

Core-Shell Nanoheterodimers: Laser-Assisted Deposition of Single Bimetallic Au@M (M = Au, Ag, Pd, Pt) Nanodots on TiO₂ Nanoparticles

Fenghuan Zhao,^{a, b, †} Qingguo Bai,^{a, b, †, &} Chenghui Xia,^c Junjie Hao,^{a, b, §} Marion Gayot,^d Jean-Pierre Delville,^{*b} Marie-Helene Delville,^{*a}

a Univ. Bordeaux, CNRS, Bordeaux INP, ICMCB, UMR 5026, Pessac F-33608, France.

b Univ. Bordeaux, CNRS, LOMA, UMR 5798, Talence F-33405, France.

c College of Materials Science and Engineering, Ocean University of China, QingDao 266100, China.

d Univ. Bordeaux, UMS 3626, Pessac F-33608, France

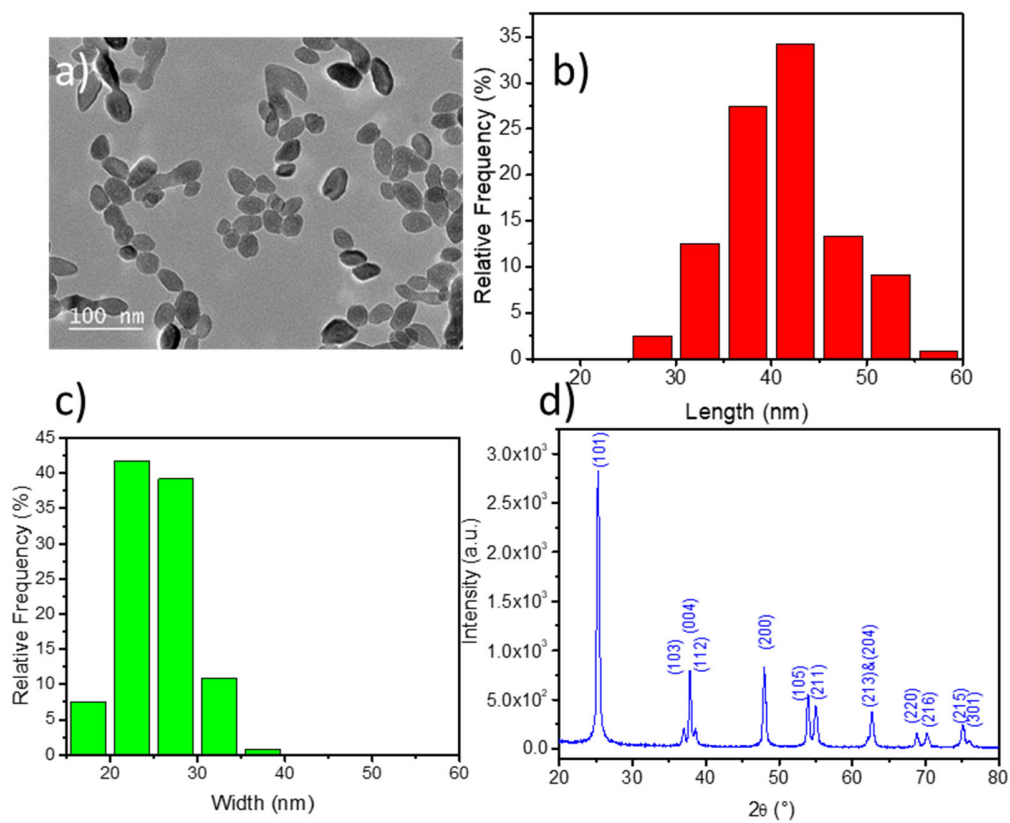


Figure S1. a) TEM image; b) length distribution & c) width distribution of the TiO₂ NPs used for photodeposition experiments; d) XRD pattern of anatase TiO₂ NPs (The peaks correspond to the JCPDS card no. 21-1272 of anatase TiO₂).

