

Supporting information:

Design of magneto-plasmonic nanostructures formed by magnetic Prussian Blue-type nanocrystals decorated with Au nanoparticles

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Experimental section

Materials:

All chemical reagents were purchased and used without further purification. Silver nitrate was purchased from Alfa Aesar. Chloroauric acid, L-ascorbic acid, potassium iodide, sodium citrate tribasic dihydrate, hexadecyltrimethylammonium bromide (CTAB), sodium borohydride and thiol polyethyleneglycole amine (HS-PEG_{3.5K}-NH₂) were purchased from Sigma-Aldrich. Ultra-pure water (18.2 MΩ) was used in the following synthesis.

Synthesis of plasmonic nanoparticles

Au Nanospheres: The synthesis was performed following the standard Turkevich's method.¹ The reduction of a gold hydrochlorate solution was achieved by adding the sodium citrate to the boiling solution with constant stirring in order to maintain a homogenous solution. A faint gray color was observed in the solution approximately one minute and in a period of 2–3 minutes later, it further darkening to deep wine and red color. Note that the color changing is a clear visual indication that the colloidal Au is actually being produced.

Ag Nanospheres: These NPs were synthesized via a citrate reduction protocol.² Firstly, 1 mL of an aqueous solution of sodium citrate (1 wt %) and 0.25 mL of an aqueous solution of AgNO₃ (1 wt %) were dropped into 1.25 mL of water under stirring at room temperature. KI was added to the mixture to set a concentration of 0.06 μL. The mixture was incubated for 5 min prior to use. 50 μL of an aqueous solution of ascorbic acid (0.10 mM) was added into 47.5 mL of boiling water, followed by boiling for an additional 1 min. After the 5 min incubation, the mixture solution was introduced into the boiling water under vigorous stirring. After its color changed from colorless to yellow, the reaction solution was further boiled for 1 h under stirring.

Au Nanorods: AuNRs were obtained through a seed-mediated growth method.³ After adding 25 μL of 50 mM HAuCl₄ solution to 4.7 mL of CTAB 0.1 M, the mixture was slowly stirred for 5 min. Then, 300 μL of a freshly prepared NaBH₄ 10 mM solution was rapidly injected under vigorous stirring. After 10 s stirring was stopped and the obtained seeds were let undisturbed 1 hour at 30 °C. After the addition of 190 μL of HCl 1M and 100 μL of gold hydrochlorate 50 mM solution to 10 mL of CTAB 0.1 M, the mixture was shaken for 5 min. Subsequently, 120 μL of AgNO₃ 0.01 M solution was added to the mixture, which was then shaken for few seconds. Quickly, 80 μL of ascorbic acid 0.1 M solution was then added to the growth solution and thoroughly shaken, turning colorless in few seconds. Finally, 24 μL of seeds were added to the mixture, and the solution was vigorously shaken and then left undisturbed at 30 °C for 2 hours. Gold nanorods were centrifuged and redispersed in water twice in order to remove the excess of surfactant.

Au Nanostars: Au NPs with star-like shapes were obtained by a seeded-growth process,⁴ using citrate-stabilized spherical Au NPs as seeds. For the preparation of the growth solution, hydrochloric acid (10 μL, 1 M) was added to a gold hydrochlorate solution (10 mL, 0.25 mM). Afterward, aqueous solutions of ascorbic acid (50 μL, 0.1 M) and AgNO₃ (100 μL, 3 mM) were added, followed by the addition of 100 μL of seed solution (0.5 mM). Finally, HS-PEG-NH₂ was added as capping agent (1 mL, 1 mg·mL⁻¹). After 30 minutes of incubation, gold nanostars were ready for further use.

Synthesis of PB and PBA nanoparticles

NiCr PBA: at room temperature, aqueous solutions of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (5 mM, 10 mL) and $\text{K}_3[\text{Cr}(\text{CN})_6]$ (5.65 mM, 10 mL) were added simultaneously to 100 mL of pure water at $2 \text{ mL} \cdot \text{h}^{-1}$ rate. After completion of the addition, the mixture was stirred for one hour before being centrifuged at 11000 rpm for 20 min. The supernatant was removed, and the white powder was redispersed in 10 mL of water.

20 nm NiCr PBA: small NPs were synthesized by the mixture of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 0.2 mM and $\text{K}_3[\text{Cr}(\text{CN})_6]$ 0.2 mM aqueous solutions under stirring during 2 hours.

FeFe PB: at room temperature, aqueous solutions of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (5 mM, 10 mL) and $\text{K}_4[\text{Fe}(\text{CN})_6]$ (5.65 mM, 10 mL) were added simultaneously to 100 mL of pure water at $2 \text{ mL} \cdot \text{h}^{-1}$ rate. After completion of the addition, the mixture was stirred for one hour before being centrifuged at 11000 rpm for 20 min. The supernatant was removed, and the NPs blue powder was redispersed in 10 mL of water.

NiFe PBA: at room temperature, aqueous solutions of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (5 mM, 10 mL) and $\text{K}_3[\text{Fe}(\text{CN})_6]$ (5.65 mM, 10 mL) were added simultaneously to 100 mL of pure water at $2 \text{ mL} \cdot \text{h}^{-1}$ rate. After completion of the addition, the mixture was stirred for one hour before being centrifuged at 11000 rpm for 20 min. The supernatant was removed, and the yellowish powder was redispersed in 10 mL of water.

CuCr PBA: at room temperature, aqueous solutions of $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$ (5 mM, 10 mL) and $\text{K}_3[\text{Cr}(\text{CN})_6]$ (5.65 mM, 10 mL) were added simultaneously to 100 mL of pure water at $2 \text{ mL} \cdot \text{h}^{-1}$ rate. After completion of the addition, the mixture was stirred for one hour before being centrifuged at 11000 rpm for 20 min. The supernatant was removed, and the green powder was redispersed in 10 mL of water.

Au/Ag-PB/PBA Decoration

Firstly, 15 mL of a $0.33 \text{ mg} \cdot \text{mL}^{-1}$ HS-PEG-NH₂ solution was added to 15 mL of a $5 \cdot 10^{-4}$ M plasmonic NPs solution and let undisturbed overnight. The resulting capped NPs were centrifuged and redispersed to obtain a final concentration of $1.9 \cdot 10^{-4}$ M. Then, 5 mL of the aforementioned solution was adjusted to a pH between 2 and 5 (depending on the Au decoration), and immediately 0.5 mL of PB/PBA was added under magnetic stirring.

