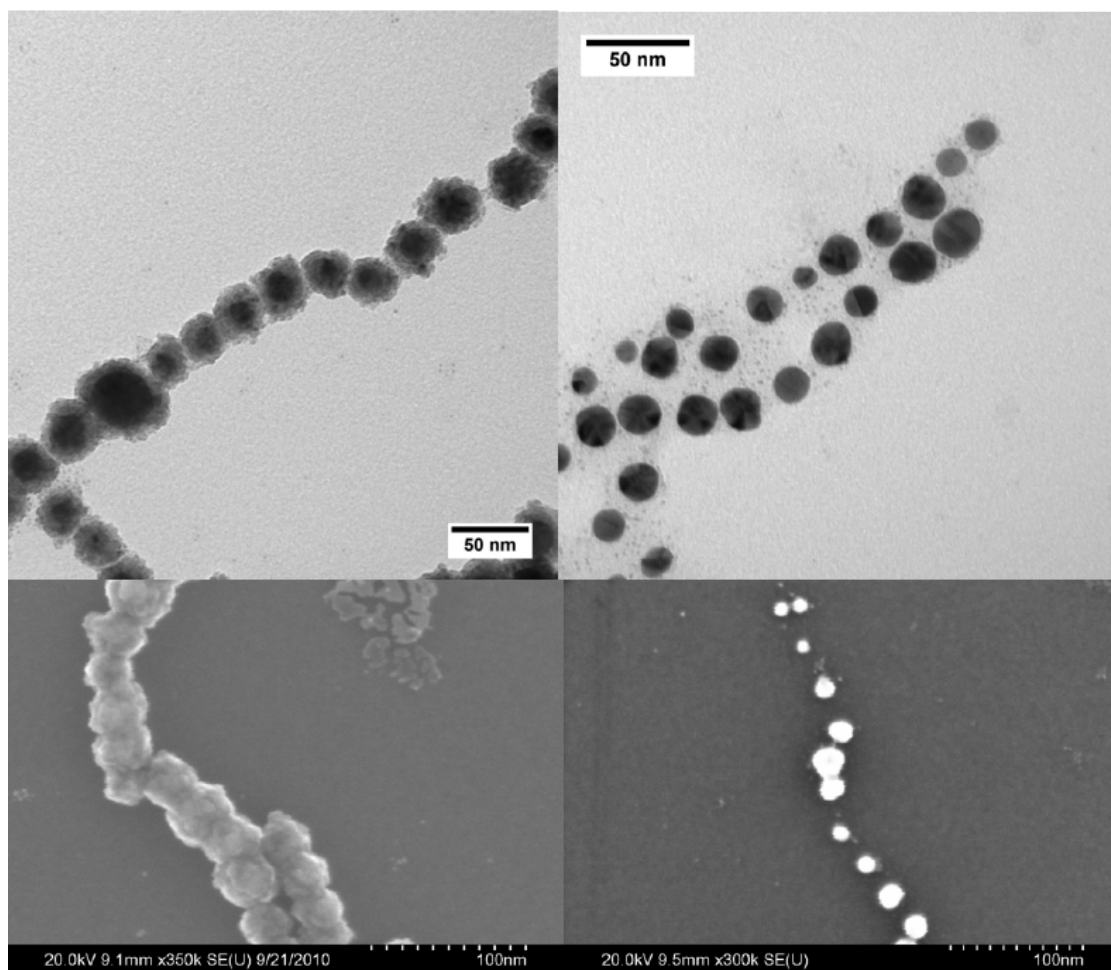
## 6. Preparation of PS-AuCoPt NPs and acid etched AuNP-PtNP chains

Galvanic reactions of PS-AuCoNPs with  $\text{Pt}(\text{acac})_2$  was conducted in DCB 175°C under Ar.<sup>4</sup> Preparation of PS ligand capped Au-CoNP core shell colloids with an outer corona of metallic PtNPs (PS-AuCoPt NPs) was performed with 1:1 (wt/wt) ratios of  $\text{Pt}(\text{acac})_2$  precursor to PS-AuCoNPs. When the feed ratio of  $\text{Pt}(\text{acac})_2$  precursor to PS-AuCoNPs was higher than 1:1 (wt/wt), we observed PS-AuCoPt NPs with excess free Pt NPs formation. With 50 mg of  $\text{Pt}(\text{acac})_2$  precursor and 50 mg of PS-AuCoNPs, a high yield of PtNP coatings along with minimum formation of free Pt NPs were observed. PS-AuCoPt NPs were isolated from free Pt NPs via centrifugation. PS-AuCoPt NPs exhibited the random chain assembly on the TEM grid same as PS-AuCoNPs (Fig. S7). TEM and SEM images exhibited roughened surfaces of nanoparticles due to the Pt deposition (Fig. S7, S8-a,c). Acid etching to remove Co phases was conducted on PS-AuCoPt NPs using identical conditions as for PS-AuCoNPs etched onto different substrates (Si and carbon coated grid). After acid etching of the Co phases, AuNPs assemblies decorated with Pt NPs were obtained (Fig. S8-b,d).