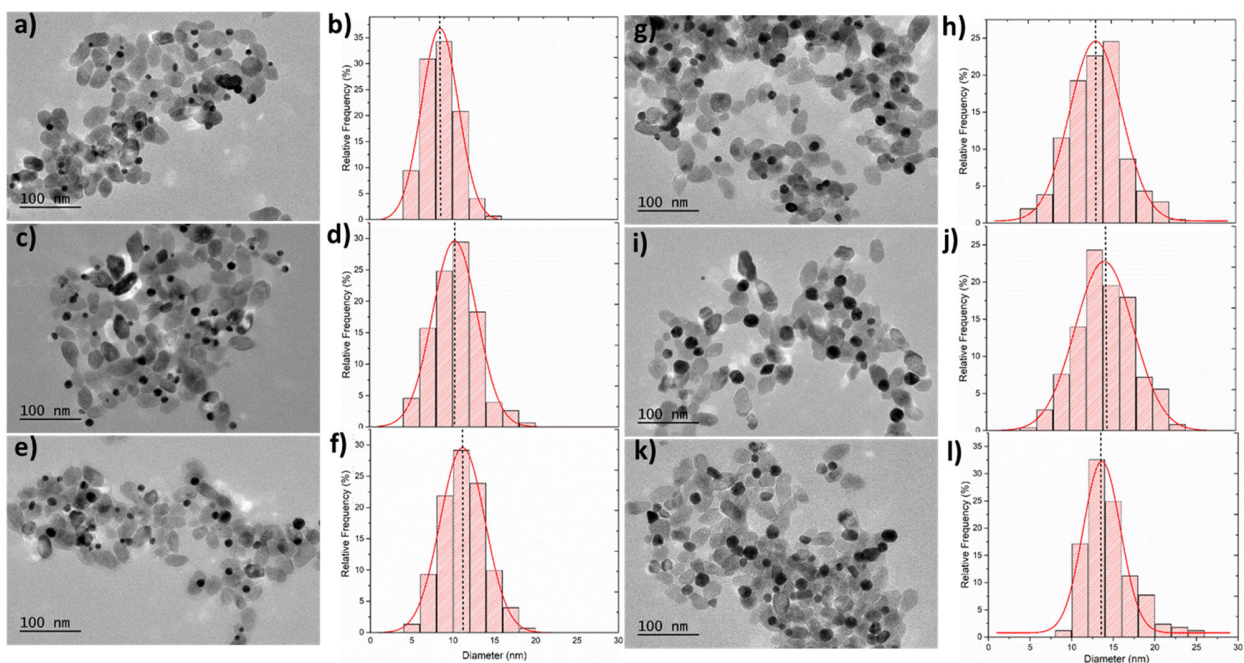


Figure S2. TEM images of Au-TiO₂ NHDs synthesized by one-step (a), and two-step deposition with different KAuCl₄ contents (c, e, g, i, and k) and their corresponding size distributions (b, d, f, h, j, and l). First step deposition: [TiO₂] = 5.5 mM, [KAuCl₄] = 0.25 mM (0.25 μmol of KAuCl₄), 50 vol. % methanol as a hole scavenger, applied power of 56.1mW, and exposure time of 4 min. Second step deposition: 0.15 μmol (c), 0.25 μmol (e), 0.35 μmol (g), 0.5 μmol (i), and 0.75 μmol (k) of KAuCl₄ were added to the prepared Au-TiO₂ solution, then this solution was irradiated for another 4 min by the same laser applied power as in the first step.

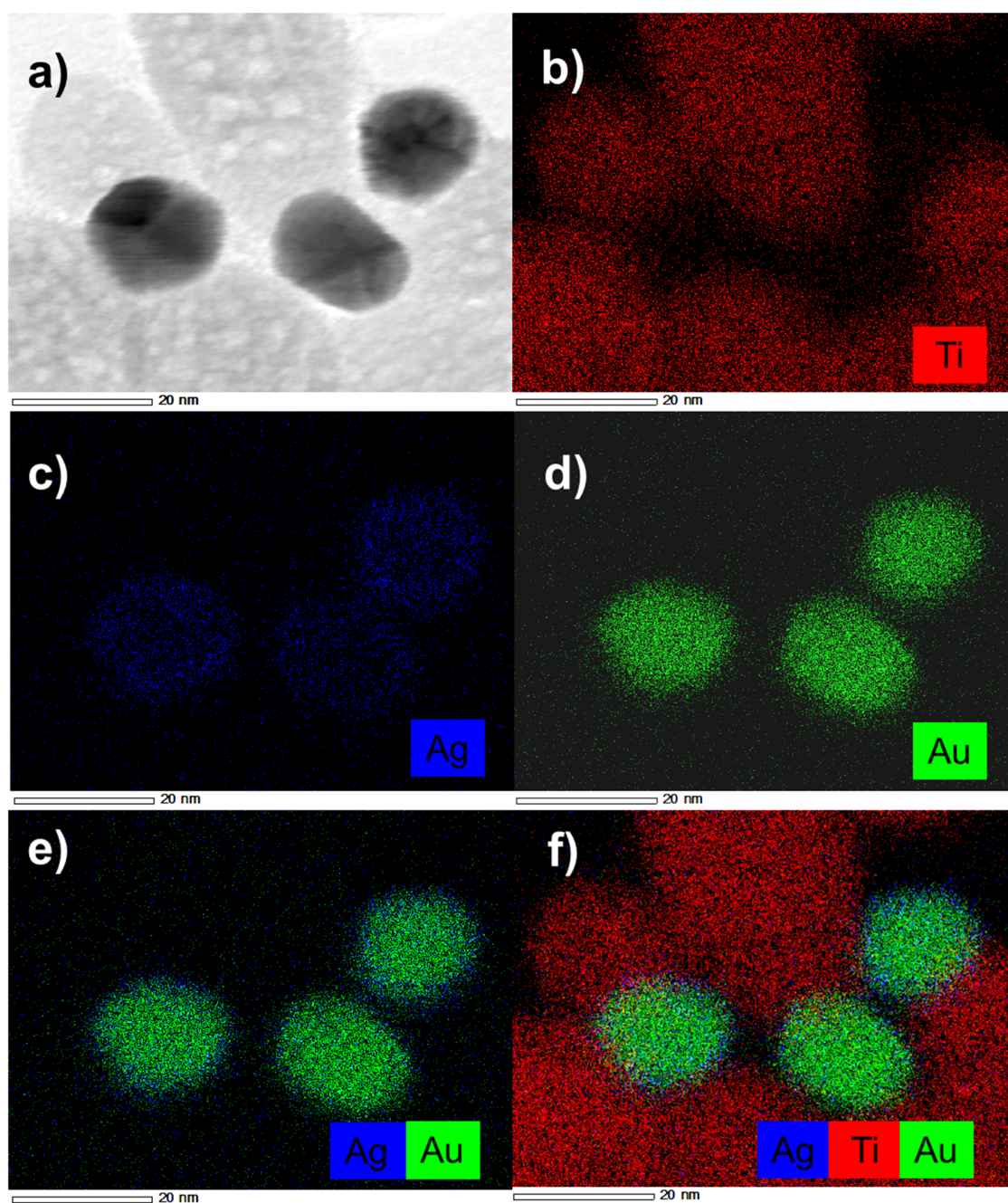


Figure S3. (a) STEM image of (Au@Ag)-TiO₂, (b)-(f) the representative EDS mapping images and their respective overlapping.

