

**Electronic Supplementary Information for
Janus nanoparticle magic: selective asymmetric modification of
Au-Ni nanoparticles for its controllable assembly onto attapulgite
nanorods**

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S1. Experimental Procedures

Materials and measurement: 3-Aminopropyl triethoxysilane (APTES) and 2-bromoisobutyl bromide were purchased from Aldrich. Monomer 2-(dimethylamino)ethyl methacrylate was obtained from Aldrich. Initiator 2-bromo-2-methyl-N-(3-(triethoxysilyl)propyl) propanamide (BMTTP) was synthesized according to the literature.¹ Initiator 2-bromo-2-methyl-N-[2-(3,4-dihydroxyphenyl)ethyl]propionamide (BMDEP) was synthesized according to the literature.² Attapulgite (APT) was purchased from Jiangsu Autobang Co., Ltd., China. Copper(I) bromide was purified by reflux in acetic acid. Ni(NO₃)₂·6·H₂O, octadecylamine (ODA), ethanol, and cyclohexane were of analytical grade from the Beijing Chemical Factory of China and were used without further purification. HAuCl₄·4H₂O was obtained from the Chemical Reagent Co. of Shanghai (Shanghai, China). 3-Hydroxytyramine hydrochloride was obtained from Aldrich. Ultrapure water used in all experiments was obtained from a NANO pure Infinity system from

Barnstead/Thermolyne Corp. The Au-Ni hybrid nanocrystals were prepared via a noble-metal-induced Reduction Process according to the literature.³ Kaiser test reagents were prepared according to the literature.⁴ Transmission electron microscopy (TEM) was carried out using a JEOL 2100FX TEM operating at an acceleration voltage of 120 kV. One drop of a single crystal suspension or nanoparticle suspension was drop cast on a carbon-coated copper TEM grid. Upon solvent evaporation, the sample was used for TEM observation without further treatment. The energy-dispersive spectrometry (EDS) and scanning transmission electron microscopy (STEM) images were obtained on a Tecnai-G2-F30 (FEI) transmission electron microscope at an acceleration voltage of 300 kV. Thermal stability was determined with a thermogravimetric analyzer (TGA) (Perkin-Elmer, PET) over a temperature range of 25-800 °C at a heating rate of 10 °C/min under a N₂ atmosphere. FT-IR was recorded on a TENSOR 27 instrument (BRUCKER).

Single face modification: 0.05 mL initiator BMTTP, 20 μL acetic acid, 20 mL toluene and 5 mL toluene based Janus Au-Ni NPs dispersion were added into a 50 mL round bottom flask. The mixture was refluxed for 24h under nitrogen atmosphere. 20 mL n-hexane was added into the mixture to precipitate the modified Au-Ni NPs, followed by magnetic separation and dried in vacuum. This procedure was repeated 5 times to remove the ungrafted initiators and replace the ODA followed by drying in vacuum. Finally, Au-Ni@BMTTP particles were dispersed into a mixed solution (methanol:ultrapure water = 1:1) for further polymerization.

Double faces modification: 50 mg Janus Au-Ni particles were immersed in a 2 mg/mL mixed solution (ethanol:ultrapure water = 1:1) solution of initiator BMDEP and stirred for 18h in the dark under N₂ at room temperature. The modified nanoparticles were isolated and purified by repeated washing with ultrapure water and ethanol using centrifugation. Finally, the particles were dispersed into a mixed solution (methanol:ultrapure water = 1:1) for further polymerization.

Surface-initiated polymerization: In a typical SI-ATRP, 0.5 mL of DMAEMA monomer and 5 mL of 1:1 (v:v) MeOH/H₂O mixture were placed in a flask under Ar flow for 20 min; then, 30.4 mg of bipyridyl and 15.2 mg of CuBr were charged into a flask and purged with Ar flow again, 20 min later 5 mg of initiator-modified Au-Ni JNPs was added. The polymerizations were performed at room temperature under Ar protection. The mixture remained maroon and stable throughout the reaction. After 2h of polymerization, the particles were taken out of the polymerization solution and washed with copious ultrapure water and ethanol using centrifugation. The polymer-grafted samples were further dried under vacuum overnight before further analysis.