Structural characterization

UV/Vis Spectroscopy: UV-vis absorption spectra were recorded on a Jasco V-670 spectrophotometer in baseline mode from 300 to 900 nm range, using 1.000-cm-optical-path plastic cuvettes.

Transmission Electron Microscopy (TEM): TEM studies were carried out on a JEOL JEM 1010 microscope operating at 100 kV, and Technai G2 F20 microscope operating at 200 kV. Samples were prepared by dropping suspensions on lacey formvar/carbon copper grids (300 mesh).

Electron tomography: Tomography series of high-angle anular dark-field (HAADF-STEM) images were acquired using the Fischione model 2020 single-tilt tomography holder over a tilt range from -75° to $+75^\circ$, with tilt increments of 3° , on an aberration corrected “cubed” FEI Titan

60–300 electron microscope operated at 300 kV. The reconstruction of the tilt series was performed using the Astra Toolbox 1.8 for MATLAB 2018a.³ Visualization of the 3D reconstructions was performed using the Amira 5.4.0 software.

Zeta Potential measurements: Zeta potential measurements were performed at room temperature with a Zetasizer Nano ZS instrument (Malvern Instruments Ltd.).

Attenuated total reflectance Fourier-transform infrared (ATR-FTIR): spectra were collected in an Agilent Cary 630 FTIR spectrometer in the 4000–500 cm⁻¹ range in absence of KBr pellets.

Magnetic Measurements: Magnetic data were collected with a Quantum Design MPMS XL-5 susceptometer equipped with a SQUID sensor. dc FC magnetization measurements were performed under a magnetic field applied of 1000 Oe. Magnetization studies were performed between -0.3 and +0.3 T at a constant temperature of 2 K

X-Ray Powder Diffraction (XRPD): PXRD patterns were collected in a PANalytical Empyrean diffractometer using copper radiation (Cu K _{α} = 1.5418 Å) with an PIXcel detector, operating at 40 mA and 45 kV at room temperature. The spherical Au diameters were estimated by applying the Scherrer formula to the (111), and (200) reflections.^{4,5} A value of 10 ± 2 was estimated.

Inductively Coupled-Plasma Optical Emission Spectrometry (ICP-OES): The ICP-OES analysis were conducted at the Universidad de Valencia (Sección de Espectrometría Atómica y Molecular). Samples were digested in an acid medium at 220 °C using a microwave oven.

Dynamic Light Scattering measurements

Table 1: ζ -potentials of Au and Ag NPs stabilized with different capping agents measured at pH near to 7.

	ζ -potential / mV		
	Citrate	CTAB	HS-PEG-NH ₂
<i>Au NPs</i>	-40 ± 6	/	9 ± 6
<i>AuNRs</i>	/	35 ± 7	12 ± 4
<i>AuNSs</i>	/	/	12 ± 4
<i>Ag NPs</i>	-35 ± 2	/	11 ± 5

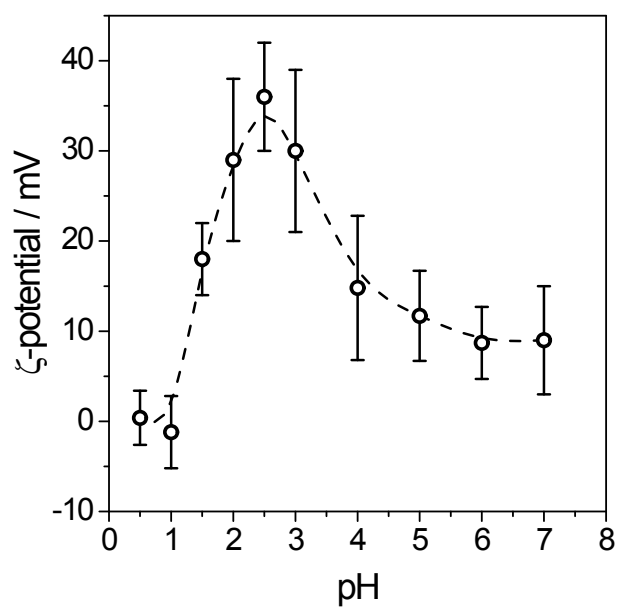


Figure S1. ζ -potential measurements of Au nanospheres stabilized with HS-PEG-NH₂ performed in water at different pH.

Transmission Electron Microscopy

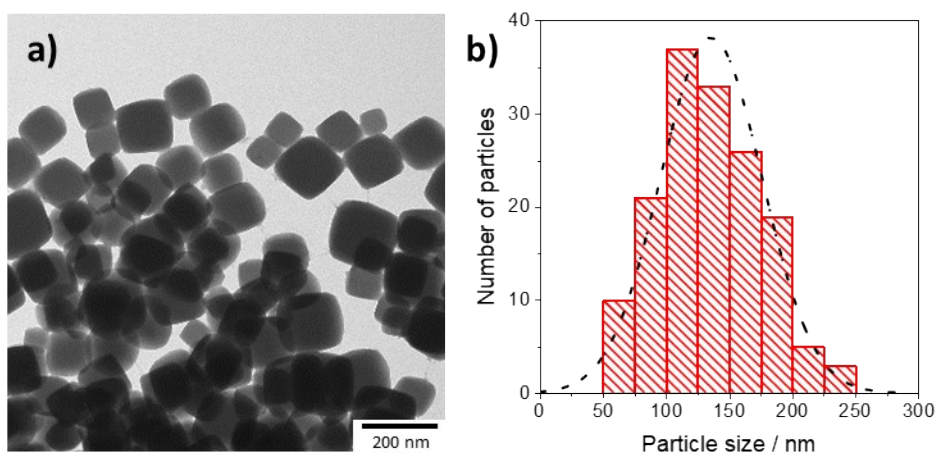


Figure S2. a) TEM image of NiCr-PBA NPs and b) Number-based particle size distribution measured by manual counting.