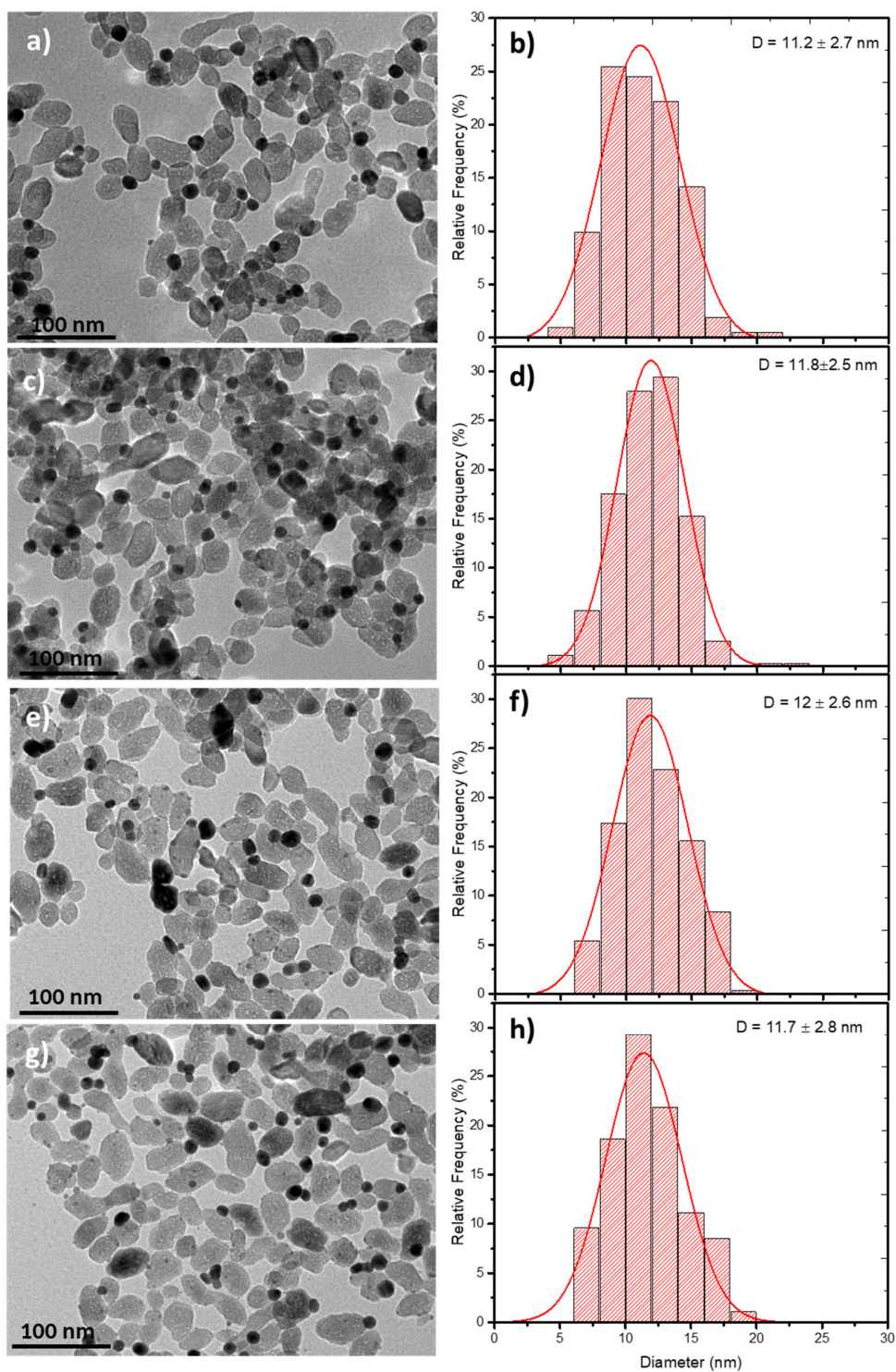


Figure S4. TEM images of Au@Ag-TiO₂ synthesized using different amounts of AgNO₃, 0.25 (a), 0.50 (c), 2.00 (e), and 4.00 μmol of AgNO₃ (g) and their respective size distributions. The condition for preparing Au-TiO₂: [TiO₂] = 5.5 mM, [KAuCl₄] = 0.5 mM (0.5 μmol of KAuCl₄), 50 vol.% methanol as a hole scavenger, P = 56.1mW, t = 4 min. Second step deposition: t = 16 min, P = 56.1 mW.

