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Segmental Janus Nanoparticles of Polymer Composites

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Experimental Details

Materials

Sodium borohydride ($NaBH_4$), sodium citrate (purity: 99%), hydrogen tetrachloroauratetrihydrate ($HAuCl_4 \cdot 3H_2O$, purity: 99.9%), ascorbic acid (AA, purity: 99.9%) and cetyltrimethylammonium bromide (CTAB, purity: 99%) were obtained from Sigma-Aldrich. PS_{5k}-SH (M_w/M_n=1.15), PS_{50k}-SH (M_w/M_n=1.06), PEO_{10k}-SH (M_w/M_n=1.08) were purchased from Polymer Source Inc. (Canada). $P4VP_{50k}$-SH (M_w/M_n=1.12) was synthesized according to the reported procedure.[1] CdSe quantum dot (size: ~8 nm) was purchased from Wuhan Jiayuan Quantum Dots Co., LTD. Deionized water (Millipore Milli-Q grade) with resistivity of 18.0 MΩ was used in all the experiments. All the glassware was cleaned by aqua regia and rinsed with deionized water prior to the experiments.

Synthesis and Modification

Synthesis of AuNPs: Monodisperse AuNPs (8 nm, 16 nm, and 24 nm) were synthesized through a modified seeding growth approach.[2] All the Au NPs solutions were used as starting materials for ligand-exchange within 1 h after preparation.

Surface Modification of Au NPs: A monodisperse Au NP (size: 16 nm) capped with CTAB was synthesized through a modified seeding growth approach.[2] Entire surface of Au NP was terminated with PS-SH through two-step ligand-exchange approach.[3] In a typical experiment, 0.4 mL of the concentrated (~0.8 mg/mL) aqueous solution of NPs was added to 10 mL of PS-SH solution in THF (0.2 mg/mL). The solution was sonicated for 30 min and incubated for 24 h. The modified NPs were washed with chloroform to remove CTAB and free PS-SH, and the precipitate was dissolved in 4 mL of $CHCl_3$. Purification was performed through three 30-min-long centrifugation cycles at 10k-12k rpm. PS-SH (4 mg) in $CHCl_3$ (10 ml) was added to the PS@Au NPs solution, followed by the same sonication, incubation and purification. Finally, the PS@Au NPs were achieved.

Preparation of the Janus NPs

Monolayer of the PS@Au NPs: The PS@Au NPs were dispersed in $CHCl_3$ at the concentration of 80 mg/mL. ~2 μL of PS@Au NPs dispersion was dropped on the surface of milli-Q water. After evaporation of chloroform, a centimeter-sized free-standing monolayer of PS@Au NPs was assembled. Subsequently, the monolayer was transformed to the silicon wafer *via* dip-coating or sedimentation

Preparation of the Janus NPs: The NPs coated silicon wafer was placed in the plasma cleaner and etched for 1 min at different power (low: 6.8 w, medium: 10.5 w, high: 18 w). The etched silicon wafer was steeped in ethanol solution of $P4VP_{50k}$-SH (0.2 mg/mL) under gentle shaking for 24 h, for the grafting onto the naked surface of the NP. The silicon wafer was cleaned with water to remove free polymers and sonicated in CH_3Cl for 30 min. The Janus PS-Au-P4VP NPs dispersion in CH_3Cl was obtained. Preparation of the Janus PS-Au-PEO NP was the similar but using PEO_{10k}-SH (0.2 mg/mL).

Characterization

Transmission Electron Microscopy (TEM) measurement was performed on a JEOL 2100 LaB_6 or FEI TEM operated at voltage of 200 kV. TEM samples were prepared on 300 mesh copper grids covered with carbon film. Before TEM measurement, the grid was treated with iodine vapor for 8 h to selectively stain P4VP, and soaked in phosphotungstic acid solution (wt% = 1%) for 30 seconds to make the polymer domain clear.

X-ray photoelectron spectroscopy (XPS) measurement was performed on an XPS (AXIS-ULTRA DLD-600W, Shimadzu, Japan) to obtain element content (Au, C, N) of three types particles (PS@Au NPs, plasma etched PS@Au NPs and PS-Au-P4VP NPs).