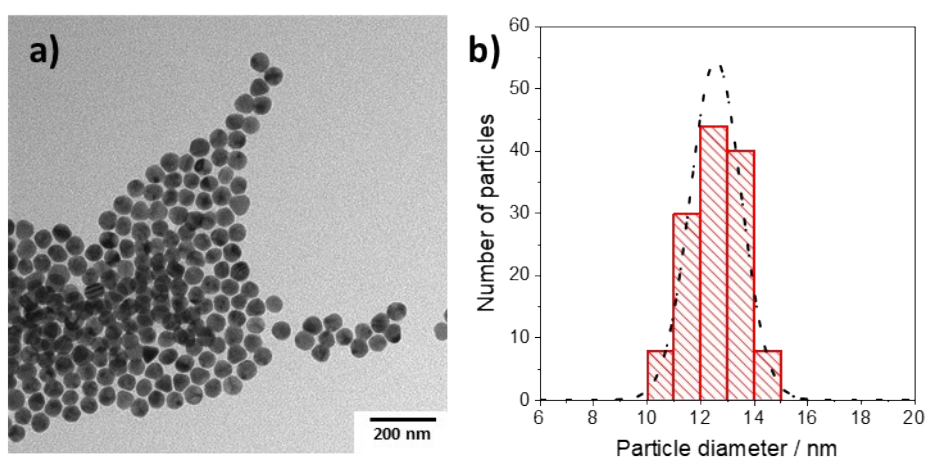


Figure S3. a) TEM image of citrate-stabilized spherical Au NPs and b) number-based particle size distribution measured by manual counting.

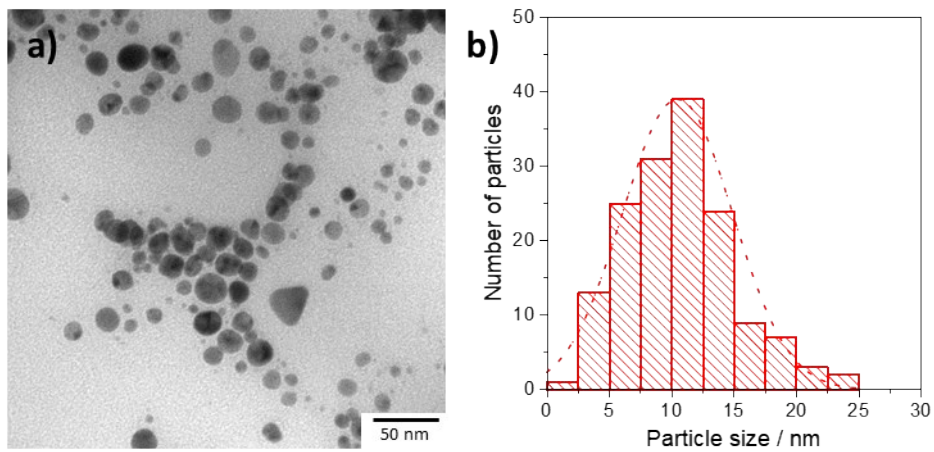


Figure S4. a) TEM image of citrate-stabilized spherical Ag NPs and b) number-based particle size distribution measured by manual counting.

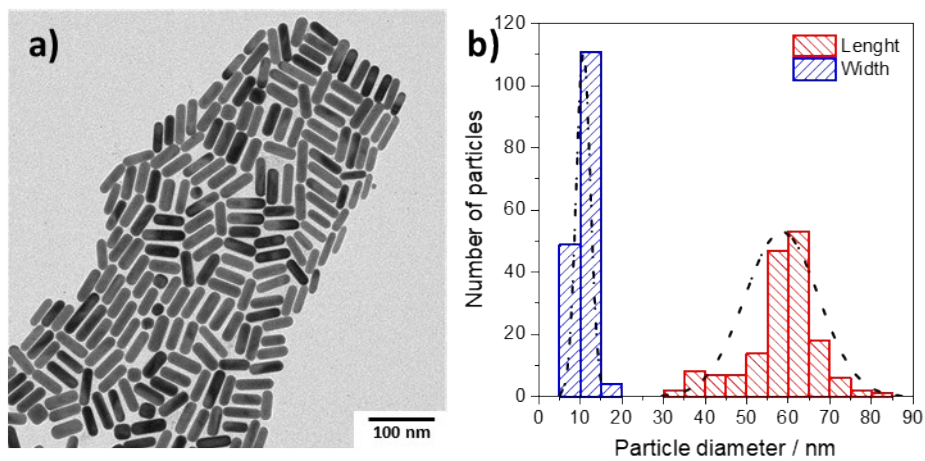


Figure S5. a) TEM image of CTAB stabilized Au NRs and b) Number-based particle size distribution measured by manual counting.

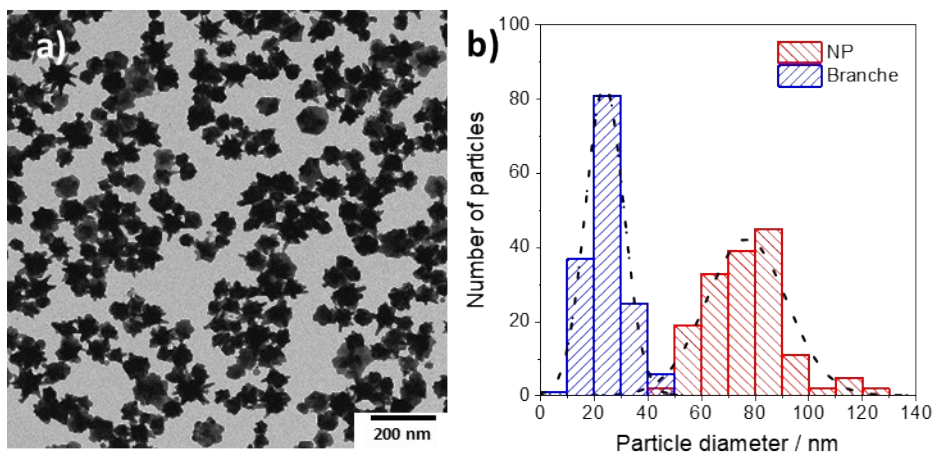


Figure S6. a) TEM image of HS-PEG-NH₂ stabilized Au NSs and b) Number-based particle size distribution measured by manual counting.

