

## Supporting Information

### **Hollow Flower Micelles from Diblock Copolymer**

Mohammad Changez, Nam-Goo Kang, Dong Woo Kim, and Jae-Suk Lee\*

[\*] Dr. M. Changez, Dr. N.-G. Kang, Dong Woo Kim, and Prof. Jae-Suk Lee  
Department of Nanobio Materials and Electronics,  
School of Materials Science and Engineering  
Gwangju Institute of Science and Technology  
123 Chemdan-gwagiro, Buk-gu, Gwangju  
500-712 Korea  
Fax: (+82) 62-715-2304  
E-mail: jslee@gist.ac.kr

### **Experimental Details**

### Formation of micelles

The amphiphilic diblock copolymer poly(2-vinylpyridine)-*b*-poly(2-(4-vinylphenyl)pyridine) (P2VP-*b*-PVPPy) (1 mg/mL) was solvated in the mixed solvent of methanol and water (95/5, v/v).

### Characterizations of Aggregates

#### DLS

The particles size analysis of the aggregates was performed by dynamic light scattering at 25 °C (DLS/Malvern Instrument, PCS). The scattered light of a vertically polarized He-Ne laser (632.8 nm) was measured at an angle of 30, 60 and 90°, and collected on an autocorrelator. The hydrodynamic diameters ( $d$ ) of vesicles were calculated by using the Stokes-Einstein equation  $d = k_B T / 3\pi\eta D$ , where  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature,  $\eta$  is the solvent viscosity, and  $D$  is the diffusion coefficient. CONTIN algorithms were used in the Laplace inversion of the autocorrelation function to obtain the size distribution.

#### SEM

For morphological study, (P2VP-*b*-PVPPy) aggregates solution was spin-coated (rpm 1500, 30s) on hydrophilic silica substrate, dried at room temperature, and coated with platinum for field emission scanning electron microscope (FE-SEM, Hitachi S-4700, Japan) analysis.

#### TEM

Field emission transmission electron microscope (FE-TEM) [JEOL, JEM-2100, 200 kV] was used for analysis. The aggregate of P2VP<sub>106</sub>-*b*-PVPPy<sub>95</sub> was drop-coated on 400 mesh carbon-coated copper grids, dried at room temperature, and finally stained with I<sub>2</sub> vapor.

#### AFM

Samples was spin coated on silica substrate and characterized by tapping mode

### **Synthesis of metal nanoparticles**

#### Synthesis of Pt DPNs

0.5 equiv ammonium hexachloroplatinate(IV)  $(\text{NH}_4)_2\text{PtCl}_6$  was coordinated with the pyridine units of  $\text{P2VP}_{106}\text{-}b\text{-PVPPy}_{95}$  solutions in mixed solvent of methanol and water (95/5, v/v) and reduction of a Pt complex itself mediated by methanol without the need of any reducing agent. The color of the solutions was changed to darkish after NPs formation.

#### Synthesis of Au NPs

0.5 equiv  $\text{AuCl}_3$  was coordinated with the pyridine units of  $\text{P2VP}_{106}\text{-}b\text{-PVPPy}_{95}$  solutions in mixed solvent of methanol and water and followed by 24 h stirring. Au NPs were finally synthesized by reducing with sodium borohydride ( $\text{NaBH}_4$ ) in block copolymer solutions. The colour of the solutions was changed from yellow to deep purple. The resultant solutions were further stirred for 5 h to complete the reduction and centrifuged for 10 min at 1000 rpm to remove the side salts and the precipitations.

#### Synthesis of Au-Pt hybrid DPNs

First 0.25/0.50 equiv  $\text{AuCl}_3$  with respect to pyridine units was coordinated with  $\text{P2VP}_{106}\text{-}b\text{-PVPPy}_{95}$  solutions in mixed solvent of methanol and water (95/5, v/v) and followed by 24 h stirring and reduction with  $\text{NaBH}_4$ . After forming the Au nanoparticles, appropriate amount of (0.25, 0.50, and 0.75 equiv, respectively)  $(\text{NH}_4)_2\text{PtCl}_6$ , were added to micelles solution, followed by 24 h stirring and reduction with  $\text{NaBH}_4$ . The color of the solutions was changed from deep purple to darkish brown.

