Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

For

Measurement of Surface Hydrophobicity of Engineered Nanoparticles using Atomic Force Microscope

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S1. Properties of nanoparticles (NPs), cantilevers and substrates

Figures S1a~g show TEM morphology images of TiO_2, ZnO, SiO_2, CuO, CeO_2, hematite (α-Fe_2O_3), and Ag NPs used in this study, and they are close to spherical shape with diameters of 25.0±5.9, 52.0±9.1, 33.2±0.8, 42.1±1.8, 20.0±3.0, 53.0±6.0, and 80.0±0.7 nm, respectively, which were consistent with the manufacturer-reported values. **Figure S1h~m** provide the particle size distribution histograms computed from TEM images via the image processing and analysis program ImageJ. TiO_2, ZnO and Ag NPs had relatively broad size distribution, while SiO_2, α-Fe_2O_3 and CuO NPs had much narrower size distribution.

Table S1. List of the NPs used in this study.

NPs	Average particle diameter (nm)	pH of the suspension	Crystal type	Vendor
Fe_2O_3	49	4.0	Alpha (hematite)	Lab-synthesized [1]
TiO_2	25	6.9	Anatase	Aldrich
CeO_2	25	4.5	Cubic (fluorite)	Aldrich
ZnO	50	6.8	--	Aldrich
SiO_2	33	5.9		Aldrich
CuO	42	7.0	Gamma and alpha	Nanostructured &AmorphousMaterials
Ag with citrate coating	80	5.0	Cubic	Ted Pella

Table S2. Summary of the cantilever tip properties.

Cantilever type	Surface functionalization	Radius of curvature (R_C) of the tip (nm)	Spring constant (N/m)[c]	Frequency (kHz)	Water contact angle (°)
Gold-coated Si_3N_4 tip[a]	CH_3-terminated end group	42±12	0.06±0.03	17±4	105
Gold-coated Si_3N_4 tip[a]	None	42±12	0.06±0.03	17±4	0
Si_3N_4 tip[b]	None	20±5	0.07±0.05	22±7	15

[a,b] more information is available at http://www.asylumresearch.com/Probe/RC800PB,Olympus and http://www.brukerafmprobes.com/p-3444-mlct.aspx. [c] spring constants (K_{sp}) were determined by the Agilent Thermal K tuning modulus (see Agilent 5500 User's Guide for details).[2]

Table S3. Water contact angles for various NP surfaces.

NPs	Contact angles (°)	Typical photos of the water droplet
Fe_2O_3	16.5 ± 0.6	
TiO_2	7.5 ± 4.3	
CeO_2	49.5 ± 0.5	
ZnO	69.0 ± 0.4	
SiO_2	63.4 ±9.5	
CuO	41.0 ± 0.6	
Ag	72 ± 3.2	

Table S4. Water contact angles for various substrate surfaces.

Gold surfaces coated with CH_3	Molar fractions of CH_3				
	0%	25%	50%	75%	100%
Contact angle (°)	30±1	60±2	82±2	100±3	105±5
SAMs	PEG-coated surface	Silane-coated surface	Biotin-coated surface	Biotin and streptavdin conjugated surface	
Contact angle (°)	10±2	96±2	18±3	23±1	