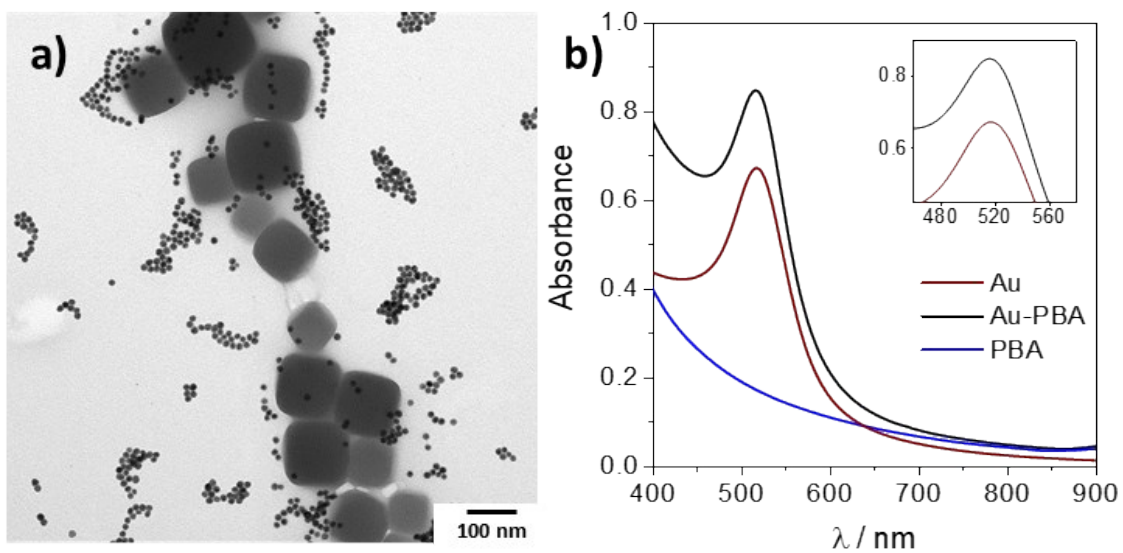


Figure S7. a) TEM image of citrate-stabilized Au NPs decorated onto Prussian blue analogue NPs
 b) UV-Spectra of Au NPs, Au-PBA and PBA.

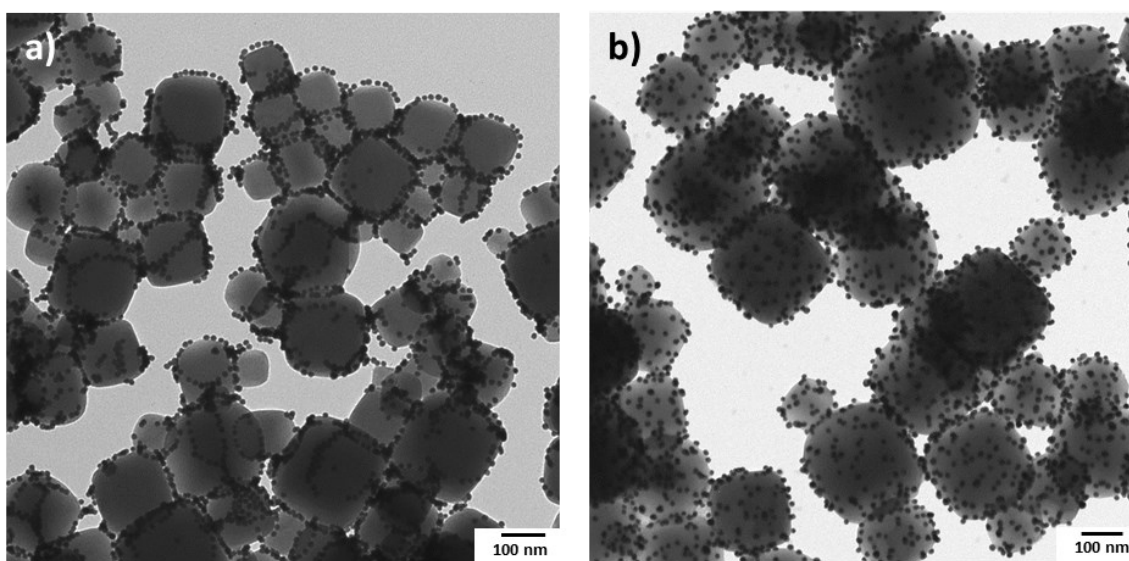


Figure S8. TEM images of the heterostructure of Au NPs with (a) preferential edge and (b) random decoration onto NiCr PBA.

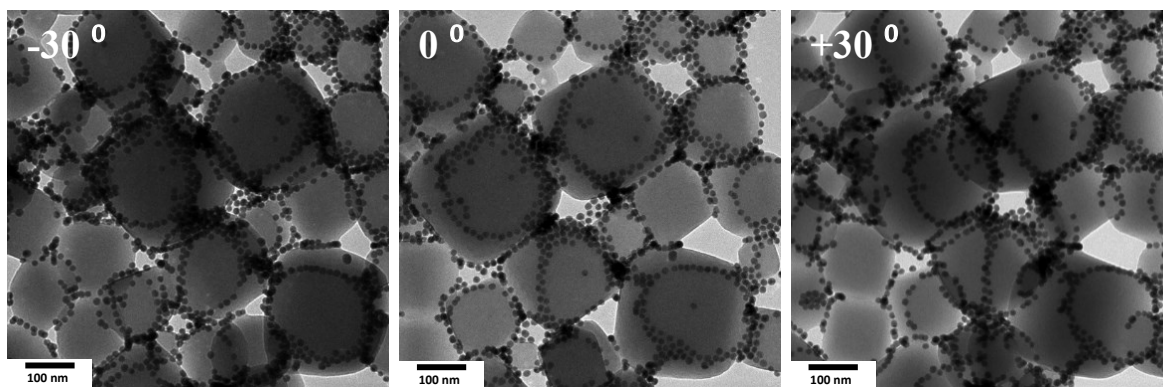


Figure S9. TEM images of Au-PBA heterostructure at different angles: (left) -30° , (center) 0° and (right) 30° .

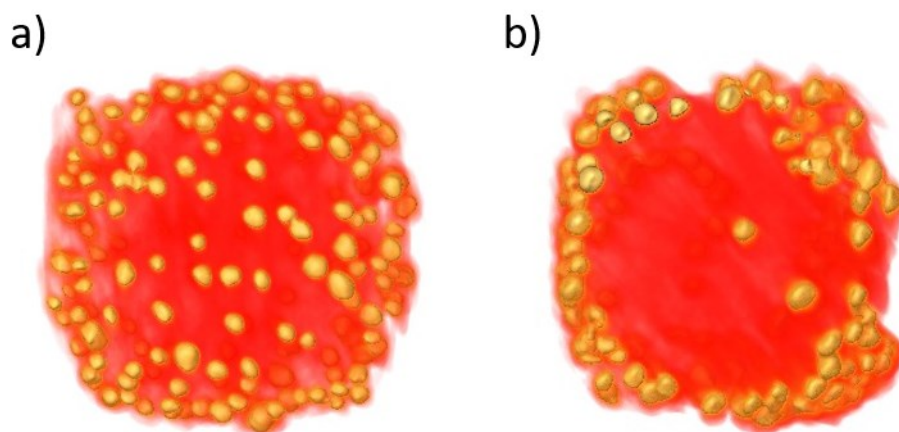


Figure S10. 3D reconstructions of Au-PBA heterostructures with (a) random and (b) preferential edge decoration onto PBA.

