# Supporting Information

## The Role of Femtosecond Pulsed Laser-Induced Atomic Redistribution in Bimetallic Au-Pd Nanorods on Optoelectronic and Catalytic Properties

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**Table S1:** Au and Pd concentrations, and Pd content (at. %) of various types of nanoparticles and their corresponding transverse and longitudinal LSPR modes. Au and Pd concentrations of nanoparticles are determined by inductively coupled plasma emission spectroscopy (ICPES). Atomic content is calculated using Au and Pd concentrations divided by the molar mass of Au (196.97 g $mol^{-1}$) and Pd (106.42 g $mol^{-1}$).

| **Catalyst** | **Au Conc. (μg $mL^{-1}$)** | **Pd Conc. (μg $mL^{-1}$)** | **Pd Content (at. %)** | **Transverse LSPR (nm)** | **Longitudinal LSPR (nm)** |
|---|---|---|---|---|---|
| Au NRs | 0.57 | NA | NA | 510 | 735 |
| $Au_{85}Pd_{15}$NRs | 0.57 | 0.055 | 15.1 | 510 | 760 |
| $Au_{75}Pd_{25}$NRs | 0.56 | 0.101 | 25.0 | 510 | 800 |

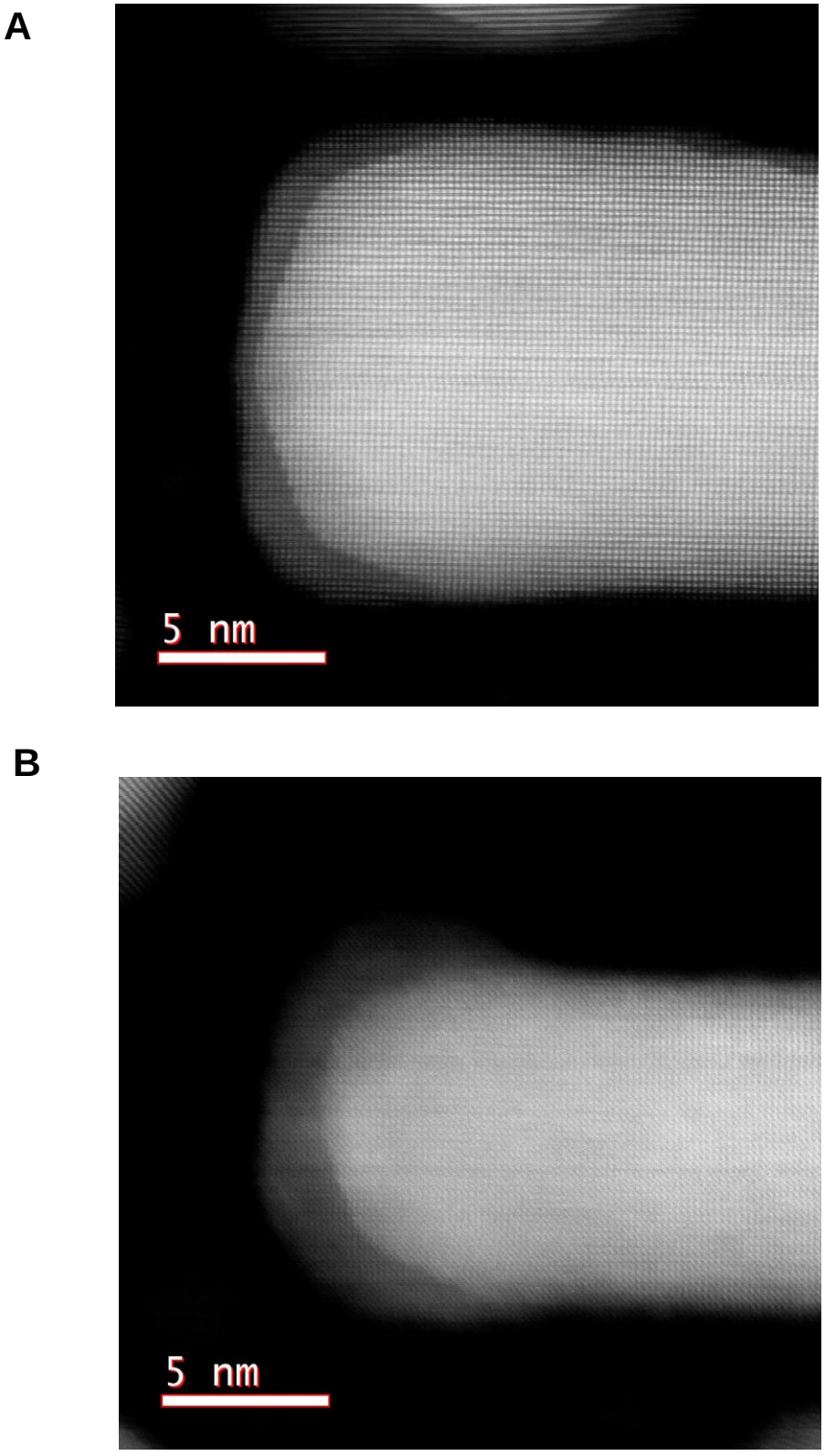


**Figure S1:** HAADF-STEM images of **A)** $Au_{85}Pd_{15}$NRs and **B)** $Au_{75}Pd_{25}$NRs.

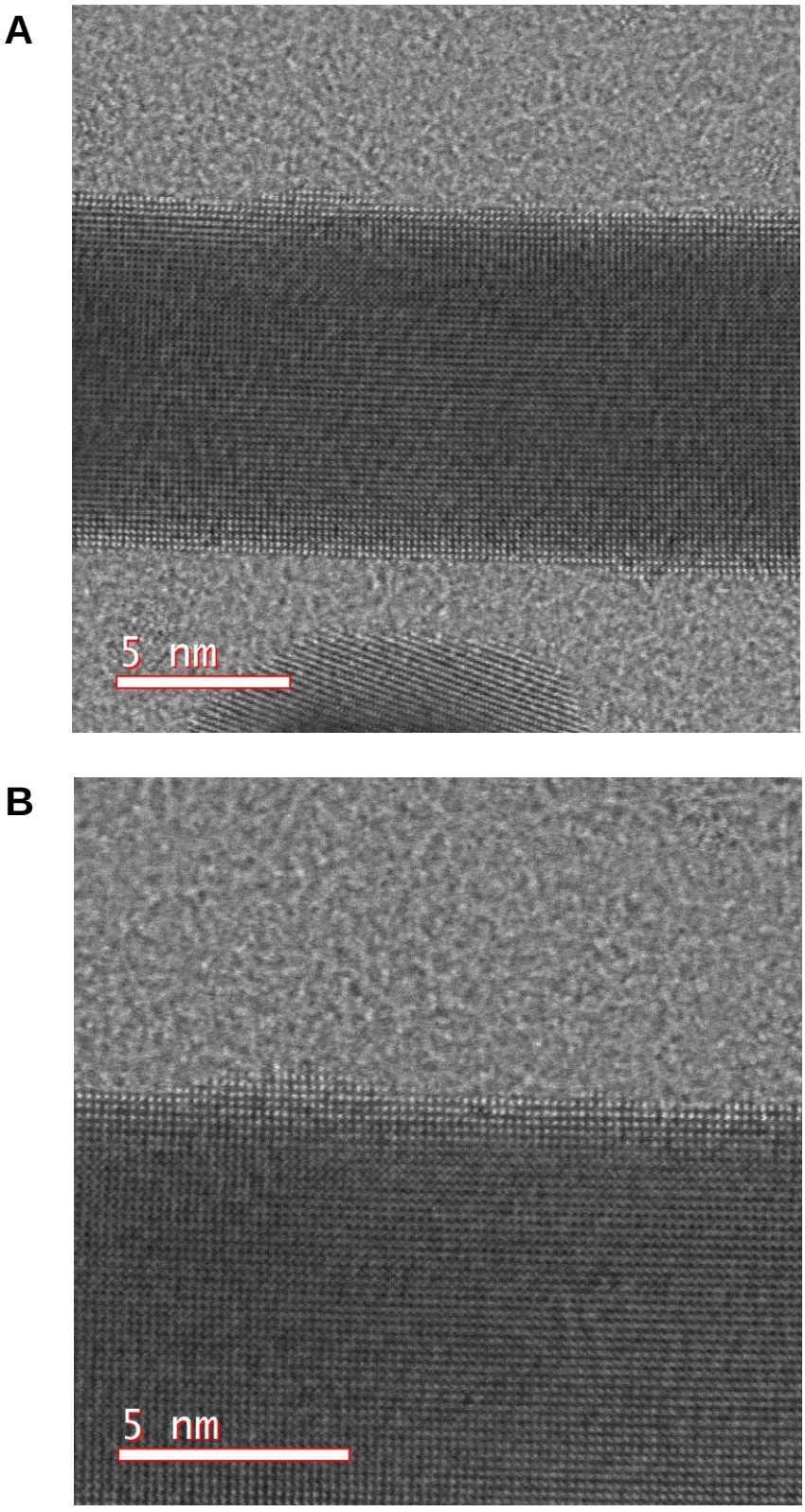


**Figure S2: A), B)** HRTEM images from the body of $Au_{85}Pd_{15}$NRs. The presence of Pd with the thickness of ~0.25 nm on the body of AuNRs is evident.

