Electronic Supporting Information

In-Stacking: A Strategy for 3D Nanoparticle Assembly in Densely-Grafted Polymer Brushes

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Experimental Methods.

AuNP Synthesis: 13 nm (in diameter) AuNPs were synthesized via Turkevich method. Briefly, 40 µL of 2.5 M $HAuCl_4$ and 100 mL of Millipore water were added to a two-neck flask. A condenser was attached and the setup was allowed to reflux. Then, 10 mL of 38.8 mM of sodium citrate was quickly added before allowing further reflux for an additional 20 min. The setup was eventually allowed to cool to room temperature before AuNPs were retrieved.

pOEGMA Synthesis: 22 x 22 mm glass coverslips and oxidized silicon wafer substrates were first cleaned in piranha solution of H_2SO_4:H_2O_2 (3:1) for 20 min. After copiously rinsing with deionized H_2O and blown dry with N_2, the substrates were immersed in ethanol for another 20 min. After rinsing with ethanol and drying, they were immersed in aminopropyltriethoxysilane (10%) in ethanol for 2 h, and were then rinsed with ethanol and baked in an oven at 120°C for 3 h. Substrates were then immersed in a solution of bromoisobutyryl bromide (1%) and triethylamine (1%) in dichloromethane for 1 h, rinsed with dichloromethane and ethanol and blown dry with N_2. Polymerization was performed by immersing the substrates at room temperature in a degassed solution of Cu(I)Br (143 mg), bipyridine (312 mg) and OEGMA (8 mL) in methanol (12mL) and deionized water (3 mL) under nitrogen purge for a stipulated duration. Finally the substrates were removed, thoroughly rinsed with methanol and blown dry with N_2.

AuNP Incorporation: Substrates were immersed in a fresh 3 mL AuNP solution for a stipulated duration. Upon removal, they were copiously rinsed with deionized H_2O. They were then rinsed 3 times in deionized H_2O under orbital shaking at 120 rpm for 2 min each and finally blown dry with N_2. For repeat immersions, the same AuNP solution was used.

Characterization: Thickness measurements were obtained from the silicon substrates by ellipsometry in air using a J.A. Woolam α-SE spectroscopic ellipsometer. UV-vis spectra were obtained using a Shimadzu UV-2540 UV spectrophotometer. Atomic Force Microscopy data were obtained in air from an Asylum Research MFP-3D AFM system conducted in tapping mode. Scanning electron micrographs were obtained from JEOL JSM-6700F FESEM microscope. Except for AuNPs on APTS, all samples were coated with Pt for 30 sec at 20 mA.

Calculations.

The graft density of pOEGMA was calculated based on the following equation[17]:

$$\sigma = \frac{h\rho N_A}{\bar{M}_n}$$

Where σ is the graft density (chains/nm^2), h is the layer thickness determined by ellipsometry, ρ is the bulk density of the polymer (1.105 g cm^{-3} was used as stated by manufacturer), N_A is Avogadro's number and $\bar{M}_n$ is the number-average molecular weight of the polymer chains on the surface.

$\bar{M}_n$ was determined by conversion (taking ideal case of 100%) x targeted degree of polymerization (ratio of [OEGMA]/[bromo-initiator]=100) x MW of OEGMA (360 g/mol)

$$\bar{M}_n = 1 \times 100 \times 360 = 36000$$

$$\therefore \sigma = \frac{18.92 \times 1.105 \times 6.022 \times 10^{23}}{36000} \times \frac{1 \text{ nm}}{10000000 \text{ cm}}^3 = 0.35 \text{ chains/nm}^2$$
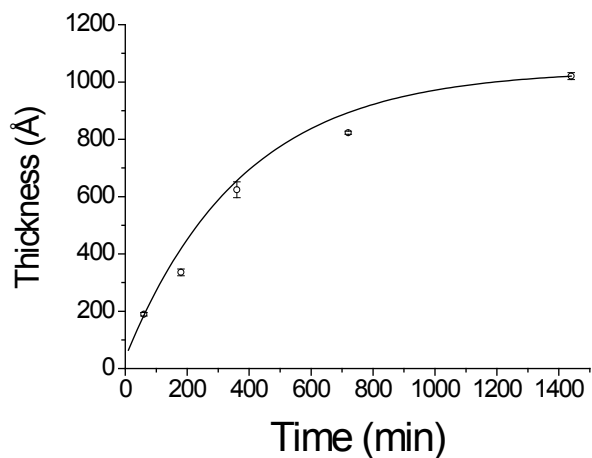
The surfacial blob size is calculated by combining equations (7) and (8) from Kim et. al.[11]:

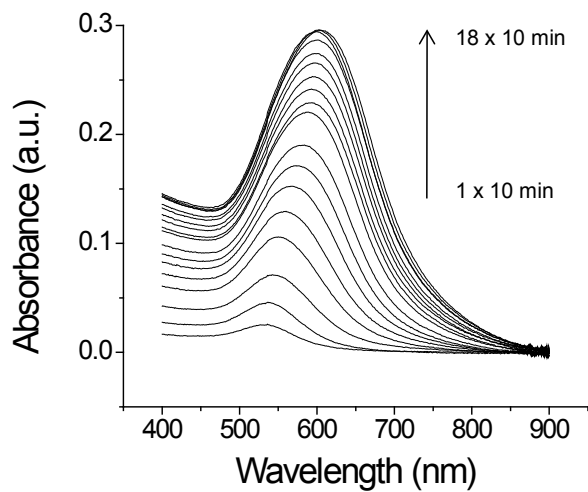$$\xi_{surf} = \frac{8h}{3\pi^2 a^2 \sigma^2}$$

a is defined as monomer size and was calculated from density:

$$a = \frac{360 \times 10000000^3}{1.105 \times 6.022 \times 10^{23}} = 0.5410$$

$$\therefore \xi_{surf} = \left(\frac{8 \times 18.92}{3\pi^2 \times 0.5410^2 \times 0.35^2}\right)^{1/3} = 5.22 \text{ nm}$$

Fig. S1 Ellipsometric thickness of polymer brush as a function of time.

Fig. S2 UV-vis spectra of 24-hr pOEGMA coated glass coverslips after each 10 min cycle for 13 nm AuNPs.