Dynamic Light Scattering (DLS) analysis was performed at room temperature on a Malvern Zetasizer Nano ZS using a He-Ne laser with a wavelength of 632 nm.

Water contact angles measurement was performed on a Contact Angle Meter (Model:

JC2000C, Powereach, Shanghai, China). A certain amount of water (~200 μL) was droplet on the surface of substrate.

References

1. H. Y. Tan, G. C. Zhang, Y. C. Lin, L. Ma, T. Tang, *RSC Adv.*, 2016, **6**, 106648-106655.
2. N. R. Jana, L. Gearheart, C. J. Murphy, *Langmuir*, 2001, **17**, 6782-6786.
3. H. Yockell-Lelièvre, J. Desbiens, A. M. Ritcey, *Langmuir*, 2007, **23**, 2843-2850.

Additional Figures:

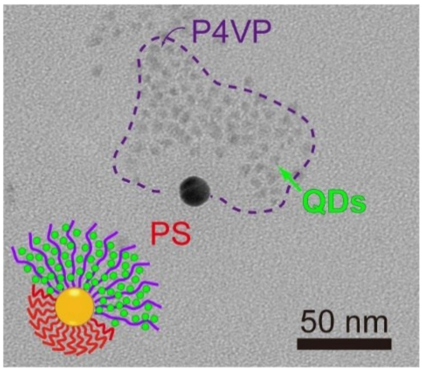

Fig. S1. TEM image and inset illustration of the coordination between CdSe quantum dots (QDs) and Janus PS_{50k}-Au-$P4VP_{50k}$ NPs.

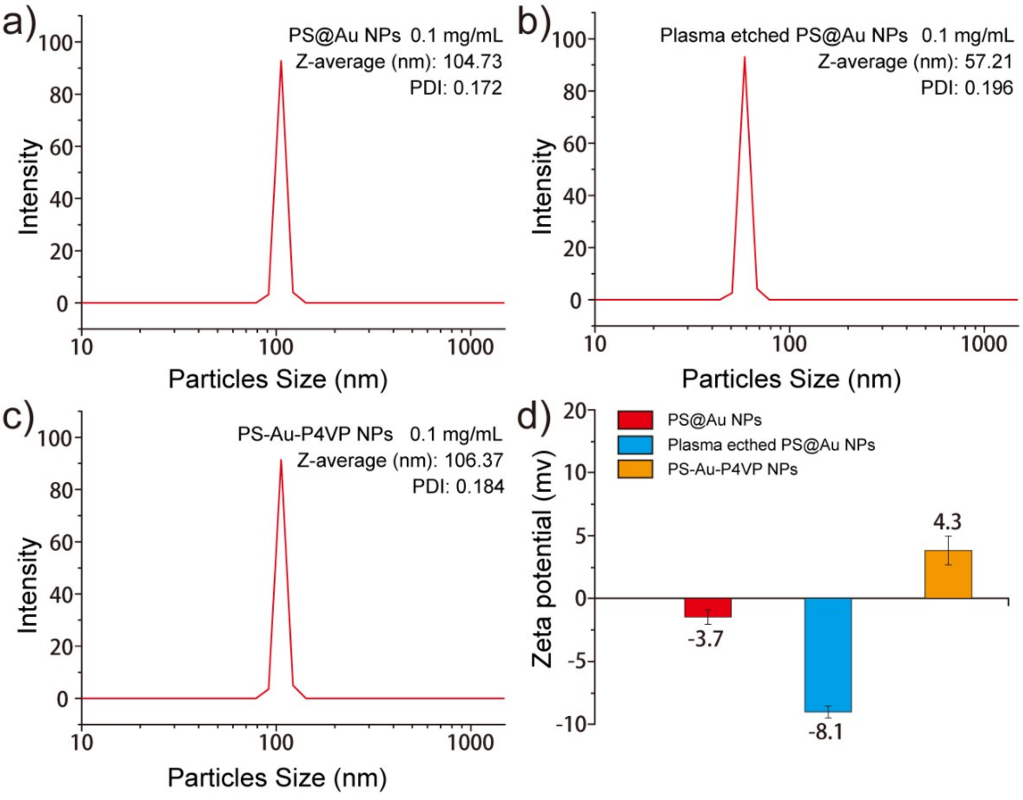

Fig. S2. The average particle size of three types NPs: a) PS@Au NPs; b) plasma etched PS@Au NPs; c) PS-Au-P4VP NPs, and d) their zeta potentials, which are measured from DLS.