**Figure S7.** TEM images of PS-AuCoPt NPs at low and high magnification

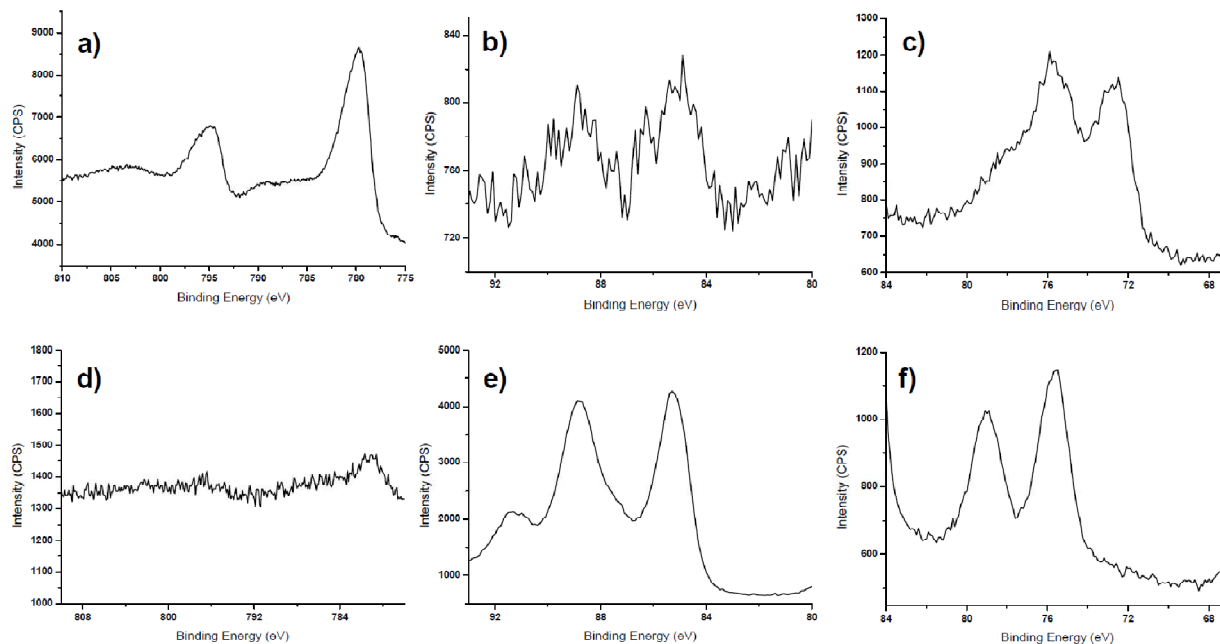




**Figure S8.** TEM images of (a) PS-AuCoPt NPs, (b) acid etched PS-AuCoPt NPs, SEM mages of (c) PS-AuCoPt NPs, and (d) acid etched PS-AuCoPt NPs after O<sub>2</sub> plasma cleaning on Si wafer

### 7. XPS of PS-AuCoPt NPs

XPS was conducted to confirm galvanic deposition of PtNPs onto PS-AuCoNPs and disappearance of Co phases after the acid etching of PS-AuCoPt NPs. XPS was performed in regions of Co<sub>2p</sub>, Au<sub>4f</sub>, and Pt<sub>4f</sub>. For PS-AuCoPt NPs, XPS in the Pt<sub>4f</sub> region showed two peaks at 76.0 eV and 72.5 eV, corresponding to Pt 4f<sub>5/2</sub> and Pt 4f<sub>7/2</sub> spin-orbit components, respectively (Fig. S9-c). XPS in the Co<sub>2p</sub> region and Au<sub>4f</sub> region exhibited similar spectrum as one from PS-AuCoNPs as shown Fig S4-a,b. Due to Pt NPs on outer shells, two peaks in Au<sub>4f</sub> region showed relatively lower intensity (Fig. S9-b). After the acid etching experiment, two peaks were disappeared in the Co<sub>2p</sub> region as shown in Figure S7-d. Two peaks both in the Au<sub>4f</sub> region and in the Pt<sub>4f</sub> region after acid etching exhibited enhanced signal to noise ratio (Fig. S9-e,f). XPS of PS-AuCoPt NPs before and after acid etching confirmed deposition of Pt NPs and complete etching of Co phases via acid treatments. We observed a shift in the XPS of Pt4f<sub>5/2</sub> and Pt 4f<sub>7/2</sub> spin-orbit components to 75.5 eV and 78 eV, respectively, after acid etching, which was attributed to surface passivation of Pt sites with Cl ions from the HCl treatment.



**Figure S9.** XPS of (a)  $\text{Co}_{2p}$ , (b)  $\text{Au}_{4f}$ , and (c)  $\text{Pt}_{4f}$  of PS-AuCoPt NPs and (d)  $\text{Co}_{2p}$ , (e)  $\text{Au}_{4f}$ , and (f)  $\text{Pt}_{4f}$  of acid etched PS-AuCoPt NPs

## References

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