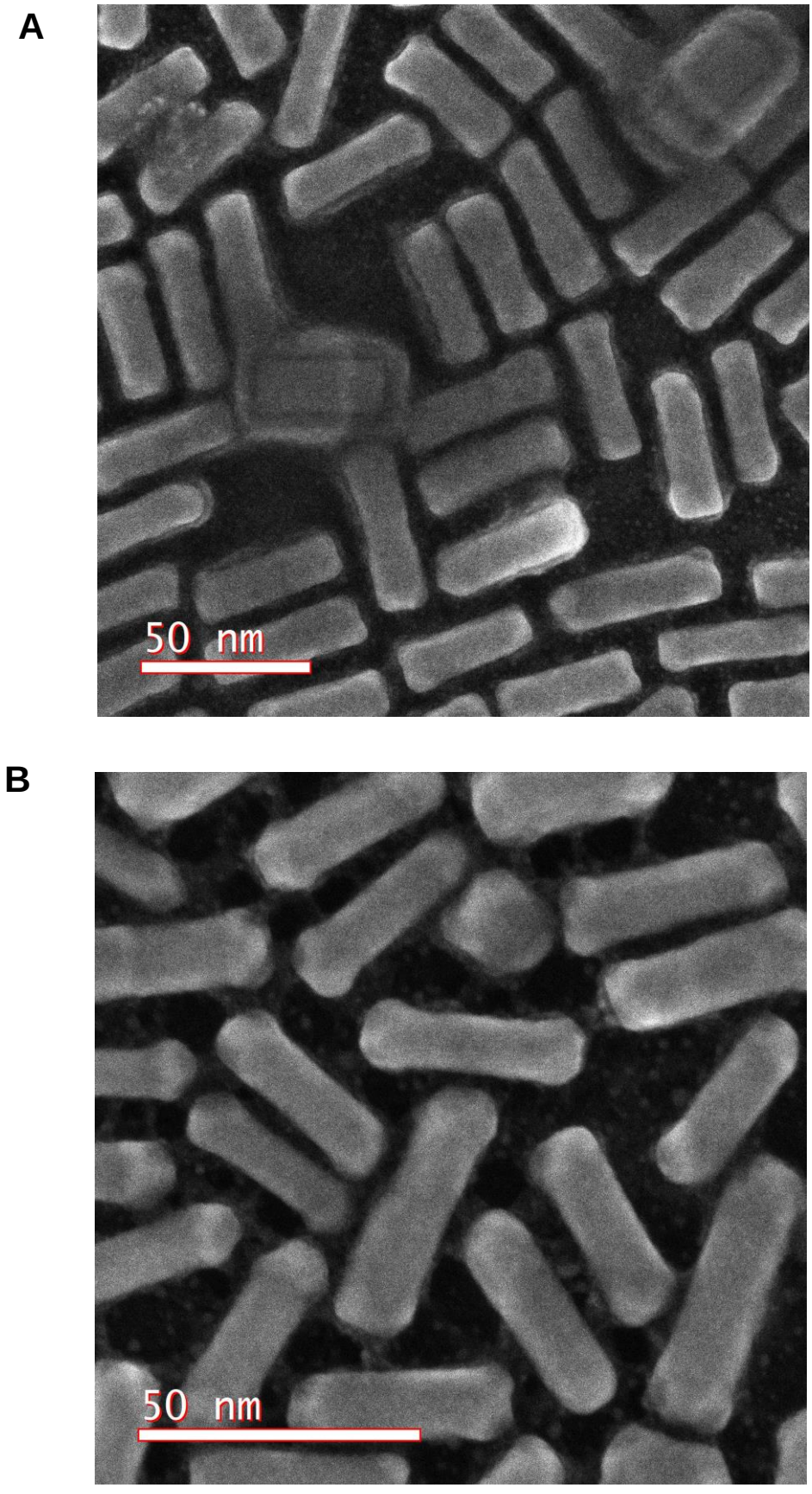


**Figure S3:** STEM images of the **A)** $Au_{85}Pd_{15}$NRs and **B)** $Au_{75}Pd_{25}$NRs.

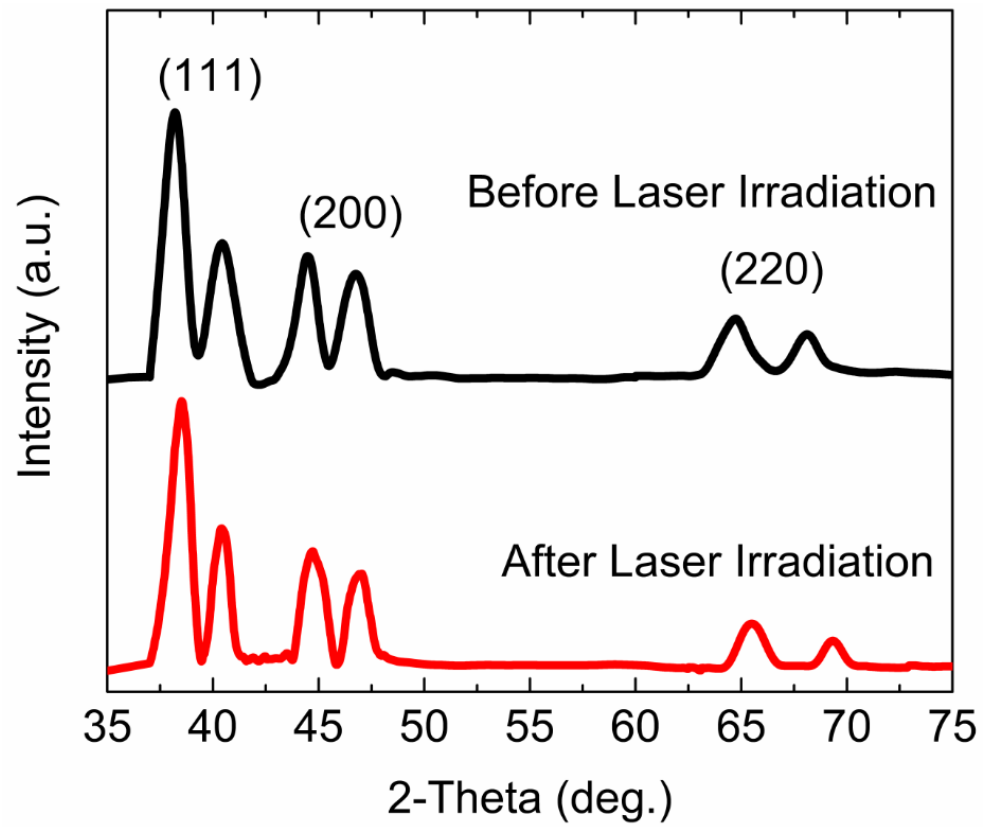


**Figure S4:** XRD patterns of bimetallic Au-Pd NRs before and after femtosecond pulsed laser irradiation. The Au and Pd peaks with minor shift are observed after laser irradiation, ruling out the possibility of the alloy formation. The Pd diffraction peaks shift to higher $2\theta$ angles due to the smaller lattice parameter (3.890Å) of Pd compared to that of Au (4.079 Å).

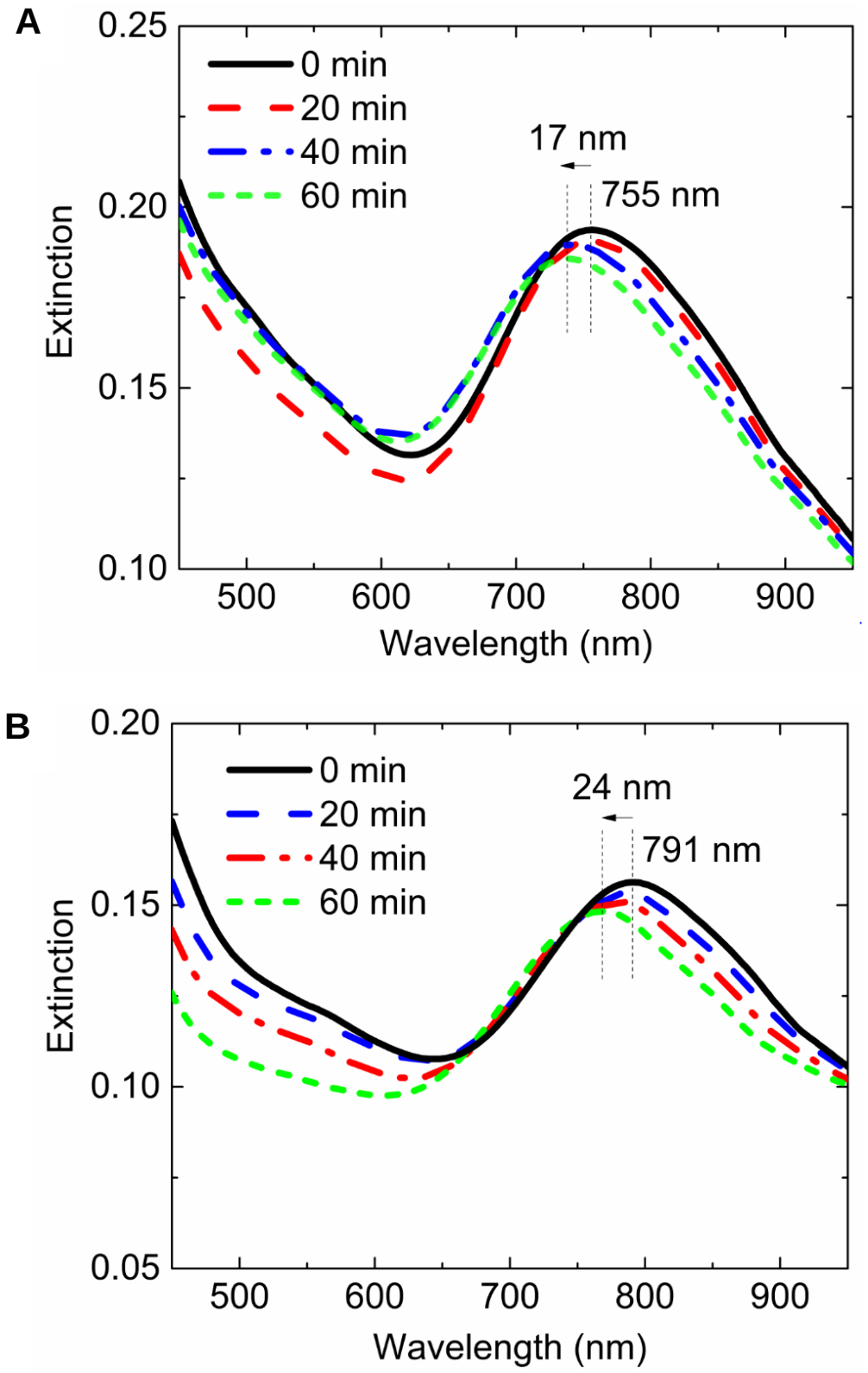


**Figure S5.** UV-vis extinction spectra of **A)** $Au_{85}Pd_{15}$NRs and **B)** $Au_{75}Pd_{25}$NRs after femtosecond pulsed laser irradiation (200 mW, 808 nm) with various exposure times (*i.e.*, 20, 40, 60 min). The plasmon intensity slightly dampens and the LSPR blue shifts after laser irradiation. The spectra were measured for nanoparticles deposited on the ITO substrate, resulting in slight blue shift in the LSPR peak position compared to those measured in **Figure 1A** in water. This is due to the change in the dielectric constant of the surronding medium.