### **Characterization of metals nanoparticles**

## TEM

Field emission transmission electron microscope (FE-TEM) [200kV, JEOL, JEM-2100] and the high voltage electron microscope (HVEM, 1250 kV, JEM-ARM 1300s, HV-GIF) were used to distinguish Pt and Au lattice in composite. TEM image processing for inverse fast Fourier transformation (IFFT) image analysis was carried out by Digital Micrograph software (version 3.0 manufactured by Gatan Inc). HAADF-STEM and EDS characterizations were performed with a FEI Technai G2 F30 Super-Twin transmission electron microscope operating at 300 kV. The effective electron probe size and dwell time used in HAADF-STEM-EDS mapping experiments were 1.5 nm and 200 ms per pixel, respectively. The compositions of Au-Pt bimetallic nanoparticles were determined by ICP–AES (ELAN 6000, Perkin–Elmer).

## Optical properties

Absorbance of metal nanoparticles containing polymer aggregates in solution were checked by UV-spectrophotometer (CARY 1E).

## Supporter Information Figures and Table

Figure S1A:

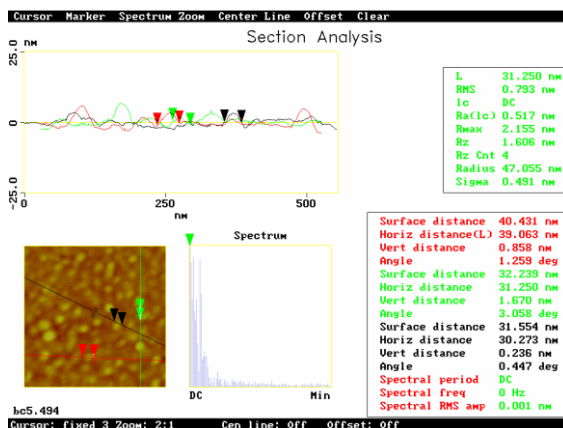


Figure S1B:

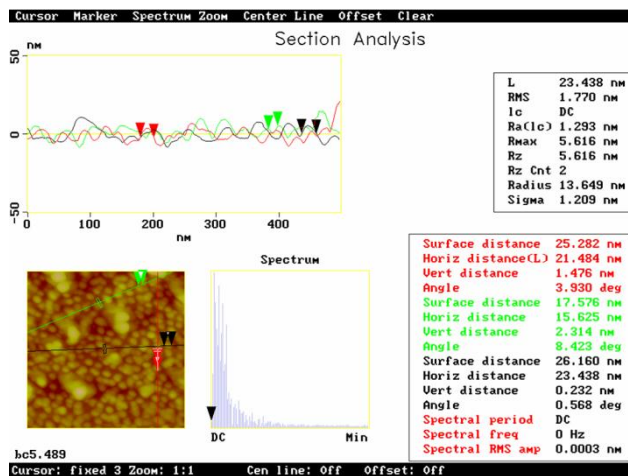
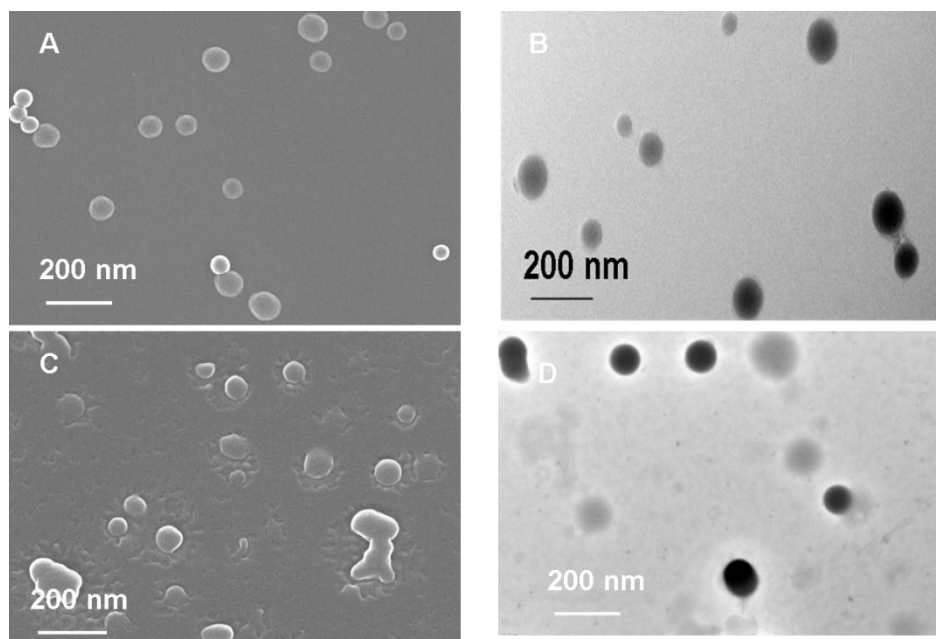
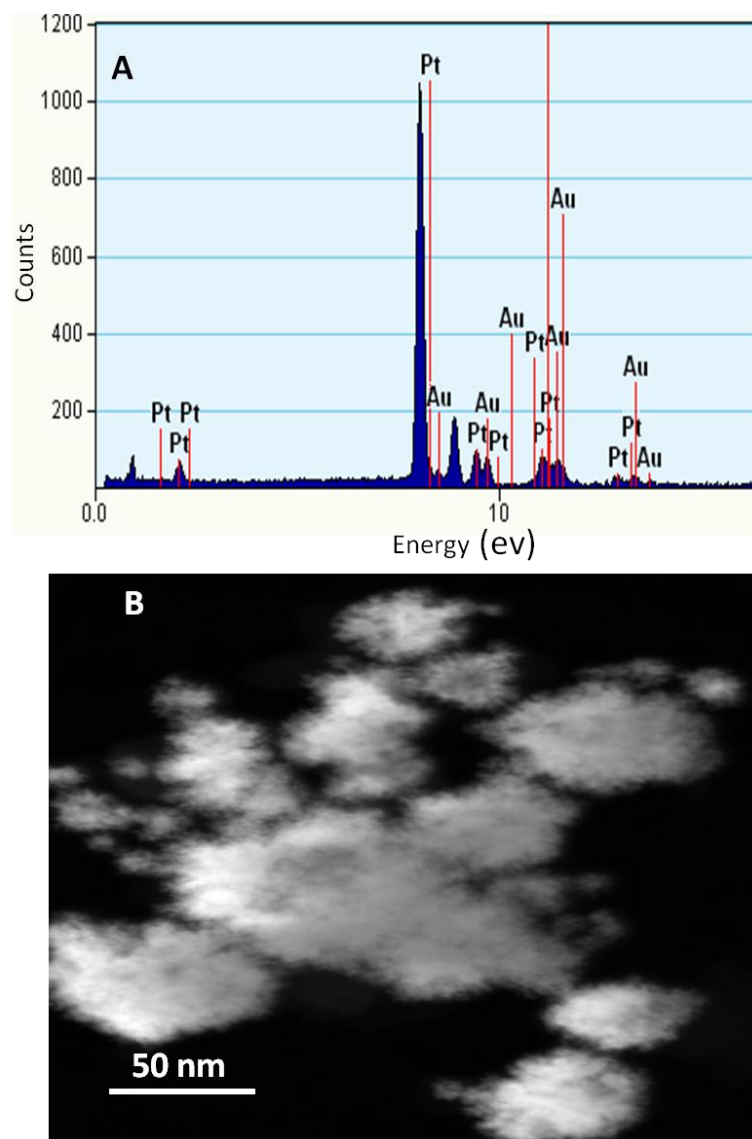


