A General Approach toward Polymer-Coated Plasmonic Nanostructures – Supporting Information

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Experimental Part

Synthesis of gold nanospheres (Au₇₀). The synthesis of large gold spheres was carried out by a modification of a previously reported method.¹ A solution gold seeds (~15 nm, [Au] = 0.5 mM, 0.5 mL) prepared by Turkevich method,² were added to a growth solution (100 mL) containing cetyltrimethylammonium bromide (CTAB, 15 mM), HAuCl₄ (0.25 mM), and ascorbic acid (0.5 mM) and the mixture was kept at 30 °C for 1h. Upon synthesis, the solution was centrifuged (4500 rpm, 30 min) to remove excess CTAB and ascorbic acid, and redispersed in water.

Synthesis of gold nanorods. Gold nanorods were prepared using Ag-assisted seeded growth.³ Seeds were prepared by reduction of HAuCl₄ (0.25 mM, 5 mL) with NaBH₄ (10 mM, 0.3 mL) in aqueous CTAB solution (100 mM). An aliquot of seed solution (24 μ L) was added to a growth solution (10 mL) containing CTAB (100 mM), HAuCl₄ (0.5 mM), ascorbic acid (0.8 mM), AgNO₃ (0.12 mM), and HCl (19 mM). The mixture was left undisturbed at 30 °C for 2h. The solution (10 mL) was centrifuged twice (8000 rpm, 30 min) to remove excess silver salt, ascorbic acid, and HCl, and redispersed in Milli-Q water.

Synthesis of gold nanostars. The surfactant-free method was used to prepare Au nanostars.⁴ A solution gold seeds (~15 nm, [Au] = 0.5 mM, 0.5 mL) prepared by Turkevich method² was

added to a solution (50 mL) containing HAuCl₄ (0.25 mM) and HCl (1 mM), followed by addition of AgNO₃ (10 mM, 0.15 mL) and ascorbic acid (100 mM, 0.25 mL). To increase the stability of the obtained nanostars, CTAB (100 mM, 2.5 mM) was added to the growth solution. Upon synthesis, the solution was centrifuged (4500 rpm, 30 min) to remove excess reactants, and redispersed in water.

Ligand exchange. Thiolated polystyrene (Polymer Source, Inc) with a molecular weight of 53 kg/mol was used. The corresponding gold nanoparticle colloid (5 mM, 1 mL) was added dropwise under sonication to a THF solution (10 mL) of PS-SH (5 molecules of PS-SH per nm² of gold surface). The solution was kept in a ultrasonic bath for 15 min. To ensure ligand exchange, the resulting mixture was left undisturbed for 12h, and then centrifuged twice. The particles were finally dispersed in THF.

Encapsulation of individual nanoparticles. In a typical encapsulation experiment, water (1 mL) was added to the mixture of Au@PS colloid (1.8 mL THF) and PS₄₀₃-*b*- PAA₆₂ (Polymer Source, Inc) in THF (6 mg/mL, 0.2 ml) under magnetic stirring. Subsequently, the water content was increased up to 50 wt%, followed by increasing the temperature up to 70 °C, which was maintained for 30 min. The final solution was centrifuged twice (3500 rpm, 20 min) and the particles dispersed in pure water.

Encapsulation of clusters. In a typical self-assembly experiment, water (0.4 mL) was added to the Au@PS colloid (1.6 mL THF) under magnetic stirring. In the final mixture the concentration of gold was 0.25 mM. The solution was left undisturbed for 10 min and then a solution of PS_{403} *b*-PAA₆₂ in THF (6 mg/mL, 0.2 mL) was added. Subsequently, the water content was increased up to 35 wt%, followed by increasing the temperature up to 70 °C, which was maintained for 30 min. The clusters dispersion was centrifuged twice (2500 rpm, 20 min) and redispersed in water.



Fig. S1. TEM images of clusters before copolymer addition. The particles form disk-like structures upon drying on the TEM grid.

References

- 1. J. Rodríguez-Fernández, J. Pérez-Juste, F. J. García de Abajo, and L. M. Liz-Marzán, *Langmuir*, 2006, **22**, 7007–7010.
- 2. J. Turkevich, P. C. Stevenson, and J. Hillier, Discuss. Faraday Soc., 1951, 11, 55–75
- 3. M. Liu and P. Guyot-Sionnest, J. Phys. Chem. B, 2005, 109, 22192–22200.
- 4. H. Yuan, C. G. Khoury, H. Hwang, C. M. Wilson, G. A. Grant, T. Vo-Dinh, *Nanotechnology* 2012, 23, 075102(1-9).