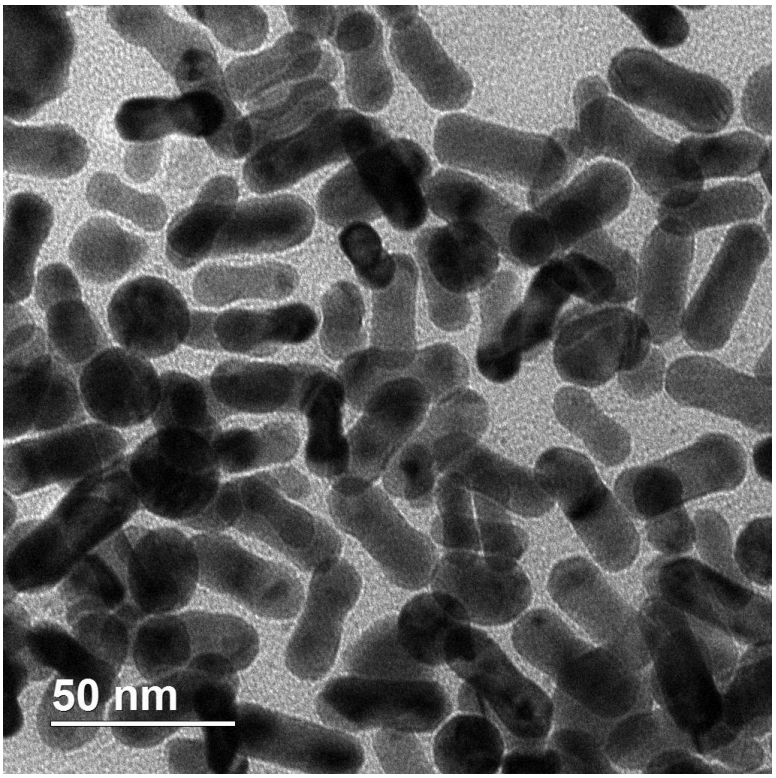


**Figure S6.** TEM image of $Au_{75}Pd_{25}$NRs after 1h femtosecond pulsed laser irradiation (200 mW, 808 nm).

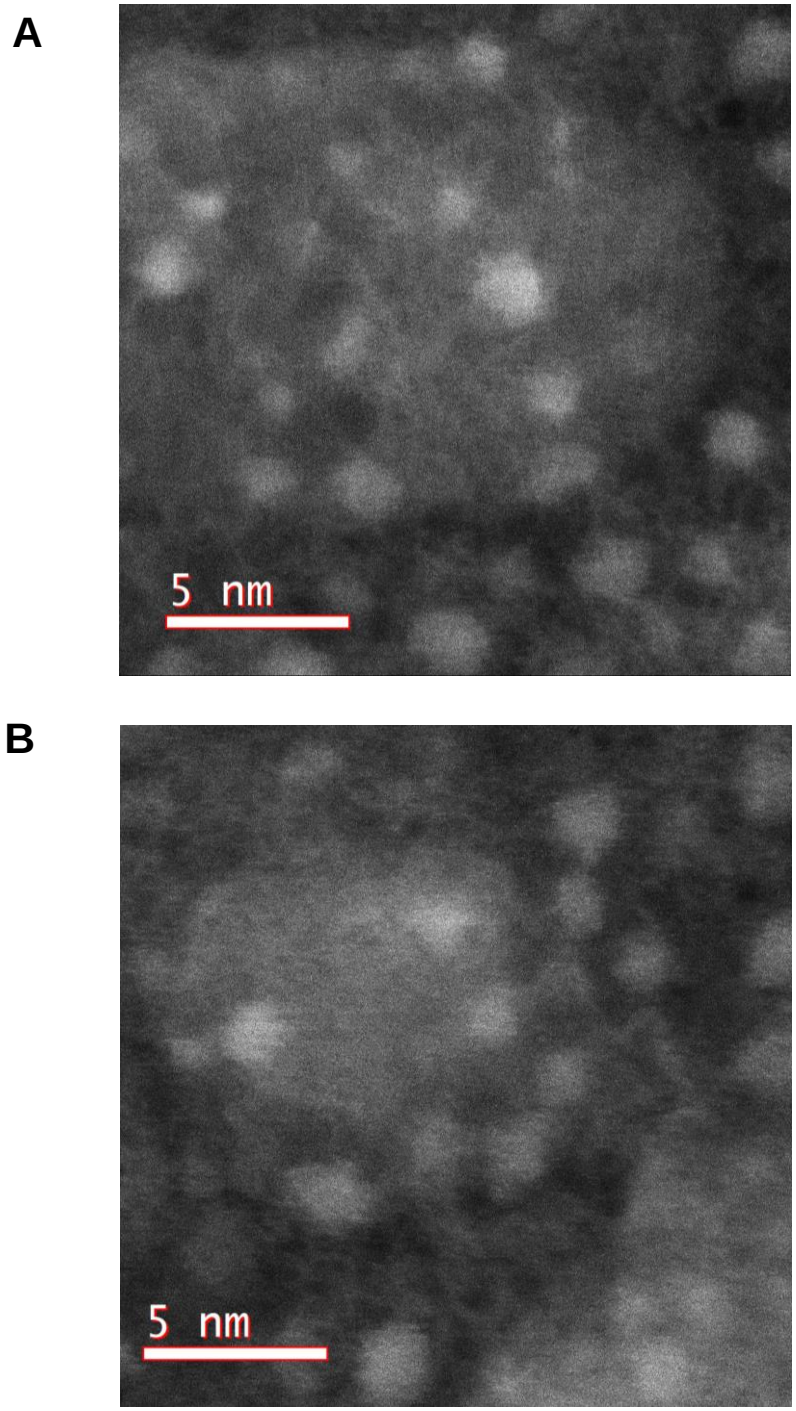


**Figure S7:** STEM images of the structurally modified $Au_{85}Pd_{15}$NRs by femtosecond pulsed laser. **A)** Dumble-shaped nanoparticles, and **B)** Sphere-shaped nanoparticles shown in **Figure 5A** in the manuscript. The Pd nanoparticles with an approximate size of 1.5-2 nm are uniformly distributed on Au nanorods surface.