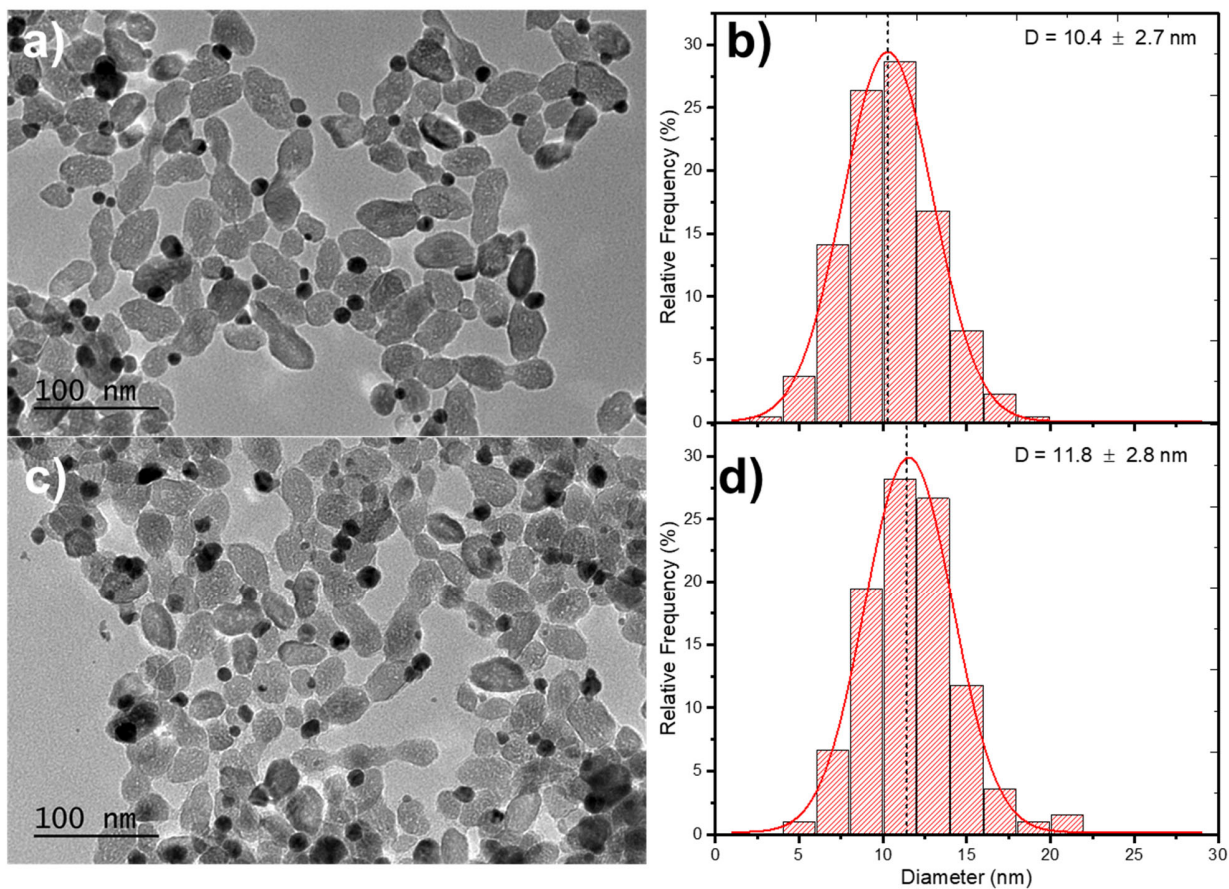


Figure S5. TEM images of Au-TiO₂ (a) and Au@Pd-TiO₂ (c) NPs and their corresponding size distributions (b and d). Experimental conditions: First step deposition, [TiO₂] = 5.5 mM, [KAuCl₄] = 0.5 mM, 50 vol.% methanol as a hole scavenger, applied power of 56.1 mW, and exposure time of 4 min. Second step deposition: 0.5 μmol of Na₂PdCl₄ was added; irradiation for 8 min with the laser (applied power of 56.1 mW).

