Fabrication of asymmetric “Janus” particles via plasma polymerization

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Materials and Methods

Materials

Single crystals of sodium chloride (NaCl, 12.5 mm square x 1 mm thick) were purchased from SPI Supplies. Silica microparticles (3.08 ± 0.13 μm and 585 ± 0.02 nm diameter) and amino-modified silica particles (3.44 μm with standard deviation of 0.07 μm diameter) were purchased from Microparticles GmbH as 5% wt suspensions and were used as received. The particle sizes were specified by the manufacturer. 1-Bromopropane (Aldrich, 99%), sodium azide (Fluka, 99%), copper sulphate pentahydrate (Aldrich, 99%), sodium L-ascorbate (Aldrich, 98%), sodium iodide (Unilab, 99%) and dimethylsulfoxide (DMSO, Merck, 99%) were used without further purification. The fluorophores Alexa Fluor 488-Alkyne and Alexa Fluor 633-NHS (N-hydroxysuccinimide ester) were purchased from Invitrogen. High purity Milli-Q (MQ) water (> 18.2 MΩ) was obtained from an inline Millipore RiOs/Origin water purification system.

Particle Monolayer Preparation

The silica microparticles were washed once with MQ water and resuspended in ethanol. This ethanolic suspension (1 – 2.5% wt, 50 μL) was drop casted onto a NaCl crystal and left in ambient conditions to allow the solvent to evaporate.

Radio Frequency Glow Discharge (RFGD) Deposition

Deposition of brominated plasma polymers (BrPP) was carried out in a custom built reactor. The plasma reactor consisted of two internal capacitively coupled copper electrodes housed in a cylindrical glass bell jar (height = 36 cm, diameter (d) = 18 cm). The electrodes are spaced 15 cm apart with the top electrode (d = 11 cm) connected to an RF power supply and the bottom electrode (d = 11 cm) being grounded. The NaCl crystals are being placed on the bottom electrode. A rotary pump kept the reactor under vacuum. A round bottom flask containing the monomer 1-bromopropane was connected to the reactor chamber via a stainless steel line and the flow of monomer vapor was controlled via a manual valve. The monomer was degassed prior to plasma deposition. The parameters chosen for RFGD deposition of BrPP films was a load power input of 20 W, a frequency of 175 kHz, a treatment time of 20 s and an initial monomer pressure of 25 Pa. Prior to plasma deposition the reactor was evacuated to a base pressure of less than 0.1 Pa. After deposition, the reactor was immediately pumped down to base pressure before venting.
Particle Release
MQ water (ca. 1.5 mL) was used to rinse the particles off the NaCl crystal into 1.5 mL Eppendorf tubes. The particles were washed with MQ water to remove residual salts by three cycles of water centrifugation and redispersion.

Azide Nucleophilic Exchange
A solution (0.5 mL, DMSO/H2O, 1:1 (v/v)) of sodium azide (1M, pH 5, 5% NaI) was added to the Janus particles and placed in a Thermomixer at 60 °C for 6 h with agitation. The particles were washed by three cycles of MQ water centrifugation and redispersion.

‘Click’ Reactive Fluorophore Attachment
Sequentially, an aqueous solution of sodium ascorbate (200 μL, 3 mM), a DMSO solution of AF 488-alkyne (100 μL, 5 μg/mL) and an aqueous solution of copper sulfate (200 μL, 1 mM) was added to the azidated Janus particles. The tube was agitated for 30 min at room temperature (RT). The particles were washed for three cycles of centrifugation and redispersion using DMSO/ Milli-Q water and then three cycles with just Milli-Q water. For reactions without copper, MQ water was added instead. The particles were finally redispersed in water for analysis by confocal laser scanning microscopy (CLSM).

Amine Reactive Fluorophore Attachment
To the monofunctionalized particles, a DMSO solution of AF 633-NHS ester (100 μL, 5 μg/mL) was added. The tube was agitated for 30 min at RT. The particles were washed for three cycles of centrifugation and redispersion with DMSO/ MQ water, and then three cycles with just MQ water. The particles were finally redispersed in MQ water for analysis by confocal laser scanning microscopy (CLSM).

Hydrofluoric acid (HF) Etching
A 2:1 ratio of 13.3 M ammonium fluoride and 5M HF was pH adjusted to 4. The Janus particles were redispersed in MQ water (200 μL), then the buffered HF was added (150 μL) and agitated for ca. 10 s. The sample was washed with MQ water by three cycles of centrifugation and redispersion.

Cryo-TEM experiment
A laboratory-built humidity-controlled vitrification system was used to prepare the BrPP half shells for imaging in a thin layer of vitrified ice using cryo-TEM. Humidity was kept close to 80% and ambient temperature was 22 °C. Copper grids (200 mesh) coated with perforated Lacey carbon film (ProSciTech) was used. An aliquot (4 μL) of the sample was pipetted onto the grid prior to plunging. After 30 s adsorption time the grid was blotted manually using filter paper (Whatman 541) for ca. 2 s. The grid was then plunged into liquid ethane cooled by liquid nitrogen. The frozen grid was stored in liquid nitrogen until required. The sample was examined using a Gatan 626 cryoholder (Gatan) and Tecnai 12 transmission electron microscope (FEI) at an operating voltage of 120 kV. At all times low-dose procedures were followed, using an electron dose of 8-10 e-/Å2 for all imaging. Images were recorded using a Megaview III CCD camera and AnalySIS camera control software (Olympus) using magnifications in the range 60 000-110 000×.
Fig. 1 (a) CLSM image of BrPP-silica Janus particles on 3.4 μm amino-modified silica templates, reacted with red fluorescent AF 633-NHS ester, and with green fluorescent ‘click’ fluorophore AF 488-alkyne but without Cu(I) in the ‘click’ reaction, showing only red fluorescence. (b) TEM image of BrPP silica Janus particles deposited on 585 nm silica sphere templates. (c) SEM image of unmodified 585 nm silica sphere templates.