The purification and functionalization of the attapulgite nanorods: Attapulgite was milled through a 320-mesh screen, treated through dispersion into (NaPO₃)₆ aqueous solution, followed by treating with HCl and H₂O₂. The purified attapulgite maintained rod shaped crystals with a length of about 600 nm and 20nm in diameter. Vacuum-dried attapulgite were treated with APTES in dry toluene at 80 °C for 5 h, then the resulting attapulgite-NH₂ was washed and dried in vacuum at 60 °C overnight. The dried NR-APT-NH₂ (1 g) was dispersed in ethanol (60 mL) and degassed through dry

Argon. 3,4-dihydroxybenzaldehyde (0.27 g, 2 mmol) and catalytic *p*-toluenesulfonic acid were added into the degassed solution and the solution were refluxed overnight. After the reaction temperature was cooled to 0°C, NaBH₄ (0.82 g, 2.1 mmol) was then added slowly into the solution. The synthesis progress was shown in Scheme 1. The mixture was stirred at 0°C for 1 h and at room temperature for 12 h. The resulting catechol group terminated NR-APTOH was centrifuged and washed several times, and then dried overnight in vacuum at 50 °C.

Immobilization of free Janus Au-Ni particles onto NR-APTOH: Typically, 3 mg of NR-APTOH was dispersed in 3 mL of CHCl₃ in an ultrasonication bath for 2 min, followed by degassing under argon for another 5 min. The NR-APTOH solution was divided into 3 vials with each having concentration 1mg/mL. Au-Ni Janus nanoparticles were added to different vials with concentration ranging from 2 mg/mL to 6 mg/mL. This was followed again by degassing for 5 min under argon before allowing the reaction to react at room temperature for 20 h in a shaker. After the reaction was completed, the samples were investigated using transmission electron microscopy (TEM).

Self-assembly of the single face or double faces grafted Janus Au-Ni particles onto NR-APTOH: Typically, 1 mg of NR-APTOH was dispersed in 1 mL of chloroform in an ultra-sonication bath for 5 min, followed by degassing under argon for another 5 min. Subsequently, 2-8 mL (from a standard solution of 1mg/mL) of corresponding Janus Au-Ni was added dropwise to the NR-APTOH solution under sonication. The reaction mixture was degassed for another 5 min before allowing it to react in an ultrasonication bath for 10 h at RT and 24 h in a shaker. The nanocomposite characterized for TEM were prepared by putting 1-2 drops of dispersed sample on a copper TEM grid followed by drying.

Section S2. Fourier transform infrared spectrum analysis data

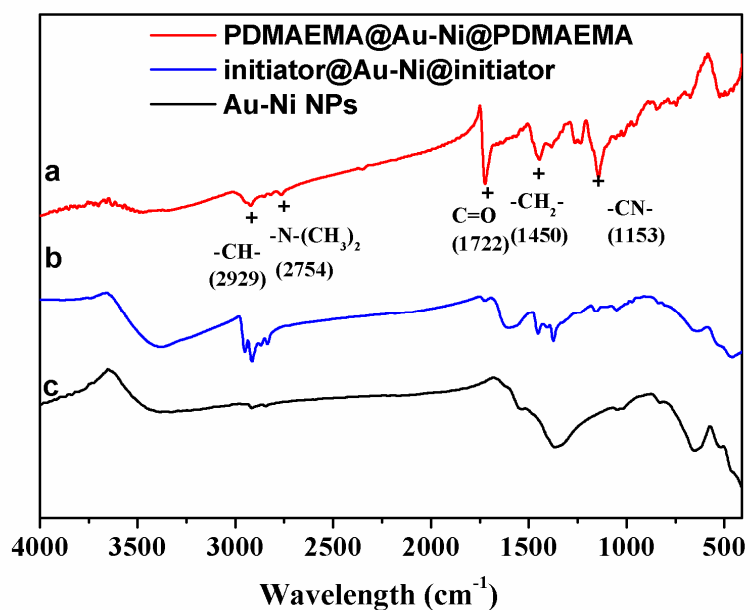


Figure S1. FT-IR spectra of (a) double faces modified Au-Ni NPs after ATRP, (b) double faces modified Au-Ni NPs with initiator and (c) Janus Au-Ni NPs without modification.