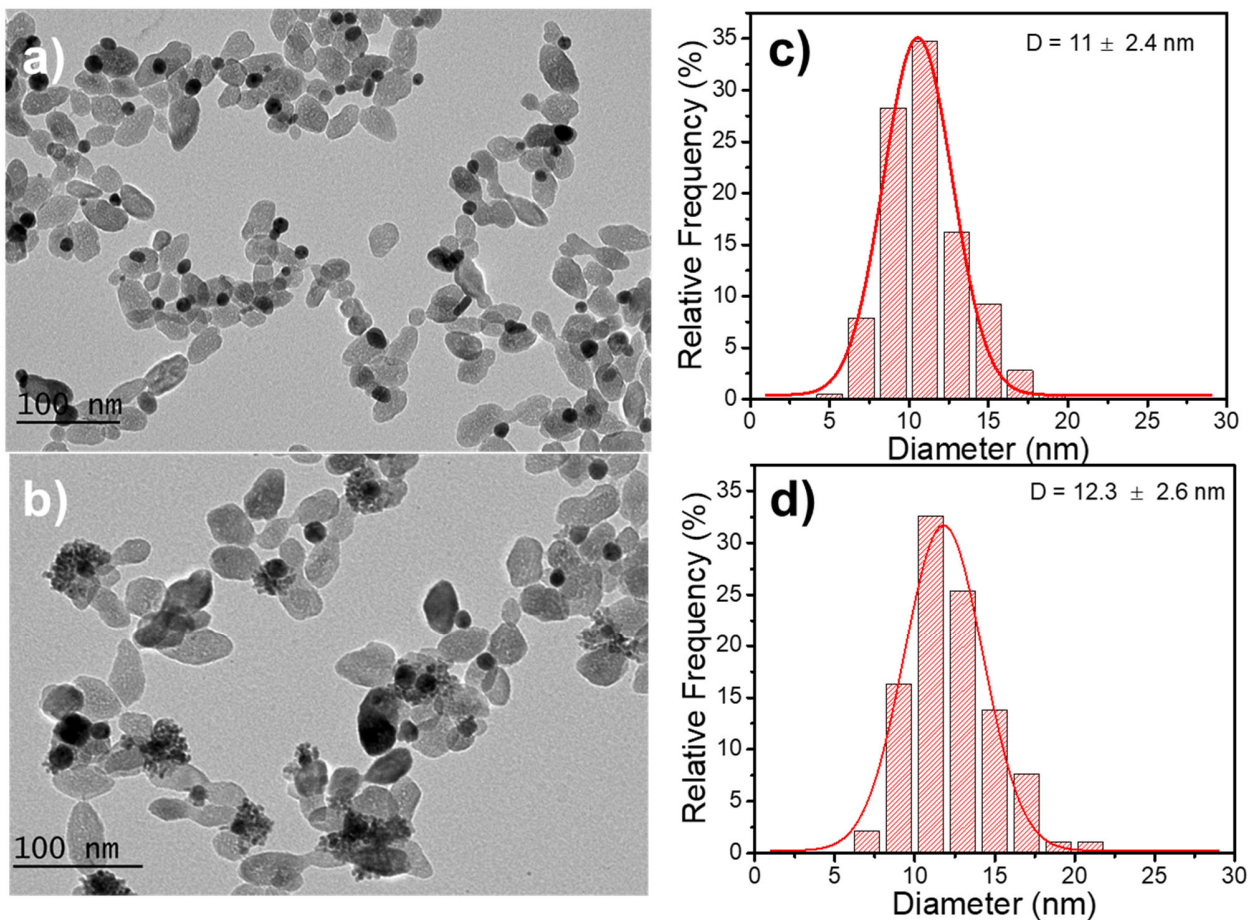


Figure S6. TEM images of Au@Pd-TiO₂ (a, b) NPs and size distributions (c). Experimental conditions: First step deposition, [TiO₂] = 5.5 mM, [KAuCl₄] = 0.5 mM, 50 vol.% methanol as a hole scavenger, applied power is 56.1 mW and exposure time is 4 min. Second step deposition: 1.0 μmol of PdCl₂ (dissolved in pH2 HCl aqueous solution) was added; then this solution was irradiated for another 4 min by the laser with an applied power of 56.1 mW.

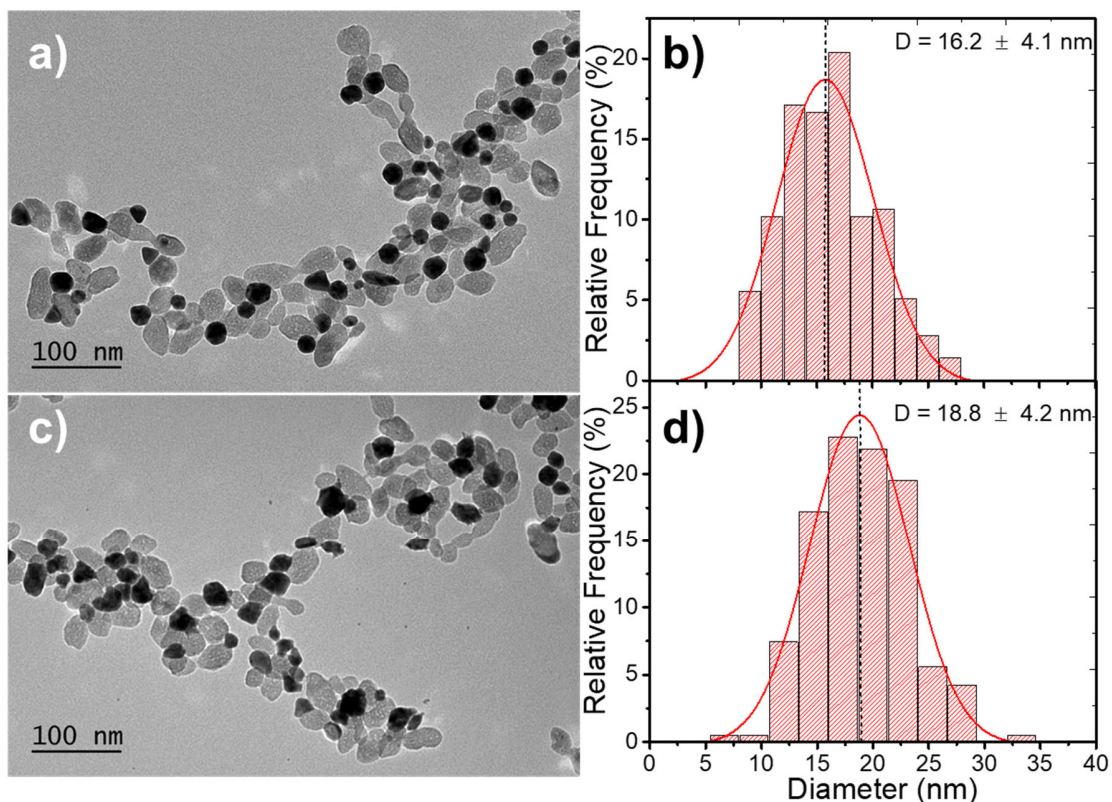


Figure S7. TEM images of Au-TiO₂ (a), and Au@Pd-TiO₂ (c) NPs and corresponding size distributions (b and d), h. Experimental conditions: First step deposition, [TiO₂] = 1.1 mM, [KAuCl₄] = 0.5 mM, 50 vol.% methanol as a hole scavenger, an applied power of 56.1 mW, and an exposure time of 4 min. Second step deposition: 0.5 μmol of PdCl₂ (dissolved in pH 2 HCl aqueous solution) was added; this solution was then irradiated for another 8 min by the laser with an applied power of 56.1 mW.

