Supporting information:

Directed Self-assembly of Hetero-Nanoparticles Using Polymer Single Crystal Template

*Hui Zhang,[†] Bin Dong,[†] Tian Zhou, and Christopher Y. Li**

Department of Material Science and Engineering, Drexel University, Philadelphia, Pennsylvania 19104. [†]The authors equally contributed to this work. *Corresponding author. E-mail: chrisli@drexel.edu

Experimental section

3nm PtNP and 6nm AuNP were synthesized following literature methods.[1,2] 4-nitrophenol, 1-butanol, 10nm iron oxide magnetic nanoparticles, triethoxy(3-isocyanatopropyl)silane, 1,6-hexane dithiol, (3-mercaptopropyl)trimethoxy silane and sodium borohydride were obtained from Sigma Aldrich Company. 15nm SiO_2NP was obtained from Nissan Chemical Company. Hydroxy terminated polycaprolactone (PCL-OH 7k g/mol) was purchased from polymer source incorporation. Silane terminated polycaprolactone (PCL-Silane) was obtained by reacting PCL-OH (300mg dissolved in 10ml anhydrous dichloromethane) with triethoxy(3-isocyanatopropyl)silane (720mg, 2.97mmol) under nitrogen protection for overnight. The solution was concentrated using a rotor evaporator to about 1ml. The mixture was then slowly added into 100ml methanol to precipitate the PCL-Silane. UV-Vis spectra were collected using an Ocean Optics USB4000 Miniature Fiber Optic Spectrometer at room temperature. TEM experiments were carried out using a JEOL JEM2100 TEM operated at an acceleration voltage of 200kV. To prepare the TEM sample, one drop of solution was cast on a carbon-coated nickel grid. After solvent evaporation, the sample was used for TEM observation without further treatment.

Polymer single crystals were prepared using self-seeding method: 9mg of PCL-OH or PCL-Silane was dissolved in 30g 1-butanol at 60°C for 10mins. Then the solution was brought to 5°C for 2hrs. The crystal solution was then heated at 45°C for 10mins to obtain the crystal seeds. Finally, the solution was allowed to crystallize at 22°C for 24hrs. The suspension of the single crystals was isothermally filtered to remove uncrystallized polymers.

Fabrication of hetero-nanoparticles: In a typical experiment, to attach Fe_3O_4NP, polymer single crystal's 1-butanol solution was centrifuged, re-dispersed in pentyl acetate. Fe_3O_4NP solution was then added with 1 to 10 weight ratio and stirred for 24hrs. Centrifugation was utilized to remove free Fe_3O_4NP. 1wt% 1,6-hexane dithiol was then added to the solution containing Fe_3O_4NP decorated

polymer single crystal. After 1hr of reaction, the solution was centrifuged to remove excess 1,6-hexane dithiol. To attach PtNP, polymer single crystal's pentyl acetate solution was centrifuged and re-dispersed in methanol. Then, a suspension of the single crystal in methanol was mixed with PtNP in methanol solution with different volume ratio and incubated for 24hrs without stirring. Free ligands and nanoparticles were then removed by centrifugation. Finally, nanoparticle were detached from polymer single crystal by dissolving it in chloroform and concentrated to a volume of about 0.5ml. This mixture was slowly added to 20ml cold methanol to remove the free polycaprolactone polymer. This process was repeated three times to ensure the complete removal of the free polymer.

Catalysis test: 100µL of 2mM 4-nitrophenol and 100µL nanoparticle's aqueous solution was added to 1.67mL of deionized water. 2mL of 0.06M $NaBH_4$ solution was then added and this solution was examined by UV-Vis Spectrometer. Deionized water used in this catalysis experiment had been purged in nitrogen gas for at least 10mins to help remove oxygen.

References:

1. N. R. Jana, X. G. Peng, *J. Am. Chem. Soc.* **2003**, *125*, 14280.

2. N. Toshima, Y. Yamada, H. Hirai, *Chem. Lett.* **1981**, 793.