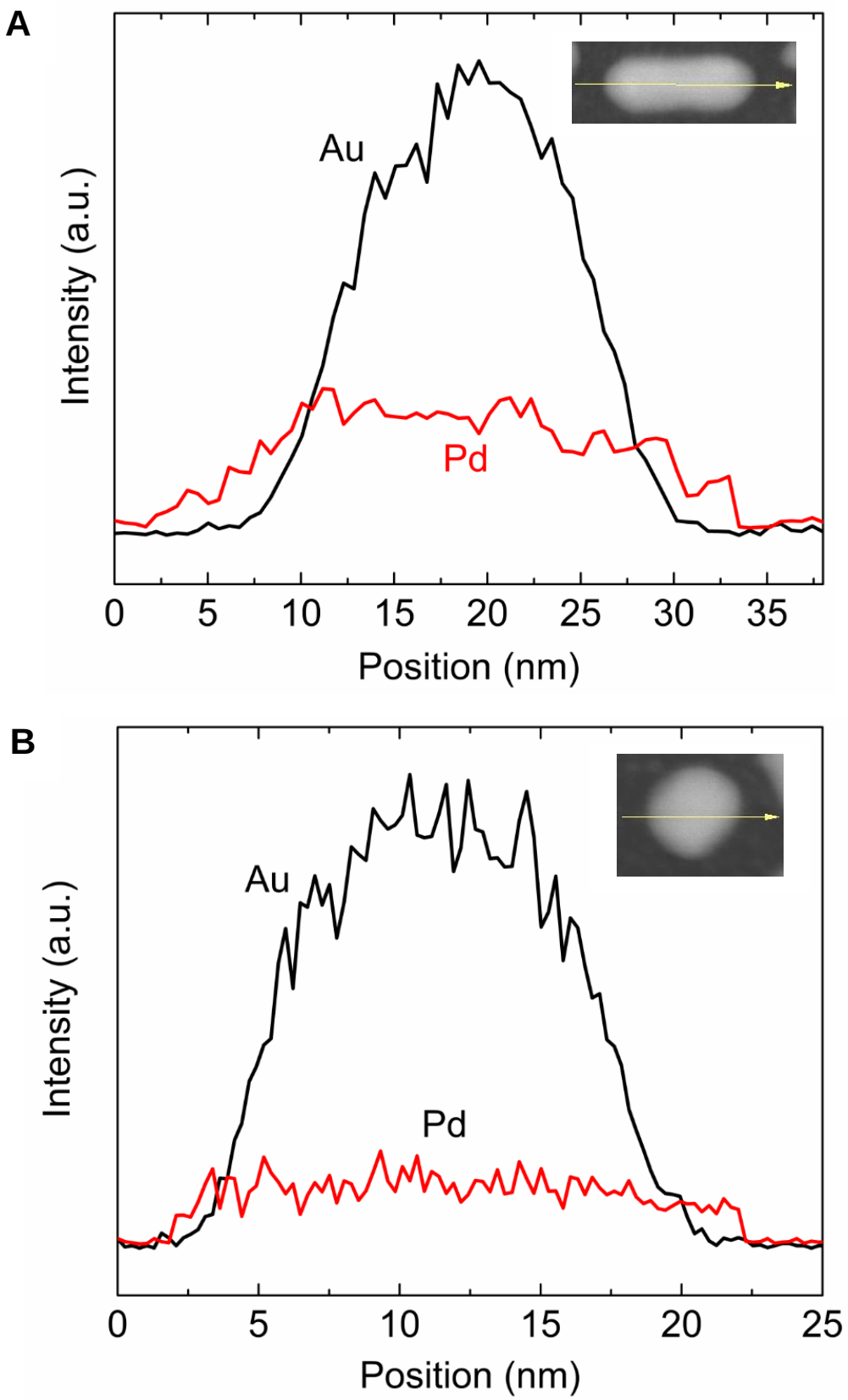


**Figure S8:** Cross sectional compositional line profiles of structurally modified $Au_{85}Pd_{15}$NRs by femtosecond pulsed laser. **A)** Dumble-shaped nanoparticles, and **B)** Sphere-shaped nanoparticles shown in **Figure 5A** in the manuscript.

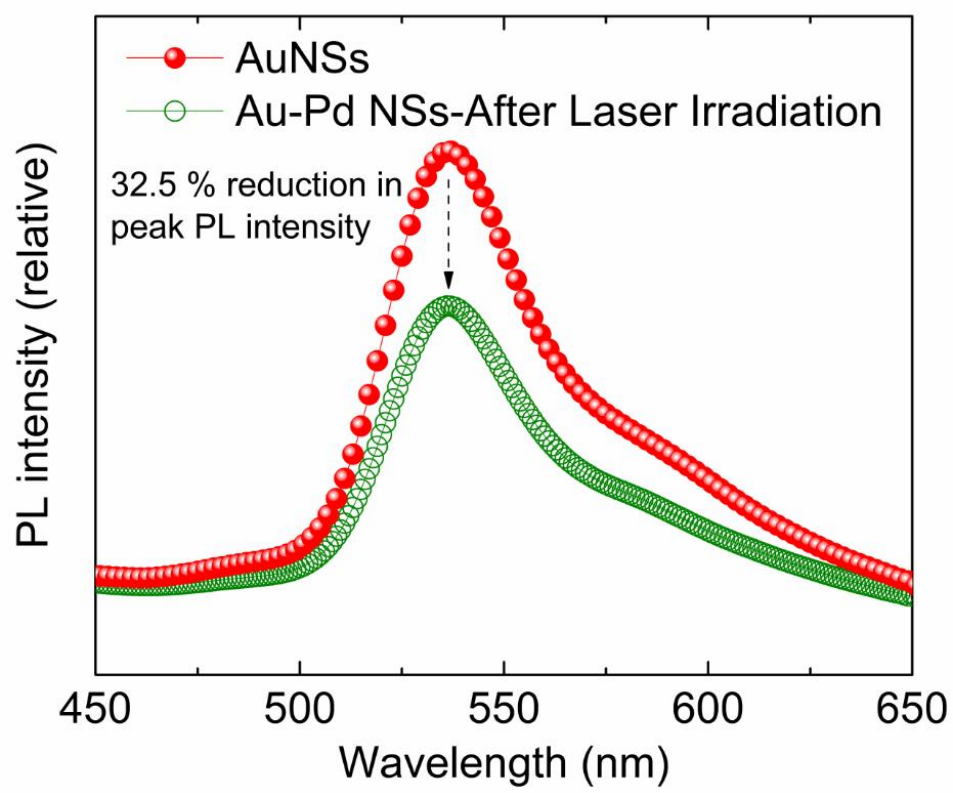


**Figure S9:** PL spectra of AuNSs and modified Au-Pd NSs after femtosecond laser irradiation. The peak PL intensity drops by 32.5%.

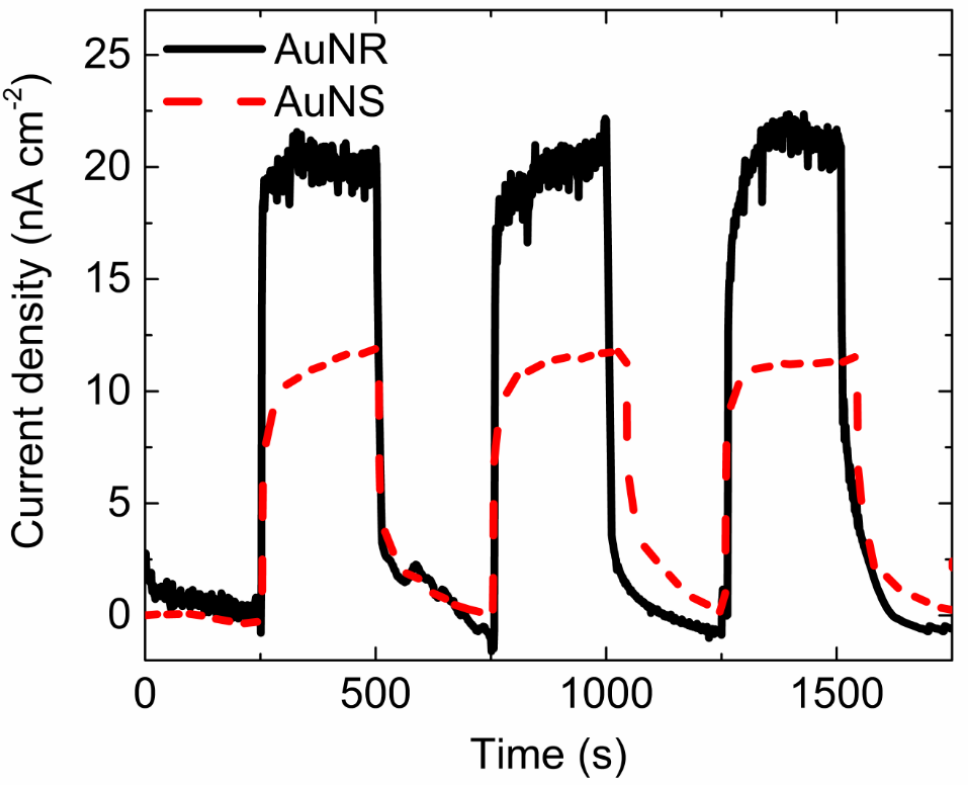


**Figure S10:** Transient photocurrent response of AuNSs and AuNRs under 1 sun illumination (100 mW $cm^{-2}$). TEM images of AuNSs and AuNRs were presented in our previous work.[1]