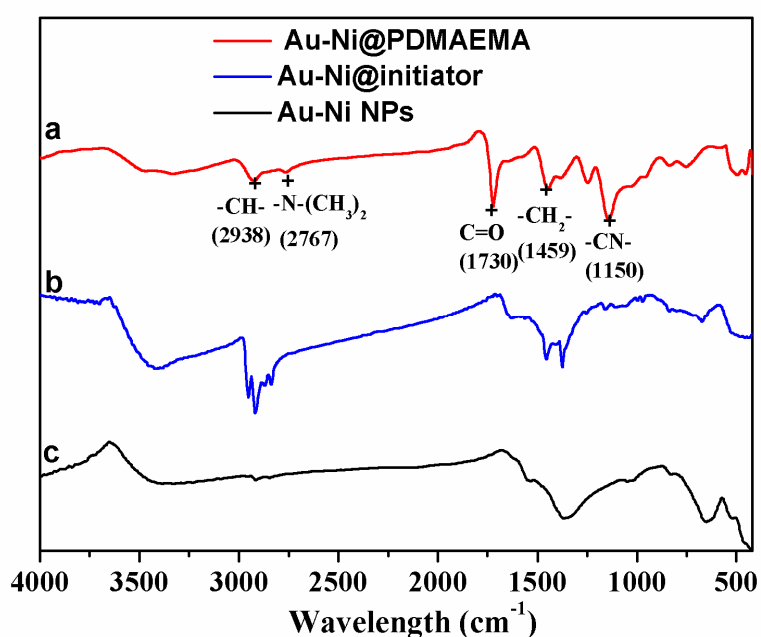


Figure S2. FT-IR spectra of (a) single face modified Au-Ni NPs after ATRP, (b)

single face modified Au-Ni NPs with initiator, and (c) Janus Au-Ni NPs without modification.

Section S3. Thermogravimetric analysis data

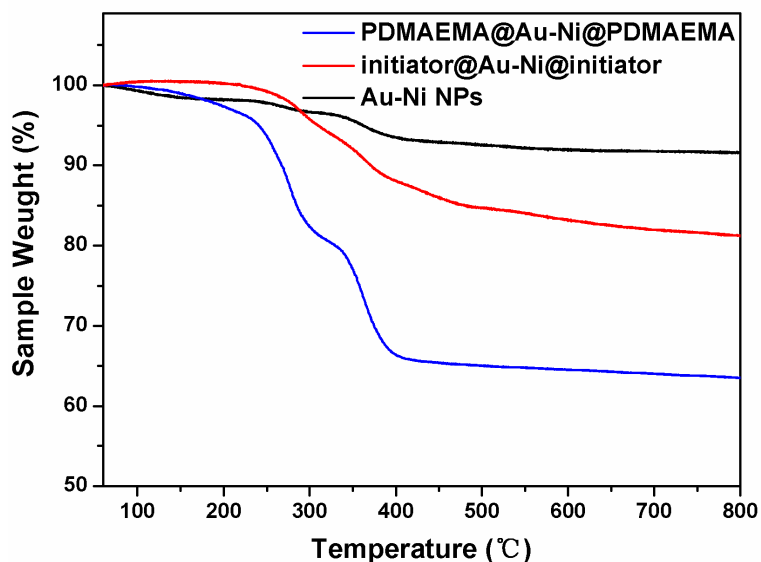


Figure S3. TGA traces of (a) Janus Au-Ni NPs without modification, (b) double faces modified Au-Ni NPs with initiator and (c) double faces modified Au-Ni NPs after ATRP.

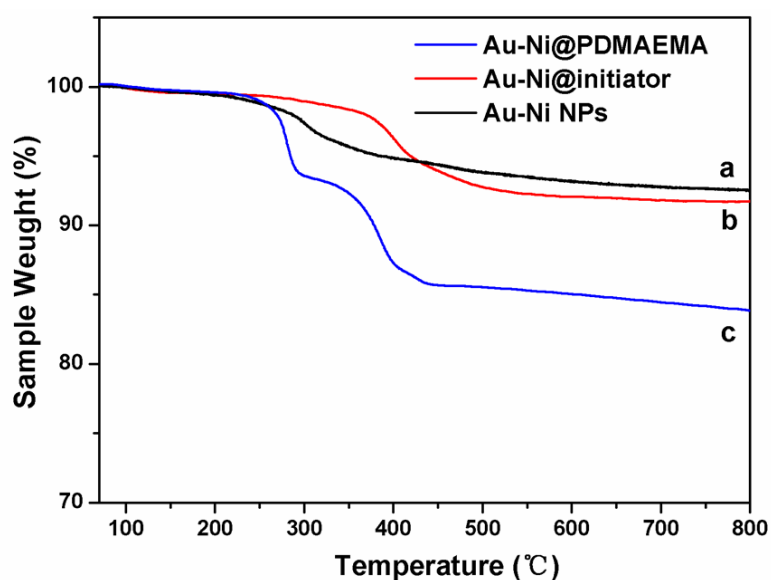


Figure S4. TGA traces of (a) Janus Au-Ni NPs without modification, (b) single face modified Au-Ni NPs with initiator, and (c) single face modified Au-Ni NPs after ATRP.