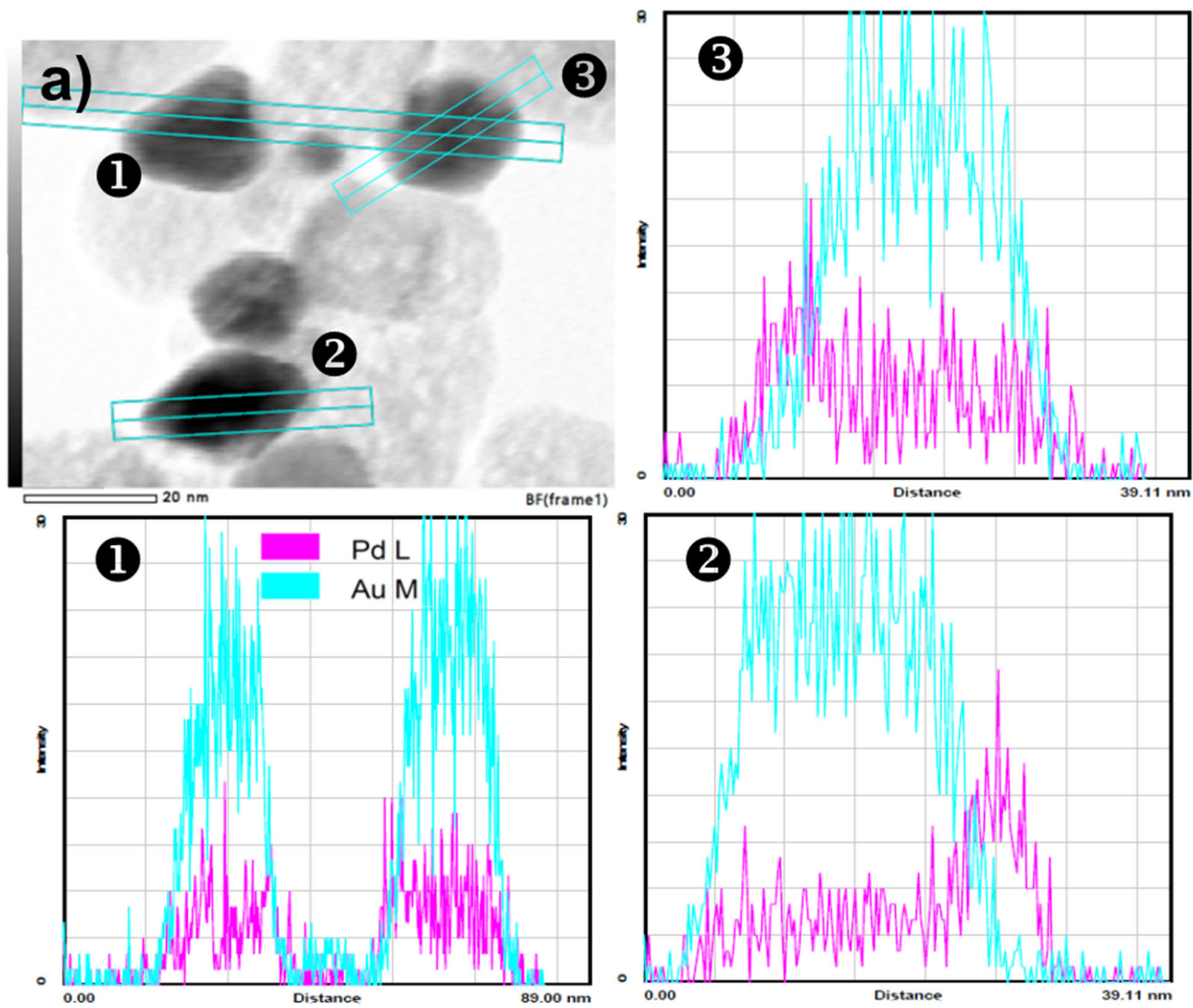


Figure S8a. STEM image of (Au@Pd)-TiO₂, and 3 line-scan distribution profiles showing that the shell layer is not that homogeneous, and the presence of the protrusions.