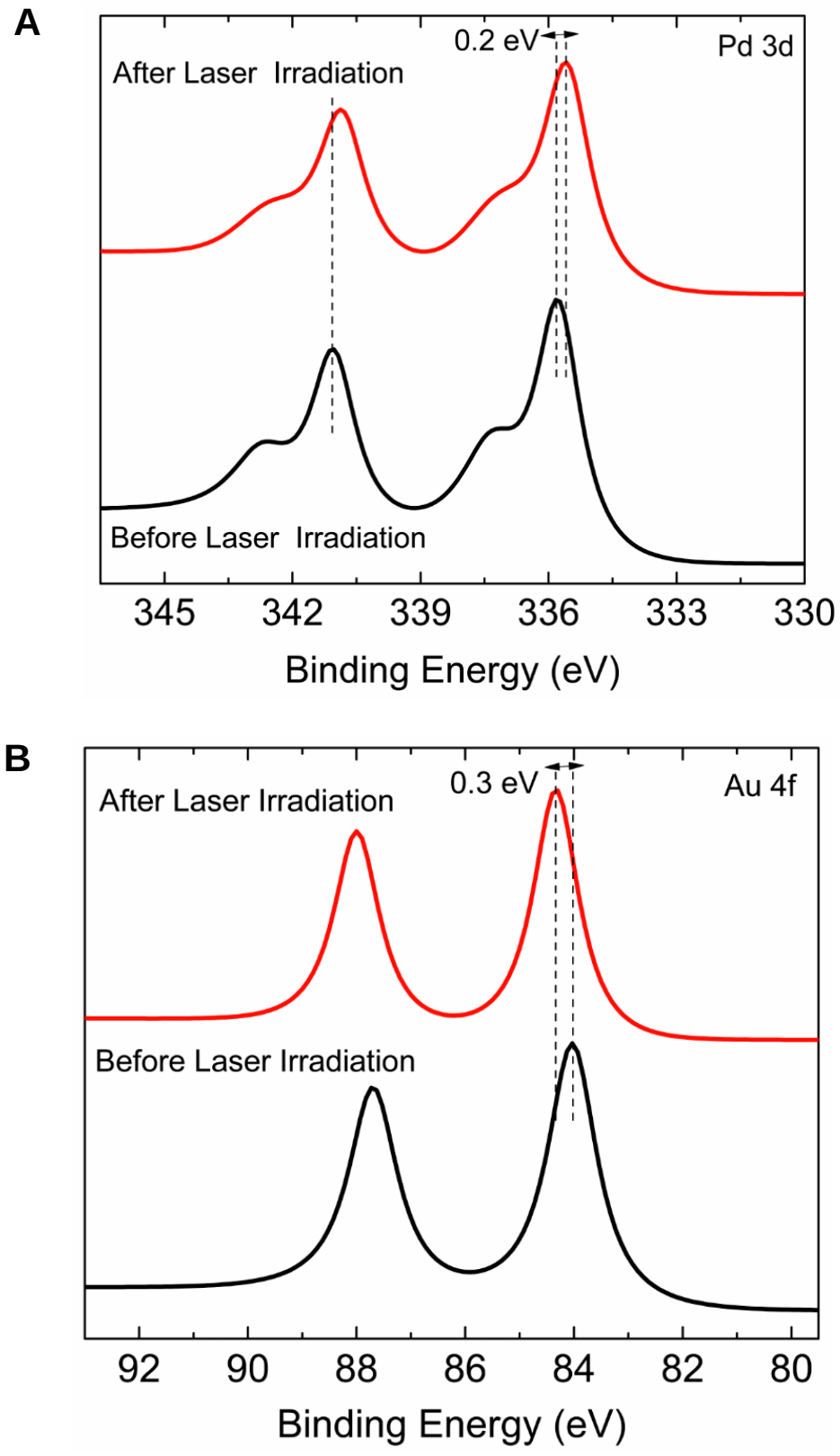


**Figure S11.** XPS spectra of **A**) Pd 3d and **B**) Au 4f of bimetallic Au-Pd NRs before and after 1 h femtosecond pulsed laser irradiation. All spectra were shift corrected using a standard reference C1s, C-C peak at 284.8 eV.

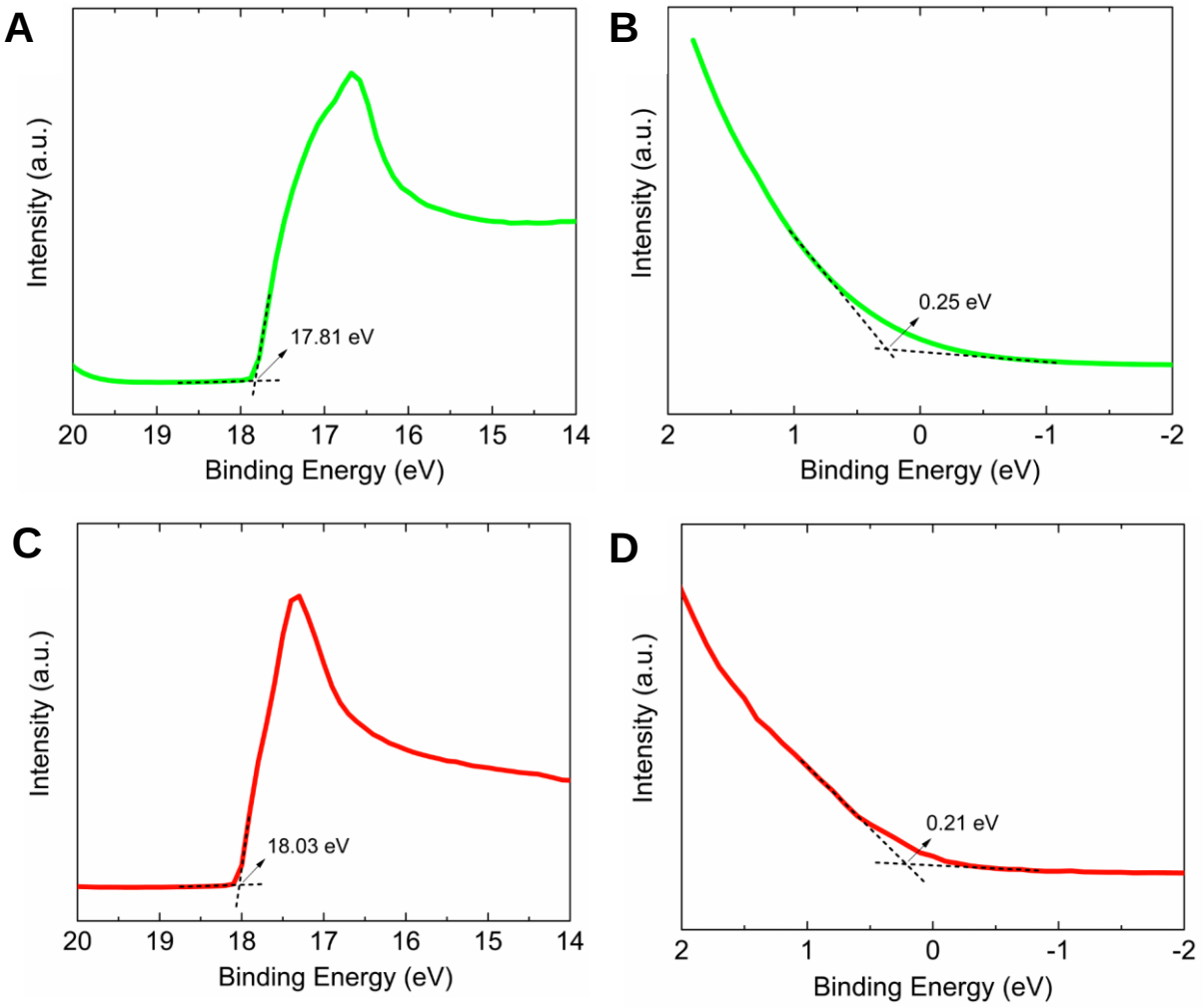


**Figure S12:** UPS spectra of bimetallic Au-Pd NRs before and after femtosecond pulsed laser irradiation. **A), C)** The secondary electron cut-off ($E_{cut\text{-}off}$) and **B), D)** the Fermi edge ($E_{FE}$) are measured with He1 (21.22 eV) source radiation. The work function ($\Phi$) is calculated by 21.21 eV − ($E_{cut\text{-}off}$ − $E_{FE}$). The $\Phi$ of bimetallic Au-Pd NRs before laser irradiation is determined to be 21.21-(17.81-0.25) = **3.66 eV**. The $\Phi$ of bimetallic Au-Pd NRs after laser irradiation is determined to be 21.21-(18.03-0.21) = **3.39 eV**.