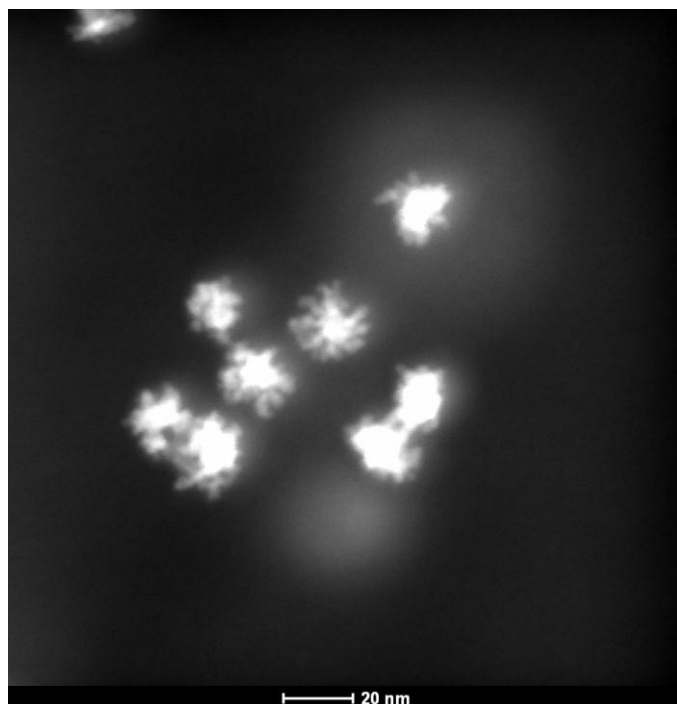
Fig. S1. AFM micrographs of the poly(2-vinylpyridine)-b-poly(2-(4-vinylphenyl)pyridine) in mixed solvent of methanol and water (95/5, v/v) at (A) pH 7 and (B) pH 8 (1 mg/mL concentration).