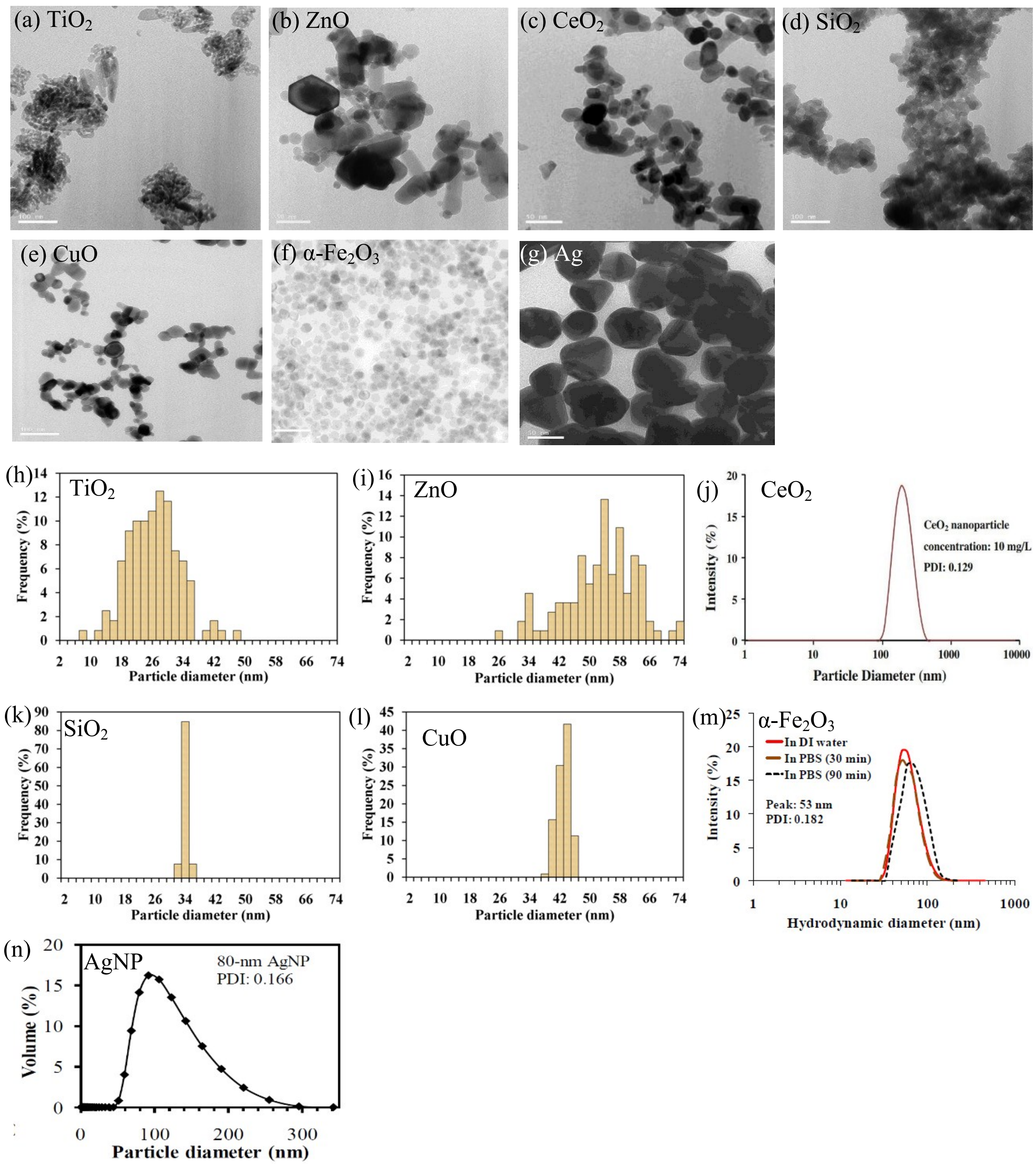

Figure S1. (a~g) TEM images of TiO_2, ZnO, CeO_2, SiO_2, CuO, hematite (α-Fe_2O_3), and AgNPs, on a carbon-coated grid. All the white bars on the bottom left equals 100 nm, except the one in (b-c, g) that equals 50 nm. (h~n) Particle diameter distribution histograms.

S2. Adhesion force measurement with AFM

An Agilent 5500 AFM (Molecular Imaging) was used for the adhesion force measurement in contact mode. Before operating the AFM, the resonance frequency and spring constant of the cantilever tips were tuned and determined. The cantilever tip used in our experiments had the nominal spring constant (K_{sp}) of 0.11 ± 0.03 N/m and the actual constant was determined by Agilent Thermal K tuning modulus (see Agilent 5500 User's Guide for details).[2] The nominal resonance frequency was 17 ± 13 Hz and the actual resonance frequency was determined for each new cantilever probe by sweeping the drive signal through a range of frequencies about the nominal resonance frequency. The drive frequency was set 0.1 kHz off the resonance frequency.[3]