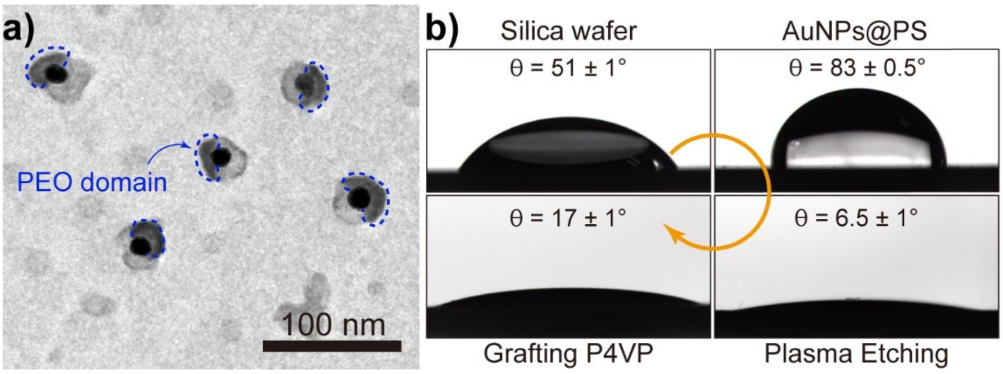

Fig. S3. a) TEM image of the Janus PS_{5k}-Au-PEO_{10k} NPs (the sample was stained with RuO_4); b) water contact angle measurement on silica wafer, monolayer from 15 nm PS_{5k}-Au NPs, after plasma etching, and grafting with PEO_{10k}.

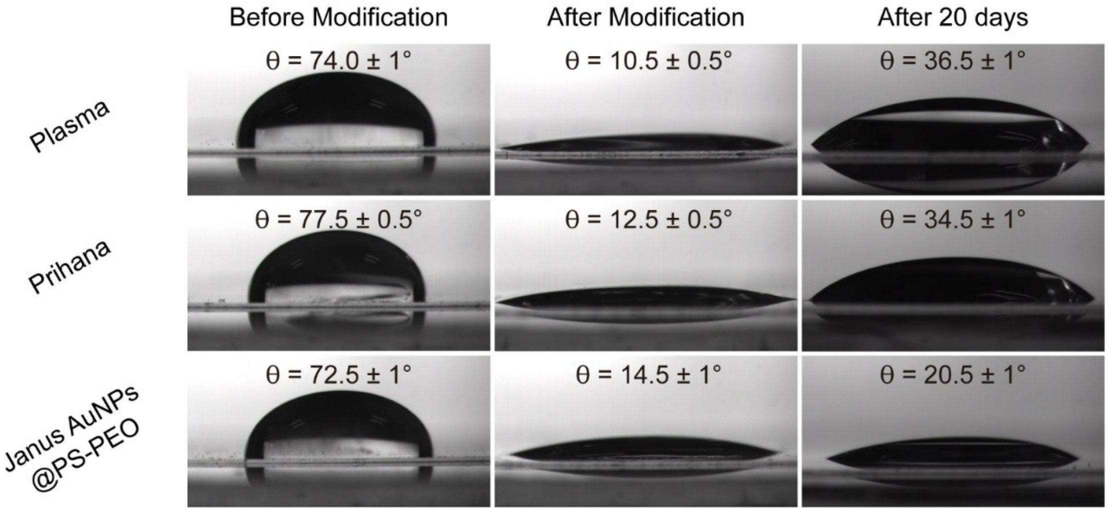

Fig. S4. Optical microscopy images showing water contact angle measurement on silica wafer after hydrophobic modification, after hydrophilic modification with plasma and after 20 days, coated with prihana, and Janus PS_{5k}-Au-PEO_{10k} NPs.