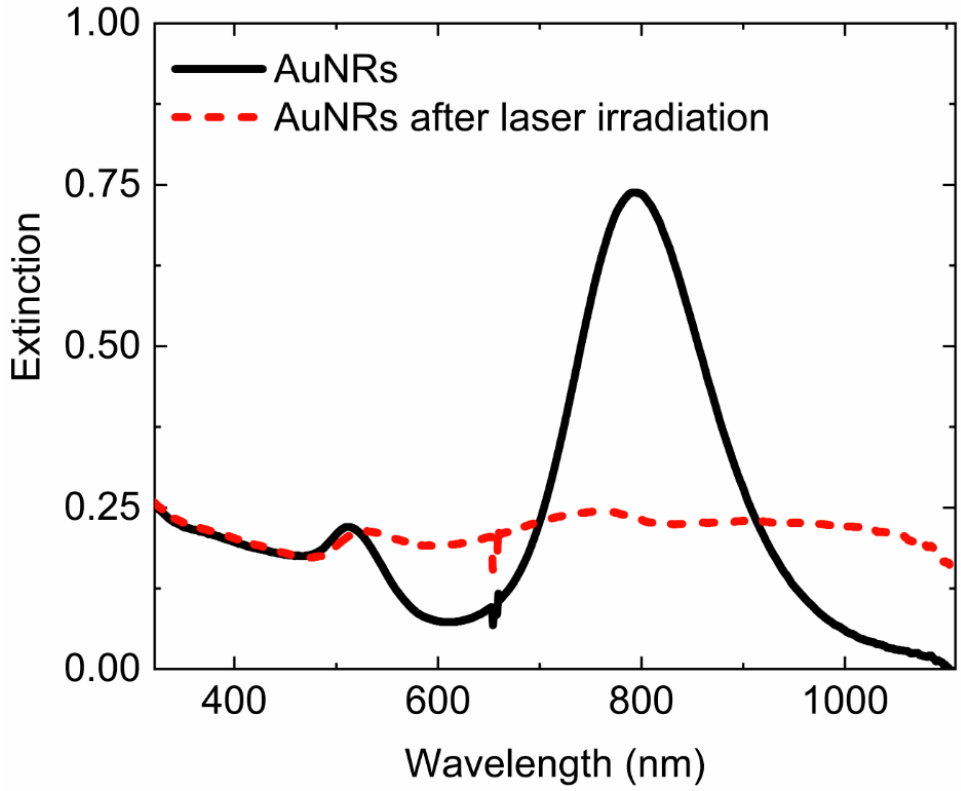


**Figure S13:** Extinction spectra of cleaned AuNRs before and after femtosecond pulsed laser irradiation for 30 min with 90 mW power.

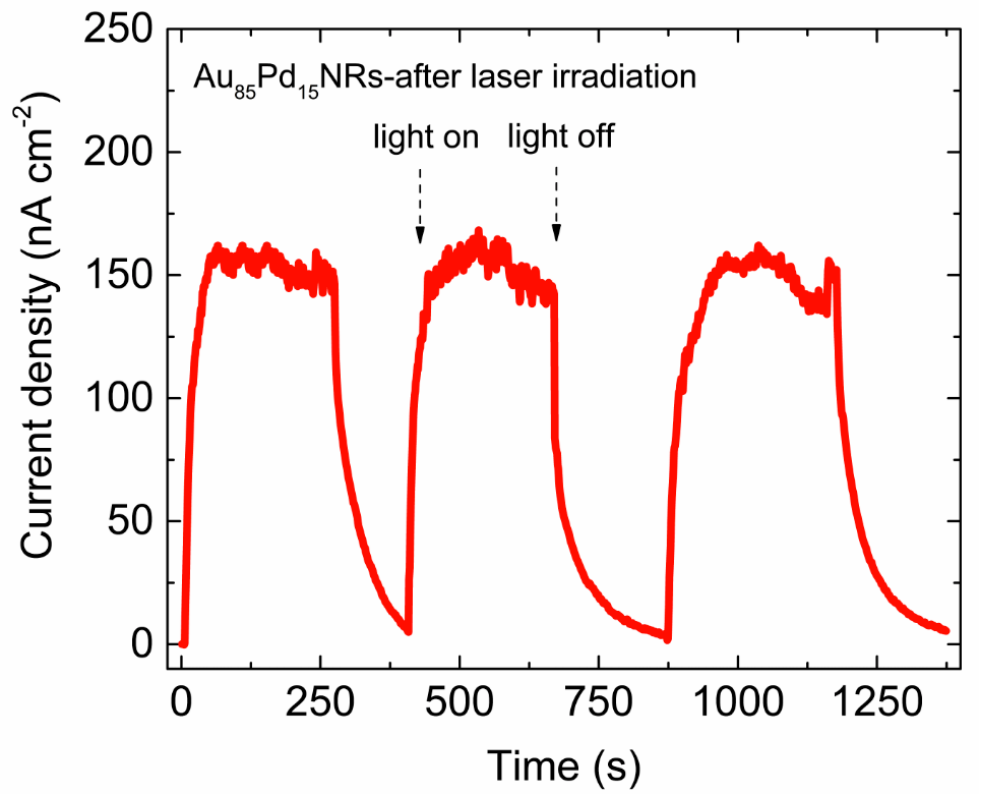


**Figure S14:** Transient photocurrent response of structurally modified $Au_{85}Pd_{15}$NRs by femtosecond pulsed laser. The light source is 808 nm femtosecond laser (200 mW).