For the adhesion force measurements, the loading force applied to the NP surface was fixed at *ca.* 6 nN by setting the maximum deflection of the cantilever at 100 nm. The initial deflection was set at -1.2 ± 0.1 V with a setpoint of 0 V, allowing a slight contact between the tip and the sample before the approaching stopped. Each cycle of force measurement includes approach, contact, and retraction as shown in **Figure S2a**. Briefly, NPs immobilized on the silicon wafer seated on a piezo scanner approach the cantilever and stop when the cantilever probe contacts the NPs with a slight compression force as specified above. As a result, the cantilever slightly bends up and the reflected laser reaches the setpoint (0 V). After the cantilever further compresses the tip against NPs for 100 nm, the cantilever begins to lift up and due to the adhesion force between the tip and the NPs the cantilever will be dragged by the piezo scanner for a certain distance, which is the recorded as the maximum deflection and converted to the cantilever displacement (*d*). After each cycle, a force-distance curve containing 500 datapoints was generated in **Figure S2b** and adhesion force (nN or pN) was obtained according to Hooke's law: $F_{ad} = K_{sp}d$, where d is the deflection displacement of the cantilever (nm). The deflection displacement relative to the baseline (no deflection of the cantilever), where the tip is no longer in contact with the sample surface, was read in deflection amplitude (V). The deflection amplitude (V) was converted to the deflection displacement (nm) also based on the Thermal K tuning modulus. A typical histogram of adhesion force distribution was generated for each sample surface as shown in **Figure S2c**.

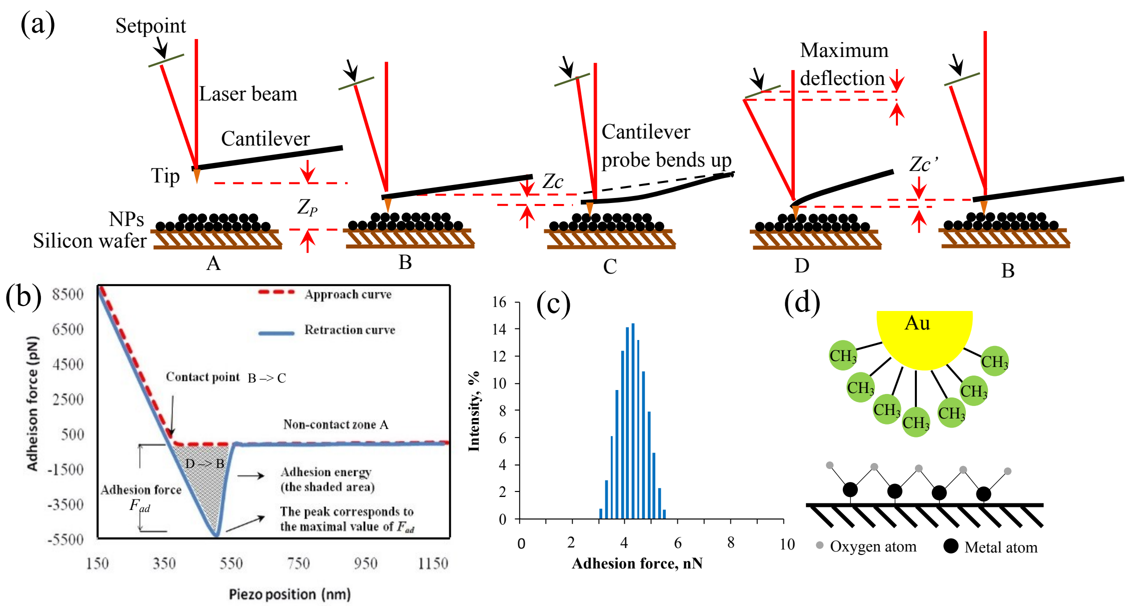

Figure S2. (a) Schematics of a complete cycle of force measurement with AFM (in order of A-B-C-D-B-A). Z_p is the initial displacement of piezo scanner away from the tip and the NPs (black dots) were immobilized on the silicon wafer substrate; Z_c is the bending distance of the cantilever probe when compressed against the NPs; Z_c' is the deflection displacement of the cantilever when pulled up away from the contact; (b) A typical force-distance curve generated by AFM; (c) A histogram of adhesion force distribution; (d) The interaction between the chemical modified gold tip (functionalized with a hydrophobic -CH_3) and a typical atomic structure of metal oxide NPs.