Section S4. Digital images

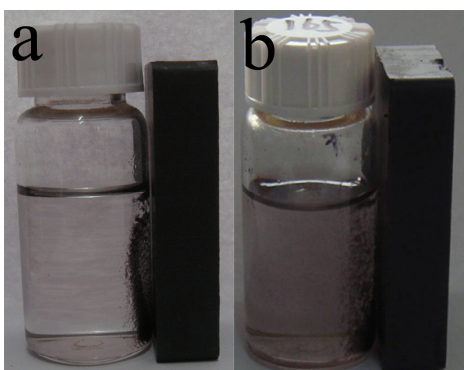


Figure S5. Digital image illustrating that Au-Ni/NR-AttaOH are attracted by the permanent magnet. (a) 2 mg/mL of Au-Ni Janus nanoparticles, (b) 10 mg/mL of Au-Ni Janus nanoparticles.

Section S5. Energy dispersive X-ray spectroscopy analysis data

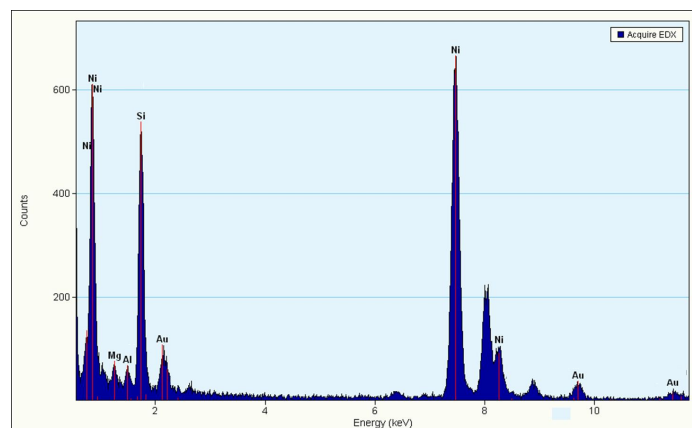


Figure S6. EDX spectrum showing the presence of silicon (Si), magnesium (Mg), aluminium (Al), nickel (Ni) and gold (Au) on the Au-Ni NPs coated NR-APTOH.

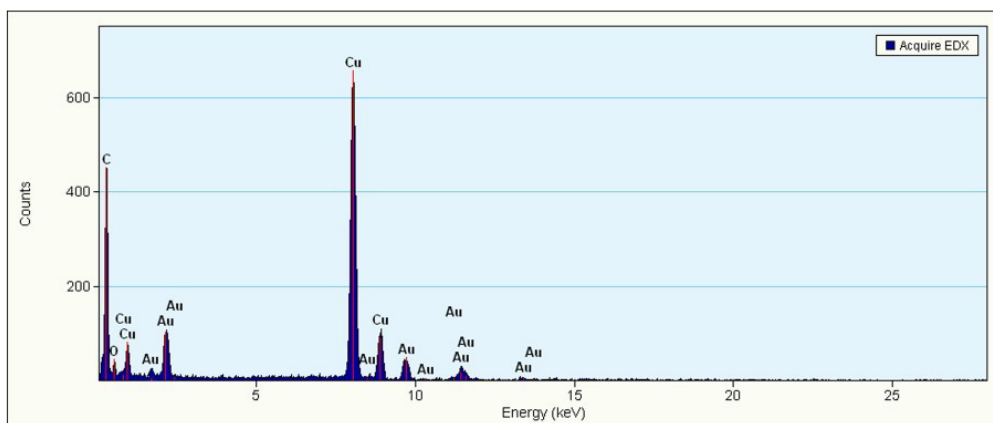


Figure S7. EDX spectrum showing the presence of gold (Au) on the BMTTP modified Au NPs.