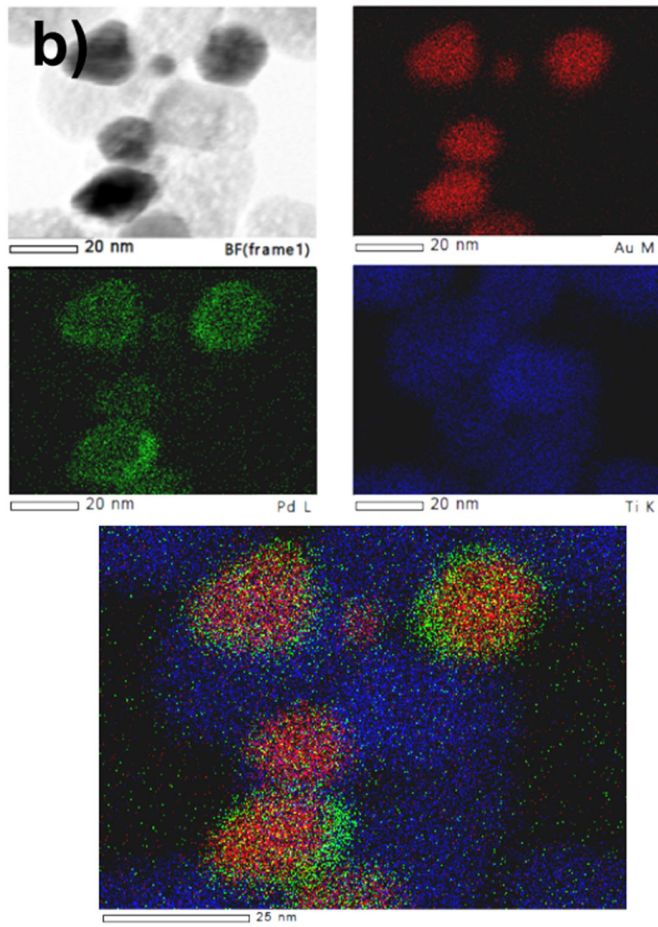


Figure S8b. STEM image of (Au@Pd)-TiO₂, and the representative EDS mapping images and their overlapping.

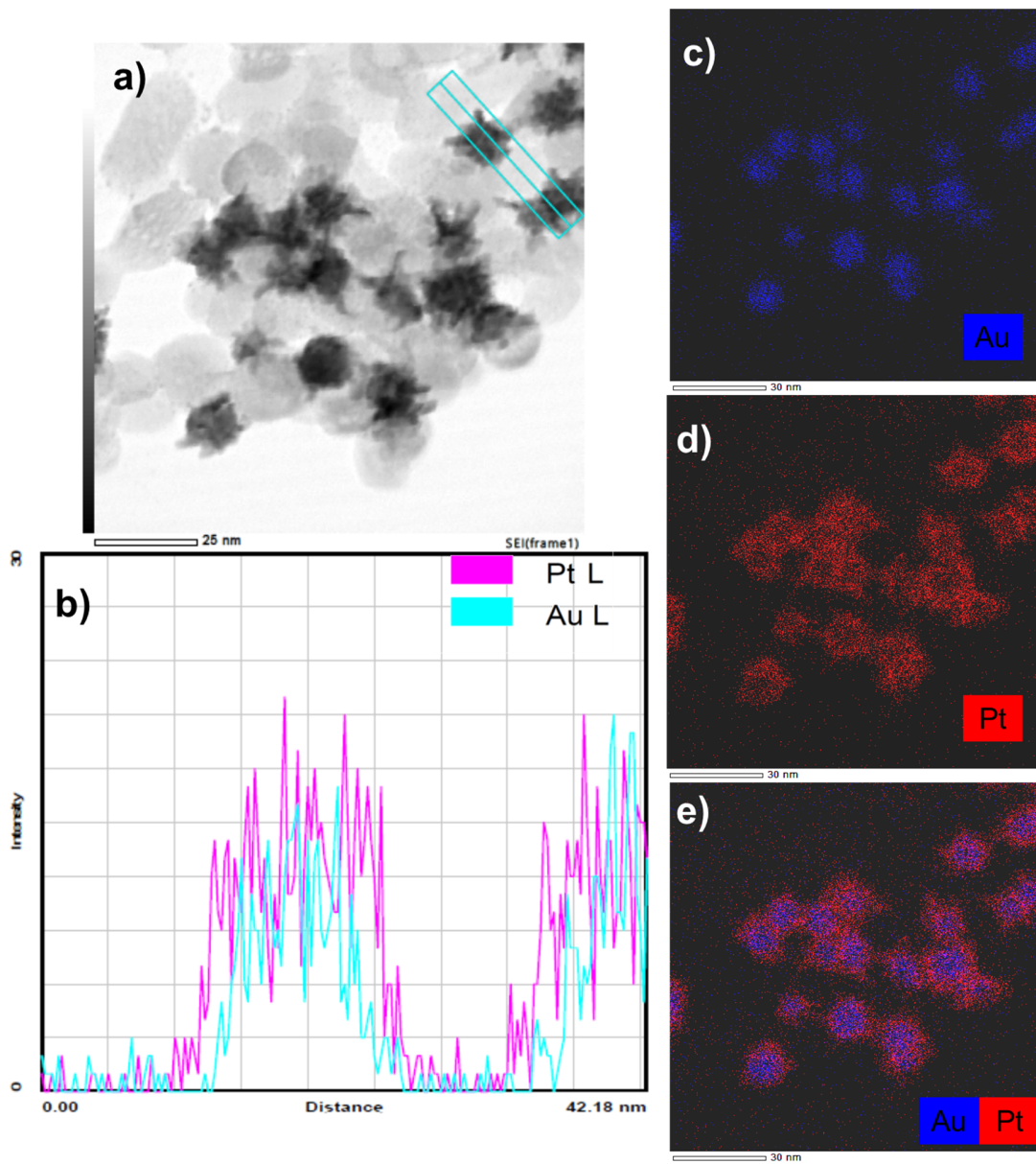


Figure S9. a) STEM image of (Au@Pt)-TiO₂ b) line-scan distribution profile showing both gold and platinum and (c)-(e) the representative EDS mapping images and overlay of the two metals.

