Electronic Supplementary Information

Comparison of RAFT derived Poly(vinylpyrolidone) verses Poly(oligoethyleneglycol methacrylate) for the Stabilization of Glycosylated Gold Nanoparticles

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Additional Experimental Details

X-ray photoelectron spectroscopy

The samples were mounted on to a sample bar using electrically-conductive carbon tape and loaded in to the fast-entry chamber of the Kratos Axis Ultra DLD spectrometer. Once the fast-entry chamber had been evacuated to an appropriate pressure, the samples were transferred in to the analysis chamber for data acquisition at pressures of less than $1x10^{-9}$ mbar. Core level XPS spectra were recorded using a pass energy of 20 eV (approx. 0.45 eV resolution), with the sample illuminated using an Al K α x-ray source (hν = 1486.6 eV). Analysis of the XPS data was carried out using the Casa XPS software, using mixed Gaussian-Lorentzian (Voigt) lineshapes. The transmission function of the analyser has been carefully determined using clean Au, Ag and Cu foils, whilst the work function of the analyser was determined using the Fermi edge of a polycrystalline Ag sample at regular intervals throughout the experiment, thereby allowing accurate composition and binding energy shifts to be determined. All binding energies have been referenced to the C 1s peak arising from adventitious carbon at 284.6 eV, a necessary correction due to the insulating nature of the oxide termination of the Si substrate.

Dynamic light scattering analysis for polymer-coated AuNPs

Polymer coating	Naked AuNP	$POEGMA_{70}$	$POEGMA_{120}$	$POEGMA_{230}$	PVP_{80}	PVP_{110}	PVP_{250}
Size (nm)	42.87	75.92	88.43	97.69	54.82	64.01	73.80

Saline stability of nanoparticle coatings

Firstly, solutions of polymer-coated AuNP in water (50 μL) were transferred to each well on a 96-well plate. The appropriate buffer (100 μL of MES, PBS, saline) was added and then mixed well. The resulting solutions were agitated at room temperature for 1 h. After that, UV-Visible absorption spectra were recorded.

LCST measurements of polymers in water and PBS

Lower critical solution temperatures (LCST) of the polymers were evaluated using an OptiMelt MPA100 system from Stanford Research Systems. The cloud points were determined by normalizing the turbidimetry curve such that the values were in the range of 0 to 1, and the transition temperature was defined as being the temperature corresponding to a normalized absorbance of 0.5. A concentration of 3 $mg.mL^{-1}$ in water or PBS and a constant heating rate of 2 °C min^{-1} were used in all experiments.

To determine the LCST of the polymer-coated AuNP, solutions of the indicated nanoparticle were prepared in HEPES or PBS at room temperature at a concentration of 0.2332 $mg.mL^{-1}$. A UV-Visible absorption spectrum was recorded for every 2-5 °C.

General procedure for the synthesis of sugar-coated gold nanoparticles

As a representative example, the dispersion of polymer-coated particles (0.5 mL) was concentrated by firstly being centrifuged (11,000 rpm) to a pellet and then diluted with MES (100 μL). To this was then added a solution (25 μL) of NHS and EDC (10 mg each in 100 μL MES). The resulting mixture was then shaken at room temperature for 30 min. Excess coupling agents and small molecule by-products were removed by washing the NHS-activated-AuNP with MES buffer (0.3 mL) thrice using the aforementioned centrifugation-resuspension cycle. After the final wash and removal of supernatant, a solution (150 μL) of the galactose(glucose)amine (0.33 mg.mL^{-1} in PBS) was added to the pellet and the resulting mixture was heated at 35 °C for 17 h. Excess sugar and by-products were removed by washing the sugar-coated AuNP with HEPES buffer (0.3 mL) by three centrifugation-resuspension cycles. After the final cycle, the particles were diluted with HEPES buffer (ca. 0.5 mL) to an OD of ca. 0.25 for lectin-binding assays. It should be noted that upon addition of sugar, particles derived from all the POEGMA-coated AuNP as well as that from PVP80-coated AuNP appear to be aggregated. As a consequence, only glucose-PVP110-AuNP, galactose-PVP110-AuNP, glucose-PVP250-AuNP and galactose-PVP250-AuNP were used for subsequent binding assays.

Carbohydrate-lectin interactions

Surface binding assays

Greiner high binding 96-well plates (half volume) were incubated for 17 h with solutions of ConA (50 μL of 0.1 mg.mL^{-1} HEPES) per well. After incubation, unbound ConA was removed by washing vigorously with nanopure water, after which the plates were dried and stored at 4 °C.

Solutions of S-PVPx-AuNP (S = glucose or galactose, x = 110, 250) were made up as ½ serial dilutions in HEPES from 0.233 mg.mL^{-1} stocks. The AuNP solutions (35 μL) were then added to 96-well plates functionalized with ConA and incubated at room temperature for 1 h. After removing the unbound AuNPs by extensively washing with nanopure water, the absorbance in each well was measured between 450 and 700 nm in 1 nm steps.