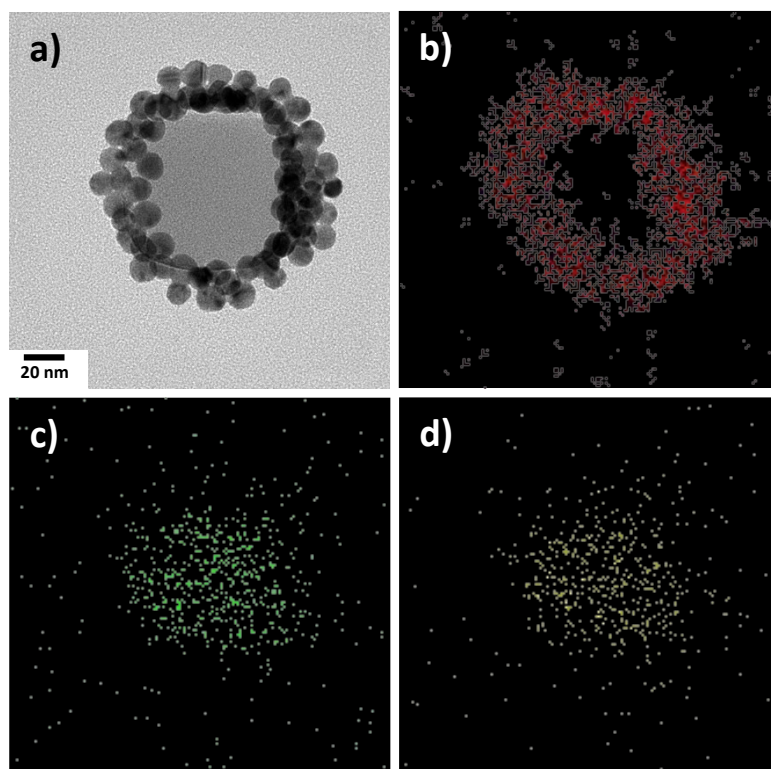


Figure S11. a) TEM image b-d) EDS Mapping of the metals present in the heterostructure (red: gold, green: nickel and yellow: iron).

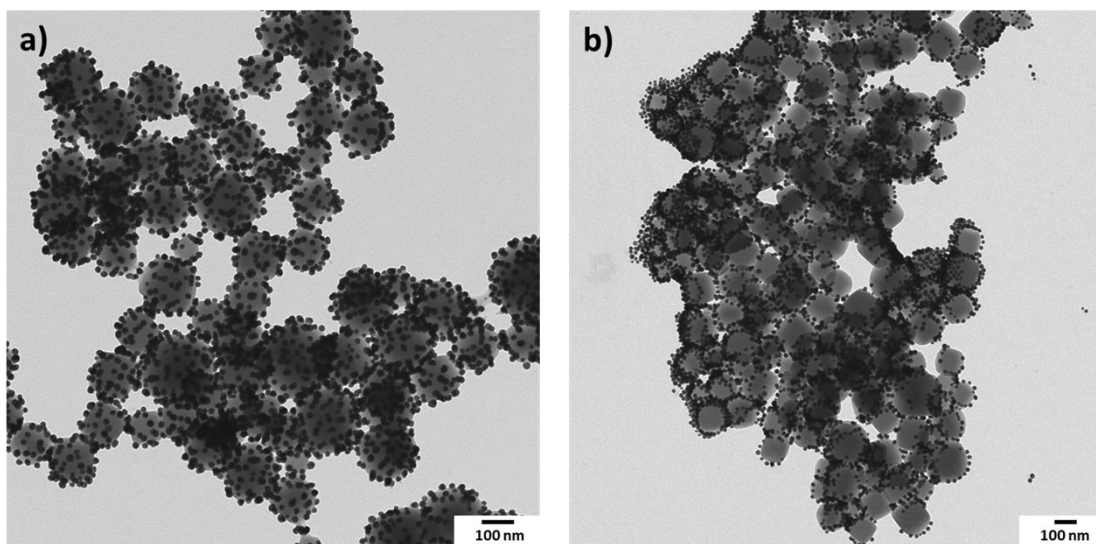


Figure S12. TEM images of the heterostructure of Au NPs with (a) random and (b) preferential edge decoration onto NiCr PBA after centrifuging and redispersing in water at neutral pH.

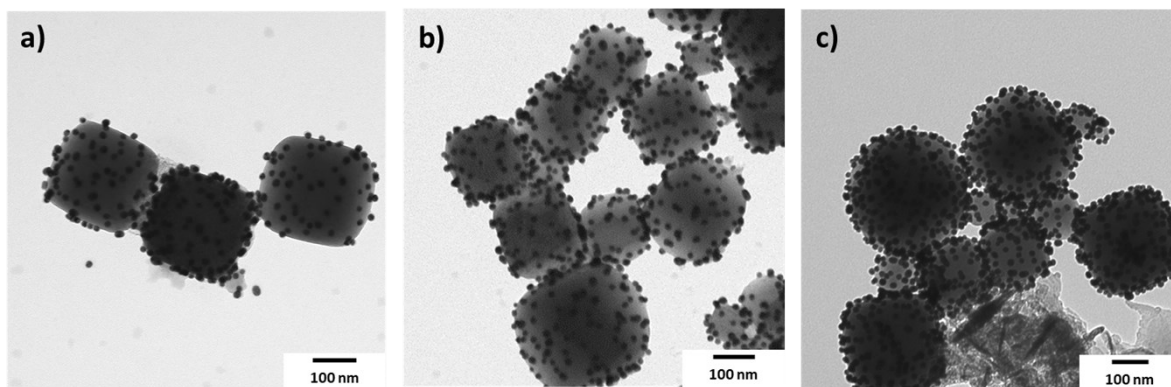


Figure S13. TEM image of decorated Au NPs onto PBA low pH 2-3 with ratio Au:PBA of (a) 0.31:1, (b) 0.40:1 and (c) 0.50:1.