Section S6. Powder X-ray diffraction data

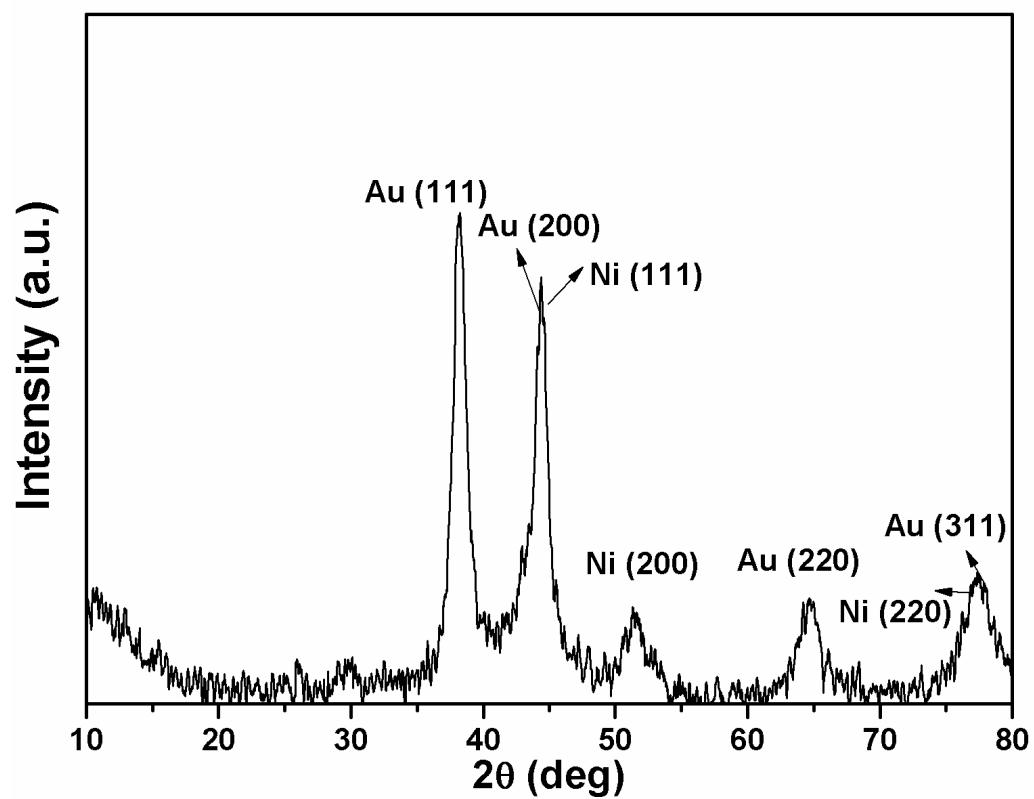


Figure S8. X-ray diffraction pattern of Janus Au-Ni nanoparticles.

Section S7. Transmission electron microscopy images

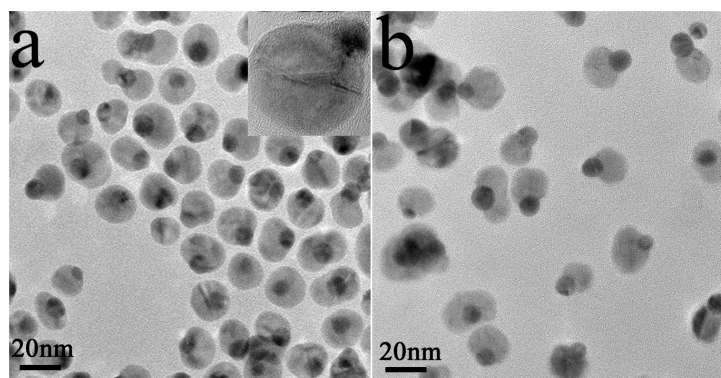


Figure S9. Overview TEM images of (a) ODA coated Au-Ni JNPs (b) initiator BMTTPP coated Au-Ni@BMTTPP JNPs

Section S8. References

- [1] R. Chen, S. Zhu and S. Maclaughlin, *Langmuir*, 2008, **24**, 6889.
- [2] X. W. Fan, L. J. Lin, J. L. Dalsin and P. B. Messersmith, *J. Am. Chem. Soc.*, 2005, **127**, 15843.
- [3] D. S. Wang and Y. D. Li, *J. Am. Chem. Soc.*, 2010, **132**, 6280.
- [4] E. Kaiser, R. L. Colescott, C. D. Bossinger and P. I. Cook, *Anal. Biochem.*, 1970, **34**, 595