

### *Experimental Procedures*

To synthesize LPS particles, we add 140 ml of deionized water, 10 ml of styrene and 22 mg of potassium persulfate into a one-neck rounded flask. The flask is sealed with rubber septum and purged with nitrogen. The flask is then placed in ultrasonication bath for ten minutes. Polymerization is performed by heating the flask to 75°C while it is tumbled at 30 RPM for 20 hours. After the polymerization, the reaction mixture is slowly cooled to room temperature. The diameter of LPS particles is ~380 nm determined by scanning electron microscopy. We then use the seeded emulsion polymerization technique for the synthesis of TMSPA-functionalized LPS. 0.5 g of LPS particles are redispersed in 2 ml of 2 w/v% polyvinylalcohol (PVA, 85~89% hydrolyzed, Mn 85,000~124,000 g·mol<sup>-1</sup>, Sigma-Aldrich) aqueous solution. We prepare a monomer solution containing 1.6 ml of styrene (St, 99%, Sigma-Aldrich), 0.4 ml of 3-(trimethoxysilyl) propyl acrylate (TMSPA, Sigma-Aldrich) and 40 mg of thermal initiator, 2,2'-azodi (2,4'-dimethylvaleronitrile) (V-65B,Wako). The monomer solution is emulsified in 8 ml of 2 w/v% PVA aqueous solution. The O/W emulsion is then mixed with the LPS seed particle dispersion and the mixture is tumbled at 40 rpm for 24 hours to allow the seed particles to be swollen by the monomer mixtures. Then, polymerization is carried out at 70°C for 24 hours and the tumbling speed is 60 rpm. The size of the TMSPA functionalized LPS particles increased by ~50 %. To make dimer particles, 0.5 g of TMSPA functionalized LPS particles are swollen by monomers containing 2 ml of St and 40 mg of the thermal initiator using the same procedure described above. The monomer mixture for the second swelling does not contain TMSPA. Dimeric shape is observed before the polymerization is conducted. Polymerization is performed under the same conditions described for the synthesis of TMSPA functionalized LPS particles.

After the polymerization, the dimer particles are washed by methanol several times to remove PVA and unreacted monomers. Asymmetrically coated dimer particles are obtained simply by mixing dimer particles with citrate-stabilized gold nanoparticles. Citrate-stabilized gold nanoparticles are prepared by the Turkevich method.<sup>22</sup> Excess amount of gold nanoparticles is added to the dimer particles dispersed in methanol. The mixture is lightly stirred with a magnetic bar for three hours at room temperature. The mixture is then washed by methanol several times to remove residual gold nanoparticles. For the growth of gold nanoparticles, we prepare reducible gold salt solution by dissolving 10 mg of potassium carbonate ( $K_2CO_3$ ) in 40ml of deionized water. 0.01 mg of Chloroauric acid ( $HAuCl_4$ , Sigma-Aldrich) and age the solution in the dark for at least one day before use. A hydroxylamine hydrochloride ( $NH_2OH \cdot HCl$ , Sigma-Aldrich) solution is prepared by adding 1.3 mg of hydroxylamine hydrochloride into 10 ml of deionized water. Then, 10 mg of asymmetrically gold-coated dimer particles is dispersed in 1ml of deionized water. After adding 0.3ml of  $K_2CO_3 / HAuCl_4$  solution, the mixture is sonicated for 10 min. Finally, 0.15 ml of hydroxylamine hydrochloride solution is added into the particle dispersion. There is a color change from red to violet. The dispersion is centrifuged and washed with deionized water. In addition to the functionalization with gold nanoparticles, gold nanorod and iron oxide nanoparticles are used to asymmetrically functionalize the dimer particles. (Fig. S.1) Gold nanorods and iron oxidized nanoparticles are prepared by the method reported by Liao et al<sup>30</sup> and Sahoo et al<sup>31</sup> respectively.

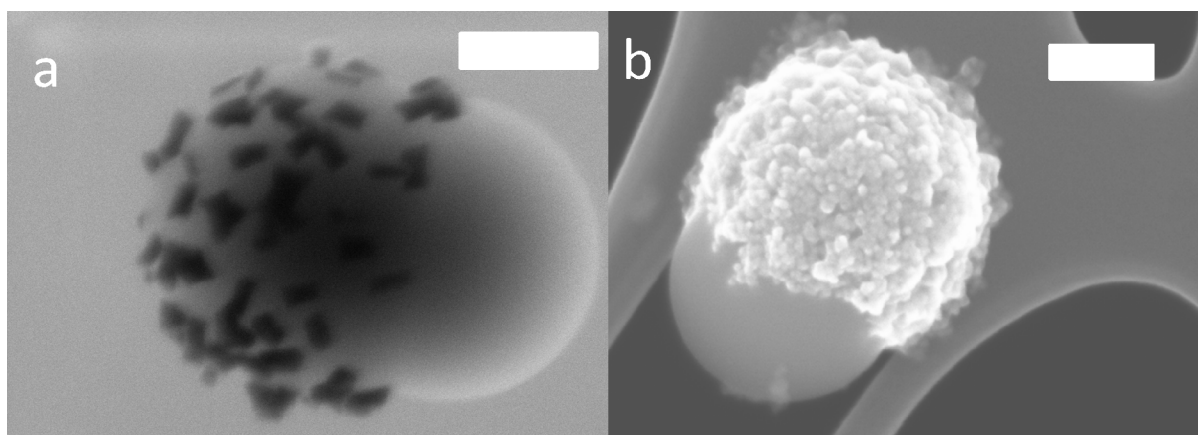


Fig. S.1 Asymmetric functionalization of dimer particles with a) gold nanorods and b) iron oxidized nanoparticles. The scale bar represents 200nm.