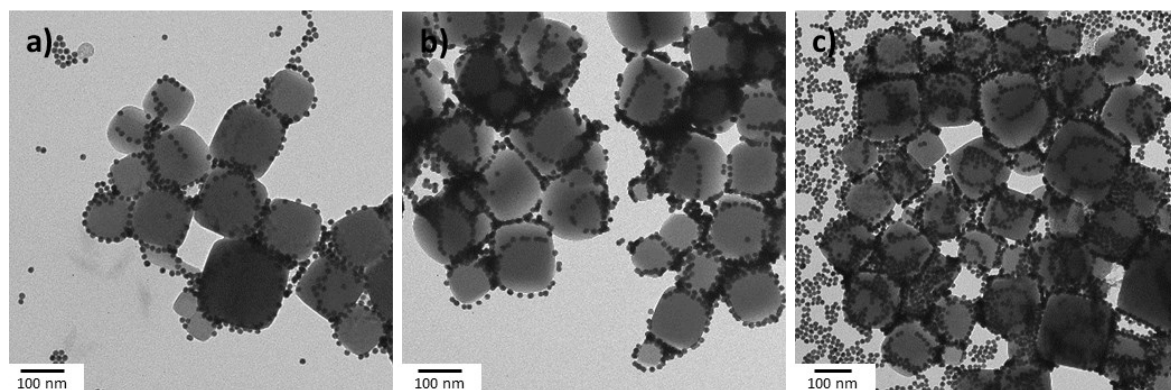


Figure S14. TEM image of decorated Au NPs onto PBA at pH 3-4 with ratio Au:PBA of (a) 0.28:1, (b) 0.41:1 and (c) 1.12:1.

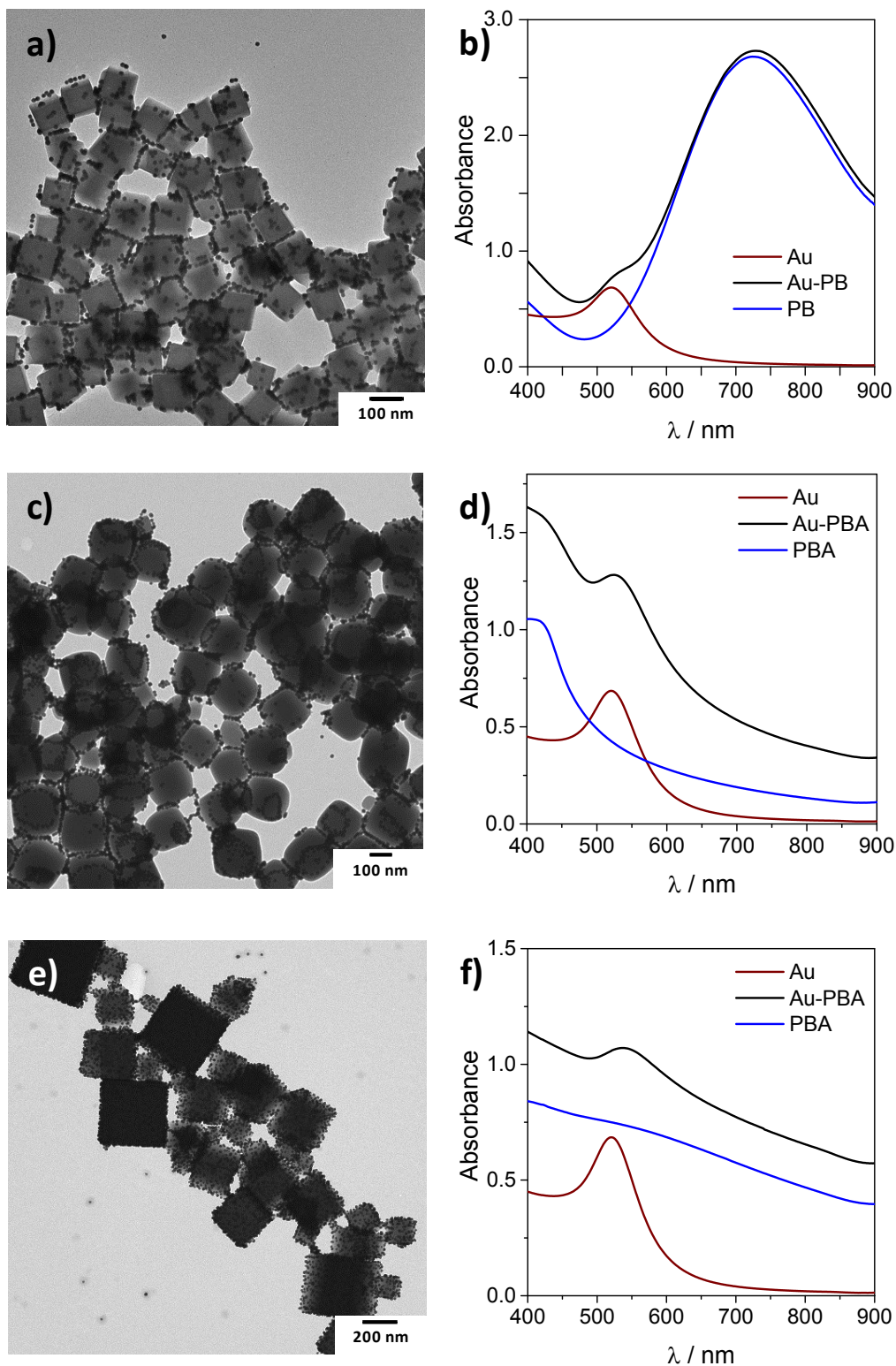


Figure S15. a) b) TEM image and UV-Vis spectrum of Au NPs decorated onto FeFe-PB NPs, c) d) decorated onto NiFe-PBA NPs and e) f) onto CuCr-PBA NPs (e) (f)

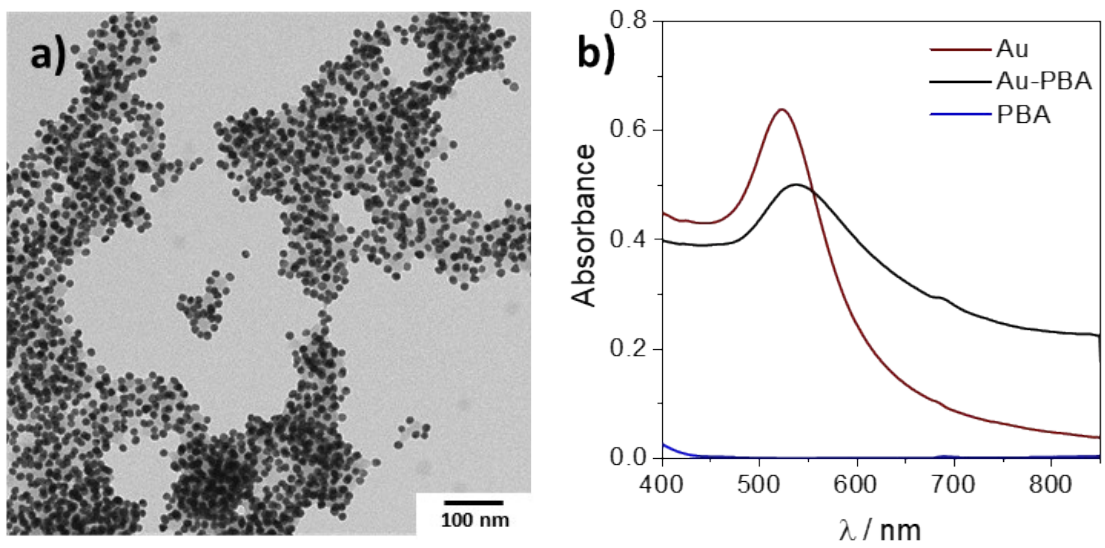


Figure S16. a) TEM image of spherical Au NPs decorated onto 20 nm NiCr-PBA NPs b) UV-Vis spectrum of spherical Au NPs decorated onto 20 nm NiCr-PBA NPs.