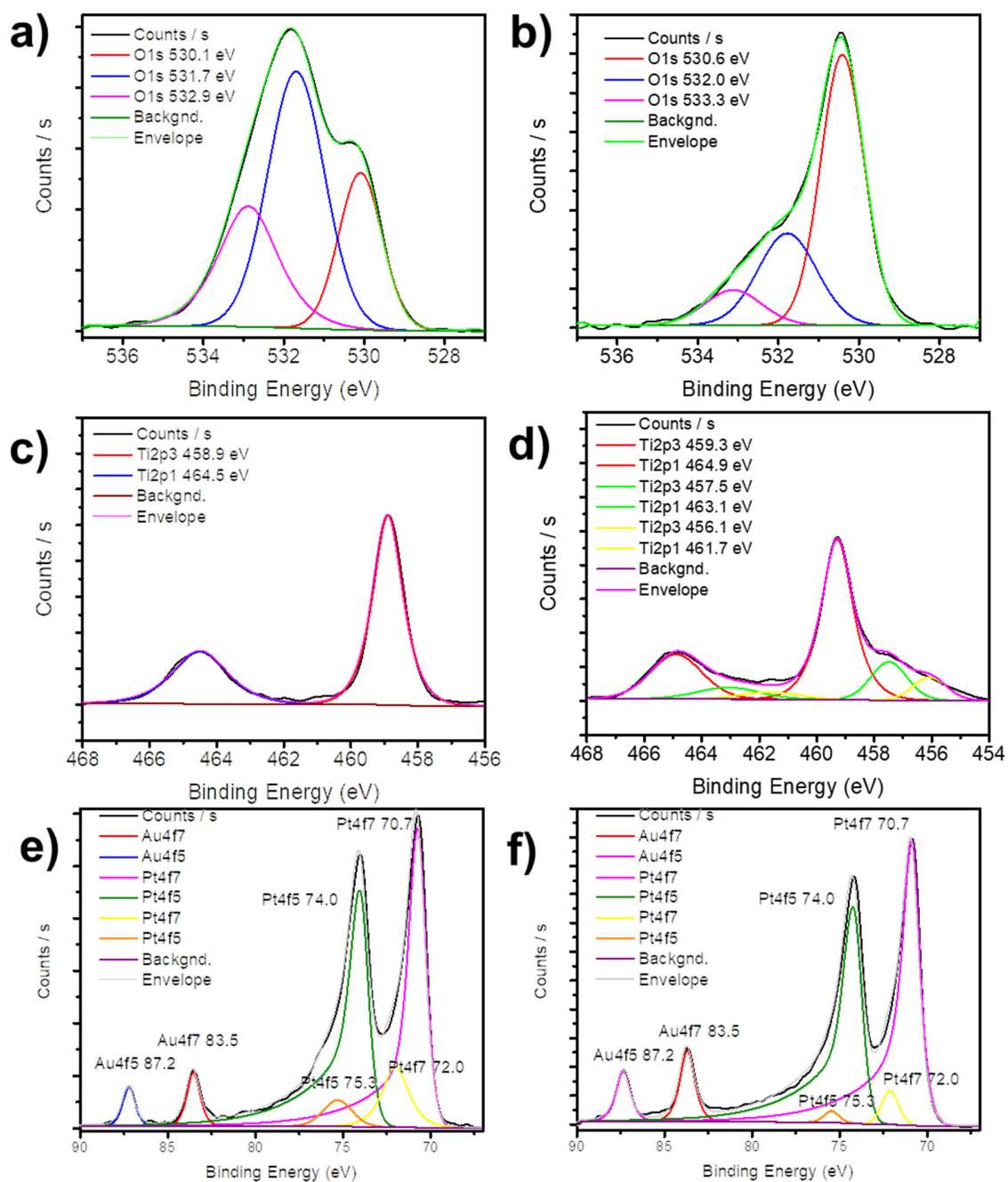


Figure S10. High-resolution XPS spectra of O_{1s}, Ti_{2p}, Au_{4f}, and Pt_{4f} in the Au@Pt-TiO₂ NHDs (a), (c), and (e) before and (b), (d), and (f) after 6 s of Ar⁺ etching.

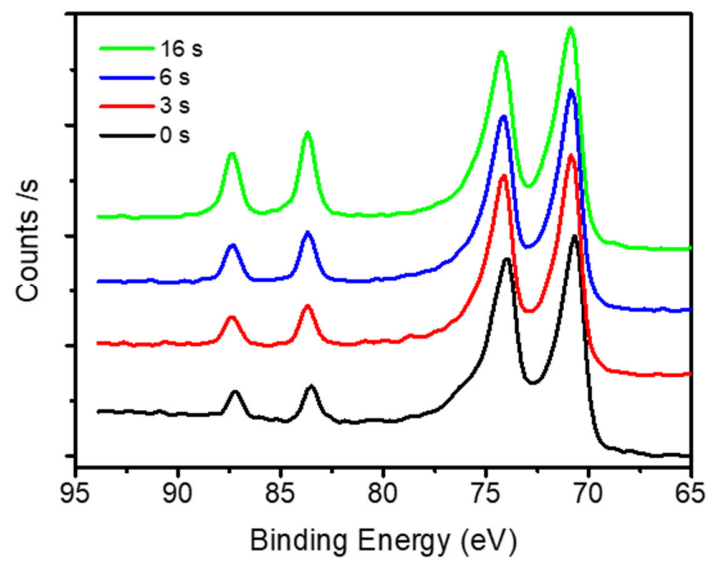


Figure S11. Variation of the XPS spectra of Au4f and Pt4f of the Au@Pt-TiO₂ NHDs with Ar⁺ etching times.