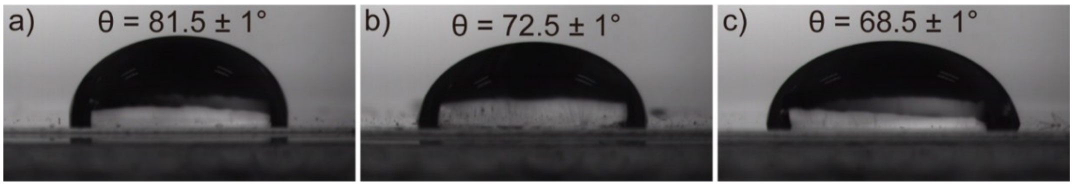

Fig. S5. Water contact angle measurement on the monolayer from: a) Janus PS_{50k}-Au-$P4VP_{50k}$ (2:1); b) Janus PS_{50k}-Au-$P4VP_{50k}$ (1:1); Janus PS_{50k}-Au-$P4VP_{50k}$ (1:2).

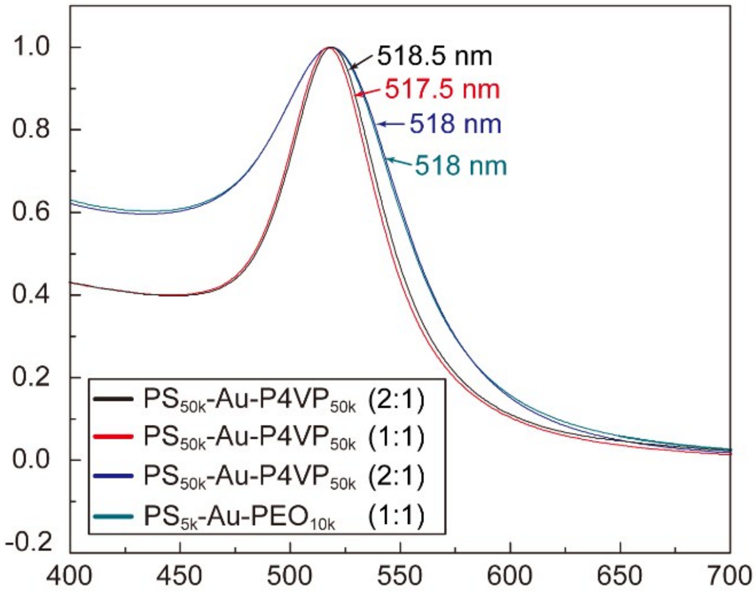

Fig. S6. The UV-vis spectra of four types Janus NPs with different surface functionalities.

Additional Tables:

Table S1. Peak positions and atomic ratio of the XPS measurement for Au, C, and N obtained from PS$_{50k}$@Au NPs monolayer, plasma etched PS$_{50k}$@Au NPs monolayer and PS$_{50k}$-Au-P4VP$_{50k}$ NPs monolayer.

	PS$_{50k}$@Au NPs monolayer			Plasma etched PS$_{50k}$@Au NPs monolayer			PS$_{50k}$-Au-P4VP$_{50k}$ NPs monolayer		
	Peak position (eV)	Atomic Ratio (%)	Absolute atom number	Peak position (eV)	Atomic Ratio (%)	Absolute atom number	Peak position (eV)	Atomic Ratio (%)	Absolute atom number
Au 4f	83.31	0.25	100	83.31	0.48	100	83.64	0.23	100
C 1s	284.68	99.75	39900	284.68	99.52	20733.33	284.35	93.96	40852.17
N 1s	/	/	/	/	/	/	399.9	5.81	2526

Table S2. The composition of three types emulsions.

Sample	Water /μL	CHCl$_3$ /μL	PS /mg	Emulsifier	Emulsifier amount / mg
A	400	50	0.5	N/A	N/A
B	400	50	0.5	PS@Au NPs	0.1
C	400	50	0.5	Janus PS$_{5k}$-Au-PEO$_{10k}$	0.1