Attenuated total reflectance Fourier-transform infrared

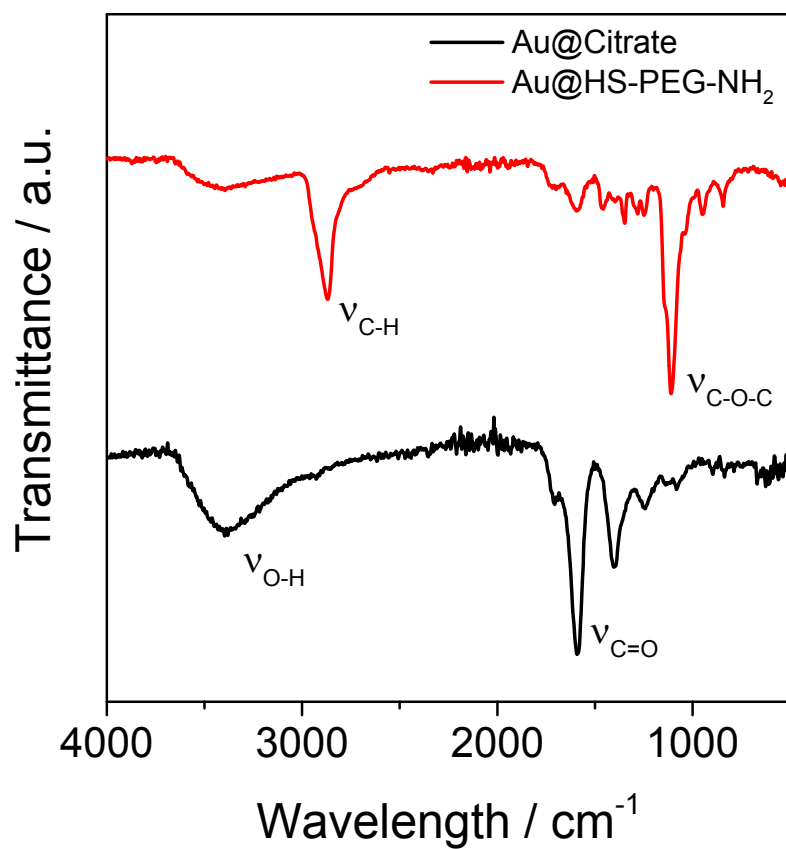


Figure S17. Infrared spectra of citrate stabilized and HS-PEG-NH₂ stabilized Au nanospheres.

PBA Crystalline Structure

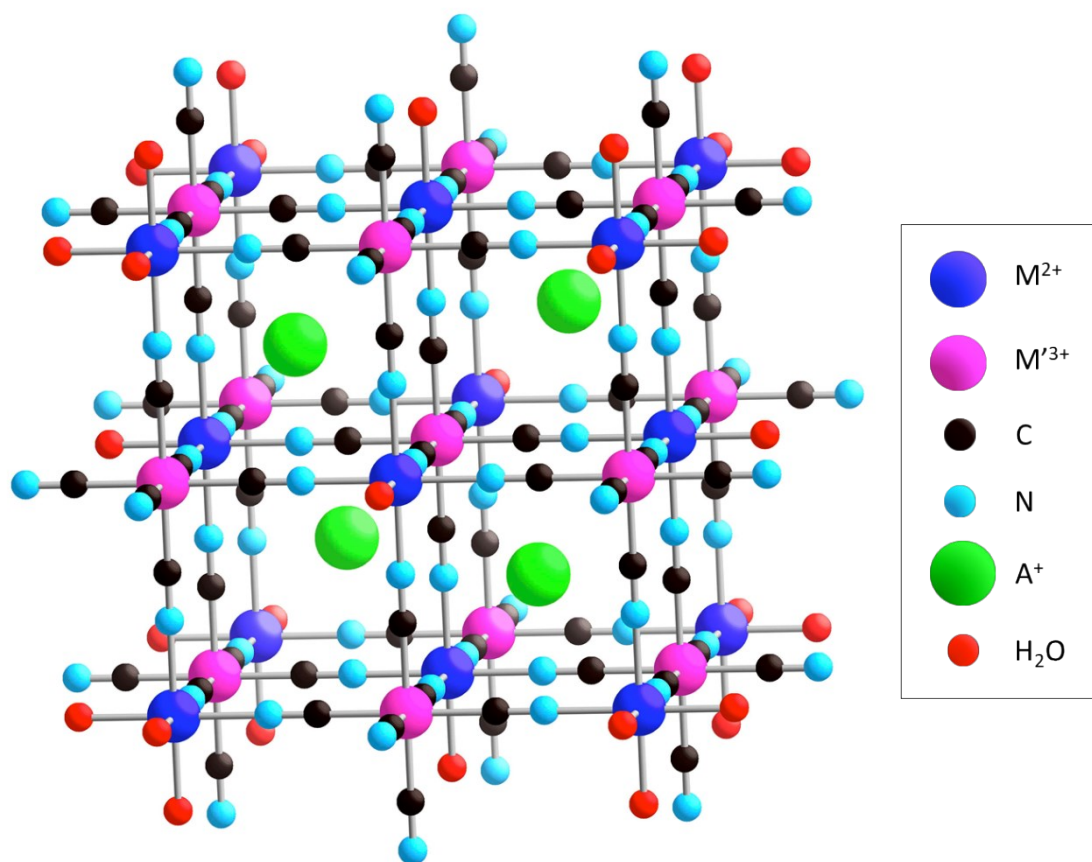


Figure S18. Schematic illustration of a general PBA structure showing the different coordination of the M^{3+} located on the edges (4 surrounding M^{2+}) and the faces (5 surrounding M^{2+}).

