Interfacial Nano and Molecular Imprinting in Particle-Stabilized Emulsions

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1. Particle size measurement using dynamic light scattering

The size of the synthesized silica nanoparticles was measured by dynamic light scattering (DLS) using a Zetasizer Nano ZS instrument equipped with a software package DTS Ver. 4.10 (Malvern Instruments Ltd., Worcestershire, UK). Silica particles were dispersed in ethanol to a concentration of ~ 10 μ g mL⁻¹ before the DLS measurement. The average particle size measured by DLS was 150 nm, 220 nm and 330 nm.

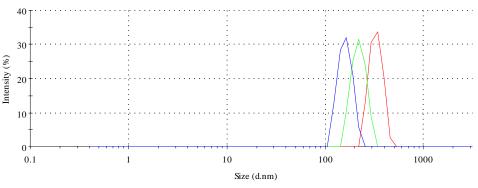


Figure S1. Size distribution of three different silica nanoparticles synthesized.

2. Colloidal stability of template-modified silica nanoparticles in water

The template-modified silica nanoparticles, Tem-I-SiO₂ and Tem-II-SiO₂, and unmodified particles (3 mg for each) were dispersed in 1.5 mL water containing 40 μ L MAA. The samples were shaken

vigorously and then left to stand at room temperature for 12 h. Figure S2 shows images of the different samples taken after 12 h standing. As seen, Tem-I-SiO₂ and Tem-II-SiO₂ remains well-dispersed after the standing, whereas the unmodified SiO₂ has sedimented to the bottom.

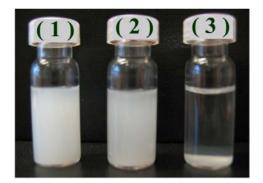


Figure S2. Colloidal stability of nanoparticles in water. The images were taken from aqueous suspensions of (1) Tem-I-SiO₂, (2) Tem-II-SiO₂, and (3) unmodified SiO₂. The size of the silica particles was 10 nm.

3. SEM imaging of MIP microspheres prepared using different sized silica nanoparticles

Scanning electron miscrope images were taken from two different MIP microspheres prepared using small (10 nm) and large (330 nm) template-modified silica particles. The instrument used was a JEOL JSM-T300 scanning electron microscope.

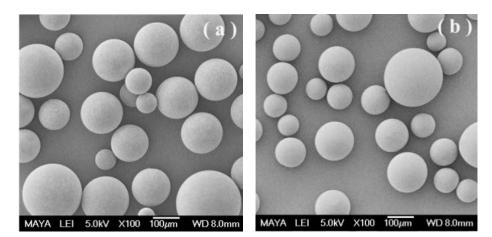


Figure S3. SEM images of MIP-I prepred using 10 nm silica (a) and 330 nm silica (b) as the stabilizing particles.

4. Titration of carboxyl groups on MIP-I and MIP-II with fluorescent AFN

The density of carboxyl groups on MIP-I and MIP-II was determined by titration with fluorescent acriflavin (AFN). The imprinted polymer particles (10 mg) were added into 1 mL of AFN solution (1 mg L^{-1} in methanol) and stirred at room temperature in dark for 16 h. After removing the solid particles,

the fluorescence intensity of the supernatant was measured. The difference of fluorescence intensity (at 488 nm) between the original AFN solution and the supernatant was used to calculate the amount of carboxyl groups on the MIP microspheres.

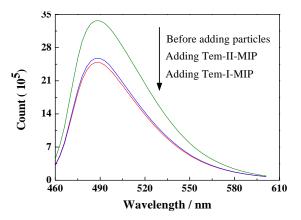


Figure S4. Fluorescence emission spectra of AFN solution before and after being exposed to different MIP particles. The excitation wavelength used was 450 nm.

5. Swelling experiment

The swelling behavior of the MIP microspheres was tested in water, 2-propanol, toluene and cyclohexane. Breifly, 1 mL of each solvent and 10 mg of dry polymer microspheres were placed in a 2-mL microcentrifuge tube, and shaken vigorously for 3 min. The particles were kept in the solvent for 12 h at 20 °C, before the excess solvent was removed by centrifugation and blotting with filter paper. The amount of solvent adsorbed by the MIP microspheres was calculated using the following equation:

$$V = \frac{m_{\rm s} - m_0}{m_0 \times d}$$

where m_0 and m_s are the mass of dry and swollen microspheres, respectively, and *d* is the density of the solvent at 20 °C.