**Fig. S2. (A) SEM and (B) TEM micrographs of the poly(2-(4-vinylphenyl)pyridine) micelles in mixed solvent of methanol and water (95/5 v/v). (C) SEM and (D) TEM micrographs of the poly(2-vinylpyridine) micelles in mixed solvent of water and methanol (60/40, v/v).**

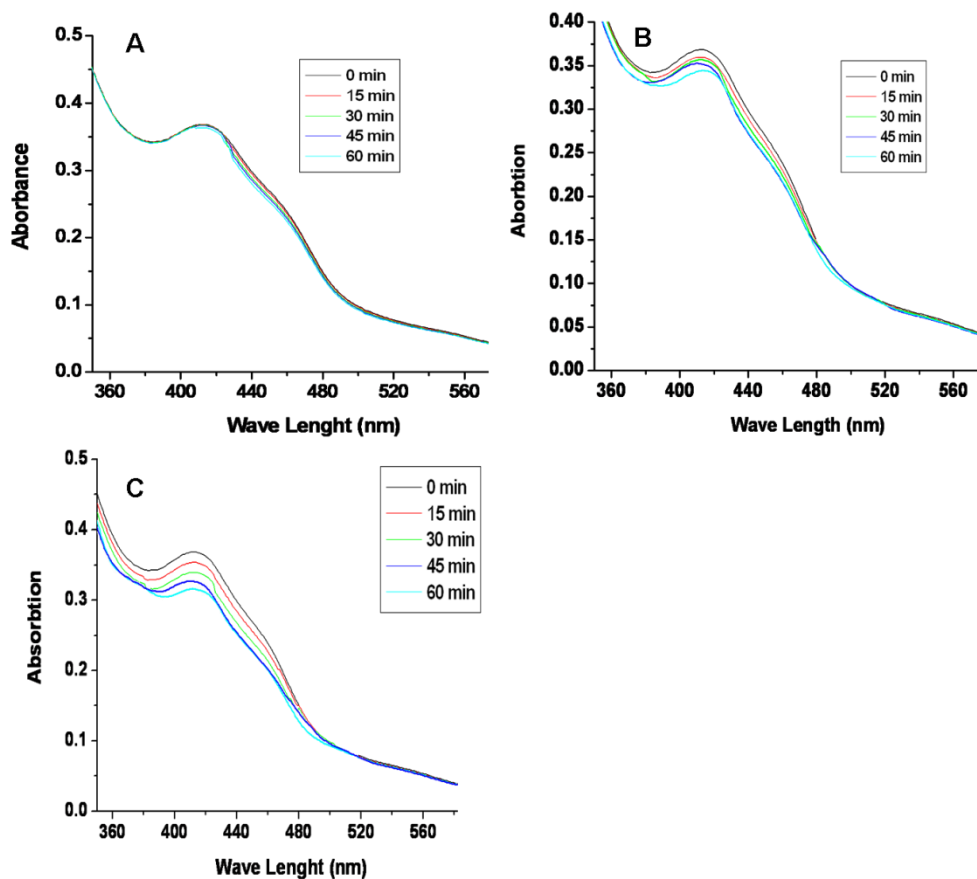


**Fig.S3. (A) Energy dispersive x-ray spectra and (B) The high-angle annular dark-field scanning TEM (HAADF-STEM) image of Pt-Au dendritic nanoparticles.**



**Fig.S4. The high-angle annular dark-field scanning TEM (HAADF-STEM) image of Pt-Au dendritic nanoparticles after 6 years of samples preparation.**





**Fig. S5. Time bound UV-vis spectra of the reaction between  $\text{Fe}(\text{CN})_6^{3-}$  and  $\text{S}_2\text{O}_3^{2-}$  at room temperature (A) in absence of catalyst, (B) presence of Pt, and (C) Pt-Au dendritic nanoparticles prepared by using poly(2-vinylpyridine)-*b*-poly(2-(4-vinylphenyl)pyridine) flower micelles as a template.**

**Table 1. Elemental analysis by the energy dispersive x-ray spectroscopy (EDS)**

<b>Element</b>	<b>Weight %</b>	<b>Atomic %</b>	<b>Uncert %.</b>	<b>Correction</b>	<b>k-Factor</b>
<b>Pt (L)</b>	<b>48.54</b>	<b>48.78</b>	<b>1.32</b>	<b>0.99</b>	<b>3.96</b>
<b>Au (L)</b>	<b>51.45</b>	<b>51.21</b>	<b>1.21</b>	<b>0.99</b>	<b>4.03</b>

**Note: Input FWHM = 134 eV @ 5.9 keV, Measured FWHM = 123.370 eV @ 5.9 keV**

**Calibration: 10.0188 eV/ch, -20.9881 eV at channel 0, Accelerating voltage: 300 kV, Alpha tilt: 15 degrees**