UV-Vis

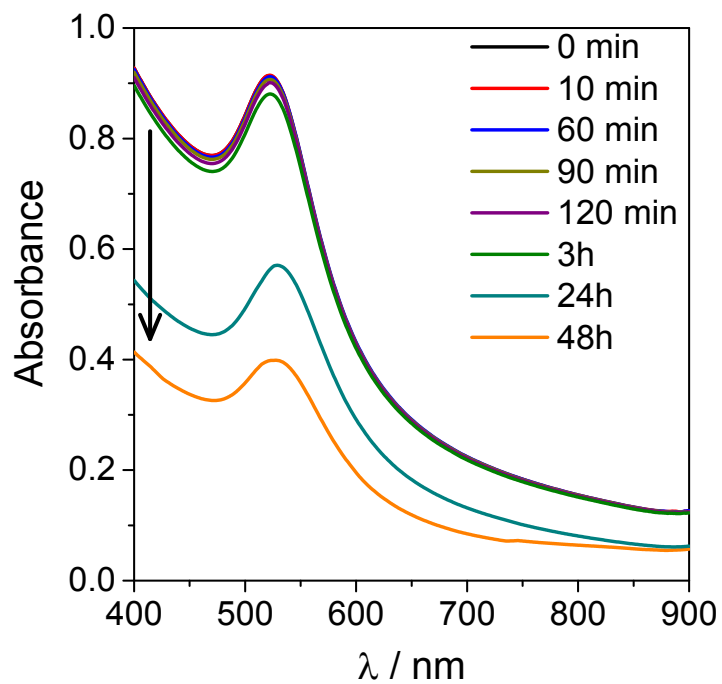


Figure S19. UV-Vis study of the stability of the Au-PBA heterostructure in aqueous solution at room temperature.

X-Ray Powder Diffraction

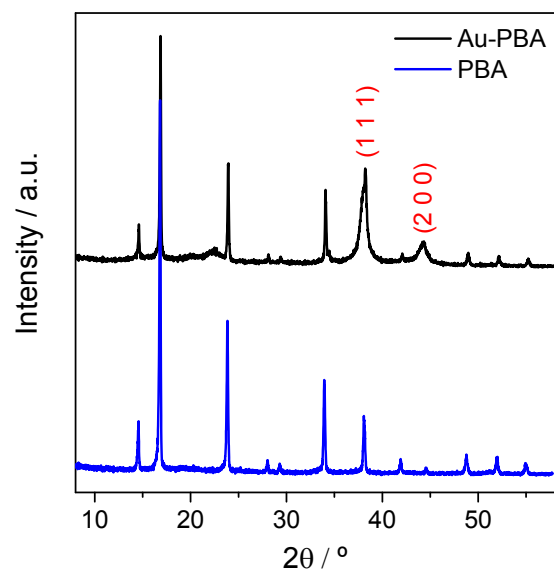


Figure S20. Room temperature XRPD for PBA nanoparticles and Au-PBA heterostructure. Au peaks are indicated in red.

The Scherrer equation was used to calculate the approximate size of the Au NPs in the hybrid. The estimated Au diameter was found to be 10 ± 2 , which is in good agreement with the TEM measurements performed before the decoration, thus confirming the Au stability in the heterostructures.

Magnetic measurements

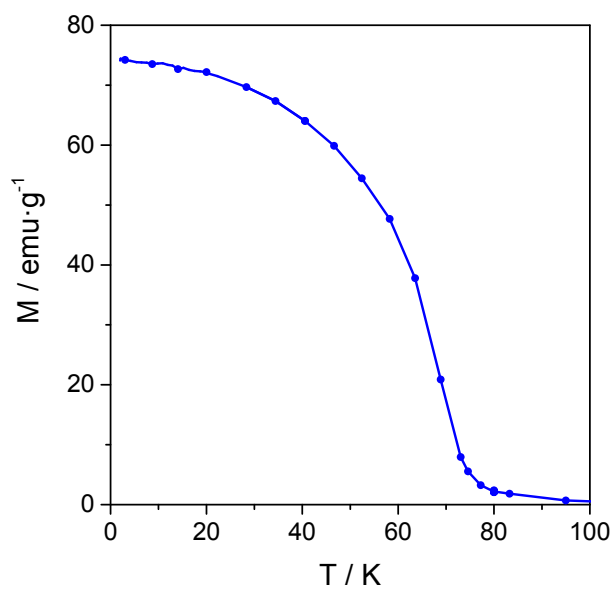


Figure S21. Temperature dependence of field cooling magnetization of NiCr PBA NPs.

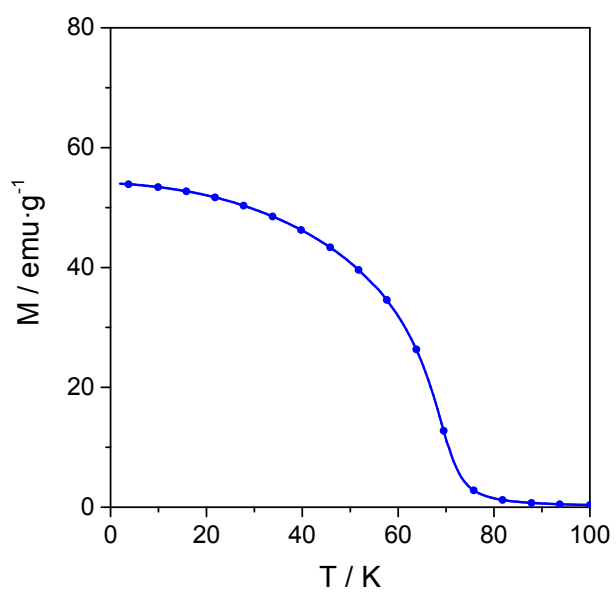


Figure S22. Temperature dependence of field cooling magnetization of the heterostructure Au-PBA.

References

- 1 J. Turkevich, *Gold Bull.*, 1985, **18**, 125–131.
- 2 H. Li, H. Xia, D. Wang and X. Tao, *Langmuir*, 2013, **29**, 5074–5079.
- 3 W. Van Aarle, W. J. Palenstijn, J. De Beenhouwer, T. Altantzis, S. Bals, K. J. Batenburg and J. Sijbers, *Ultramicroscopy*, 2015, **157**, 35–47.
- 4 H. Borchert, E. V. Shevchenko, A. Robert, I. Mekis, A. Kornowski, G. Grübel and H. Weller, *Langmuir*, 2005, **21**, 1931–1936.
- 5 V. Tallapally, D. Damma and S. R. Darmakkolla, *Chem. Commun.*, 2019, **55**, 1560–1563.