Solution binding assays

A stock solution of 1 mg.mL^{-1} ConA was made up in HEPES buffer (10 mM with 0.5 mM $CaCl_2$, 0.5 mM $MnCl_2$ and 0.5 mM $MgCl_2$). Serial dilutions (35 μL) of ConA were made up in the same buffer in a 96-well microtitre plate so that when the nanoparticles were added the resultant concentration was 0.5 mg.mL^{-1} – 0.02 mg.mL^{-1} and a control with 0 mg/mL of ConA. Solutions of S-PVPx-AuNP (S = glucose or galactose, x = 110, 250) (35 μL) was added to each concentration of ConA and incubated at room temperature for 10 min. An absorbance spectrum between 450 nm and 700 nm was then recorded.

Saline stability testing of the nanoparticles

Figures showing the spectrophotometric analysis (absorbance) of each differently coated nanoparticle between 450-700 nm in each of the 6 solutions.

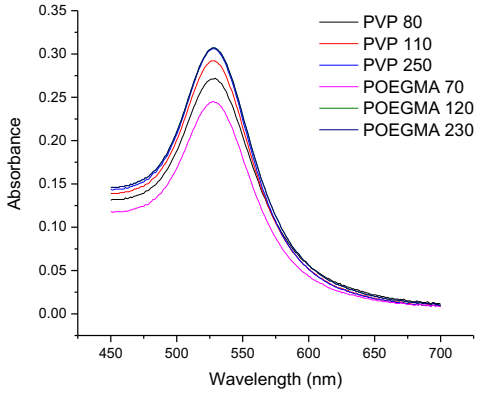

Figure S1 Spectrophotometric analysis showing the absorbance of each coated nanoparticle in 0.5M NaCl

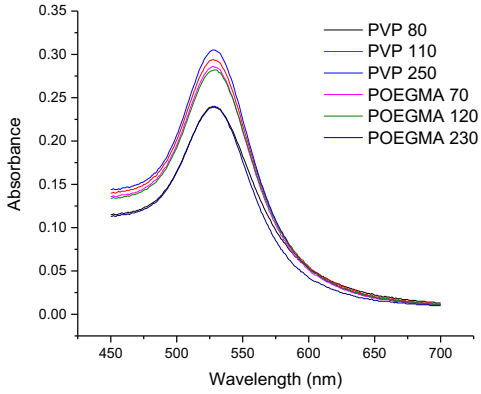

Figure S2 Spectrophotometric analysis showing the absorbance of each coated nanoparticle in 1M NaCl

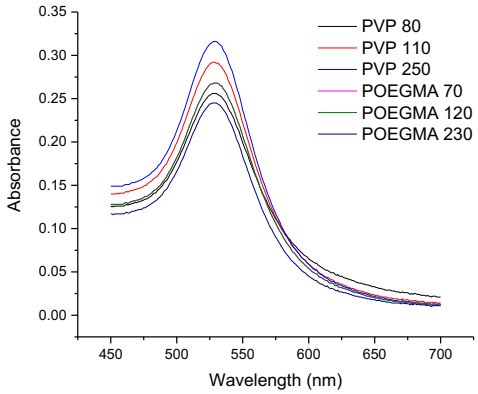

Figure S3 Spectrophotometric analysis showing the absorbance of each coated nanoparticle in 2M NaCl

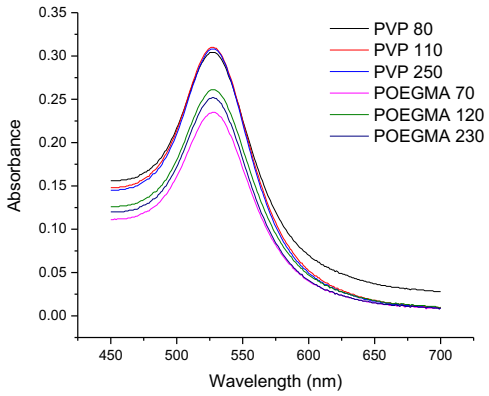

Figure S4 Spectrophotometric analysis showing the absorbance of each coated nanoparticle in MES buffer

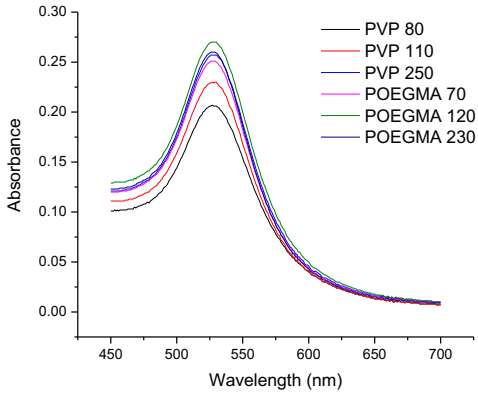

Figure S5 Spectrophotometric analysis showing the absorbance of each coated nanoparticle in PBS

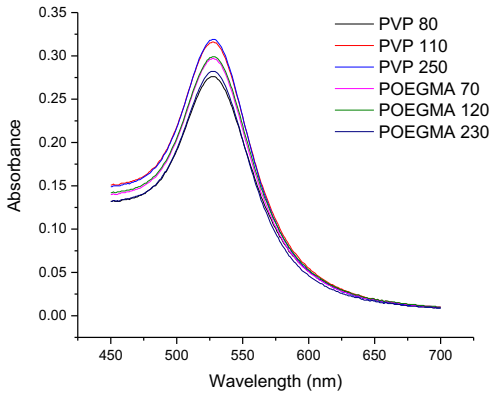

Figure S6 Spectrophotometric analysis showing the absorbance of each coated nanoparticle in water