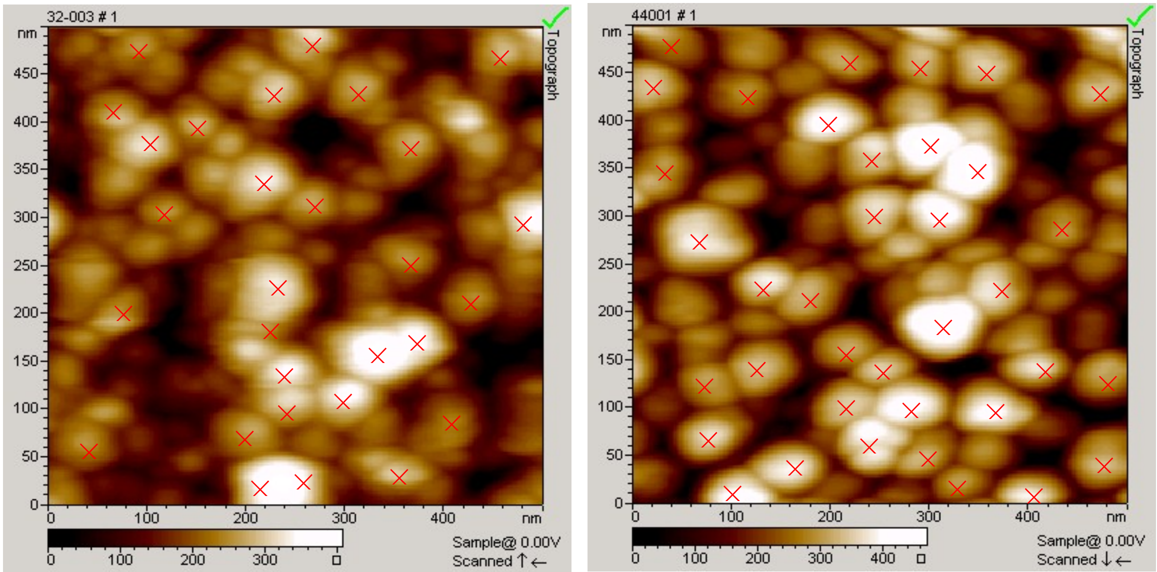

Figure S3. Adhesion force curve collection positions (red crosses) on the AFM height image (500 nm × 500 nm). The samples are CeO_2 NPs deposited on silica wafer.

S3. Quality Assurance (QA)/Quality Check (QC) for adhesion force measurements

To verify the coating integrity of the functionalized tips during the force measurement, adhesion force measurements are carried out on the gold substrate surface functionalized with 100% CH_3- group after 20-30 force measurements on sample surfaces. The measured adhesion force values should have variations of less than 10% of that obtained with the newly prepared tips. Otherwise, the cantilever tip would be changed. Duplicate values are taken for each measurement point and the variation should be within 5% of the average. To avoid the artifacts from the tip engagement on silica substrate without nanomaterial deposition, the topographical images of nanomaterials were first obtained (e.g., **Figure S3**) and then, the adhesion force measurements were conducted only on the nanomaterial surfaces, which can be visualized and located from the topographical images.

References

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2. N. A. Burnham, X. Chen, C. S. Hodges, G. A. Matei, E. J. Thoreson, C. J. Roberts, M. C. Davies and S. J. B. Tendler, *Nanotechnol.*, 2003, **14**, 1-6.
3. E. Balnois, K. J. Wilkinson, J. R. Lead and J. Buffle, *Environ. Sci. Technol.*, 1999, **33**, 3911-3917.