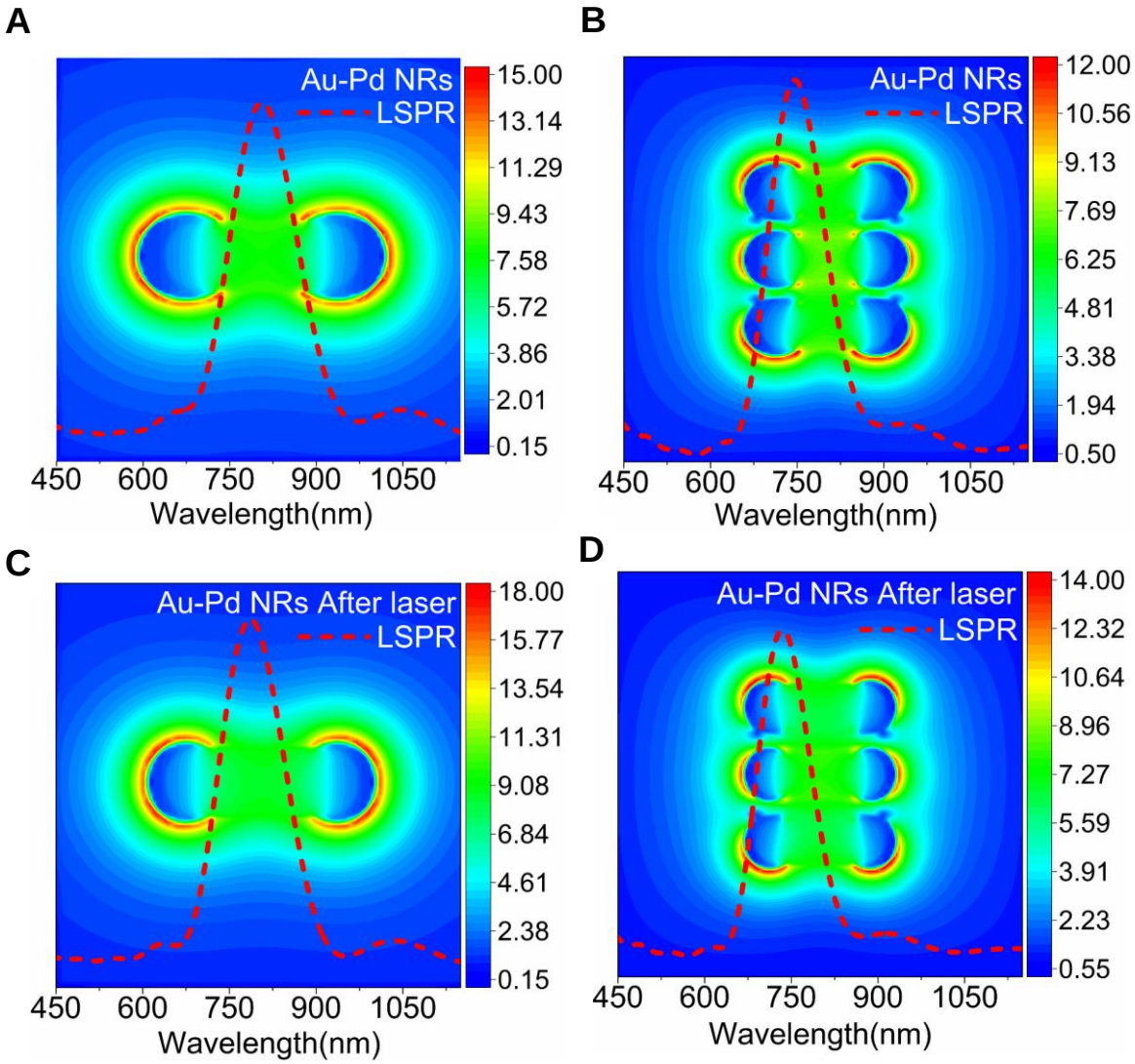


**Figure S15.** LSPR spectra and plasmon field intensity and distribution of **A, C)** Individual Au-Pd NR, and **B, D)** Three Au-Pd NRs before and after femtosecond pulsed laser irradiation, respectively.

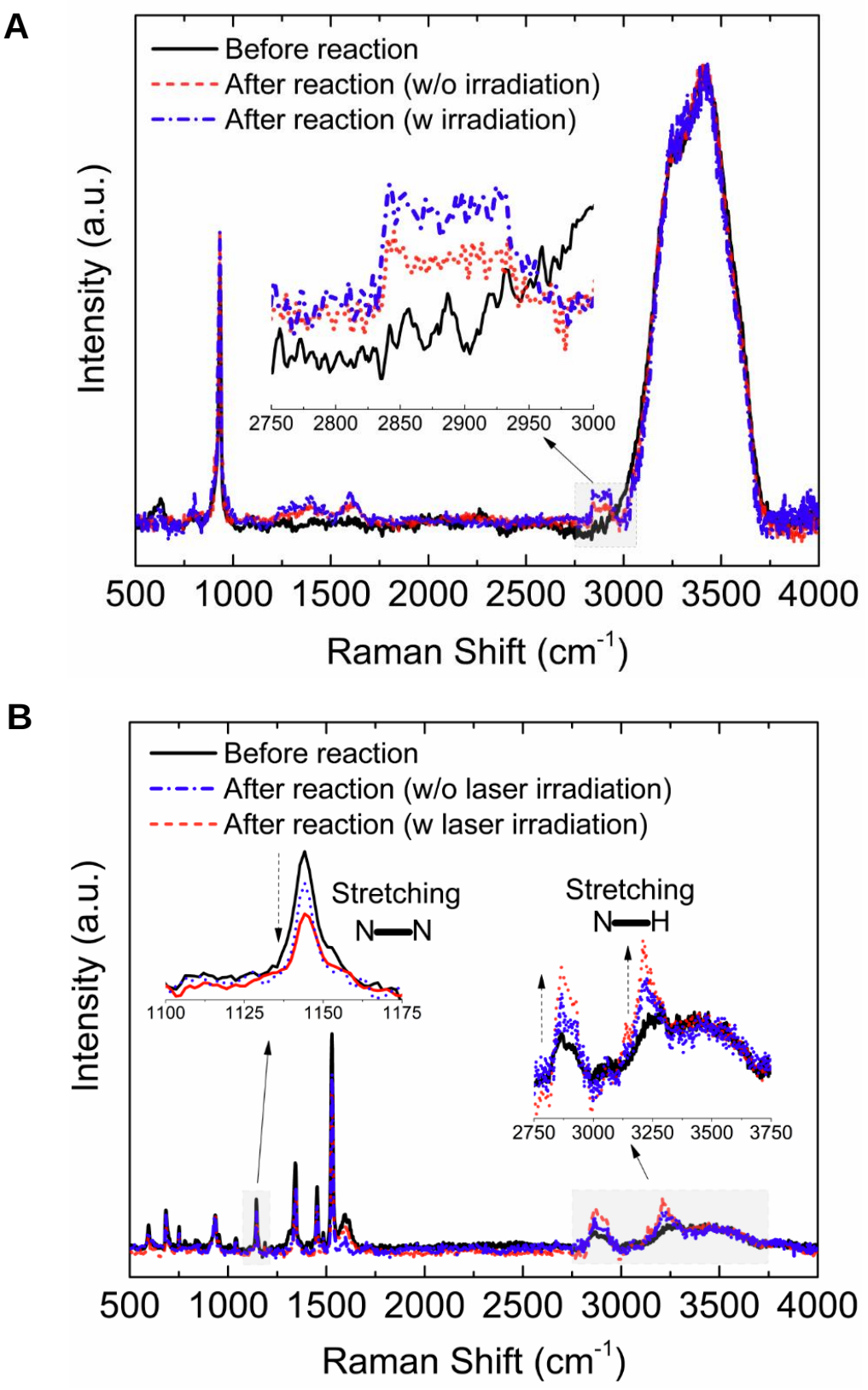


**Figure S16:** SERS spectra of photoelectrochemical **A)** $N_2$ and **B)** $N_2H_4$ reduction using bimetallic Au-Pd NRs before and after femtosecond pulsed laser irradiation. Photoelectrochemical measurements were performed at −0.4 V *vs.* RHE under 1 sun illumination for 12 h using the experimental apparatus shown in **Figure 4A** in the manuscript.

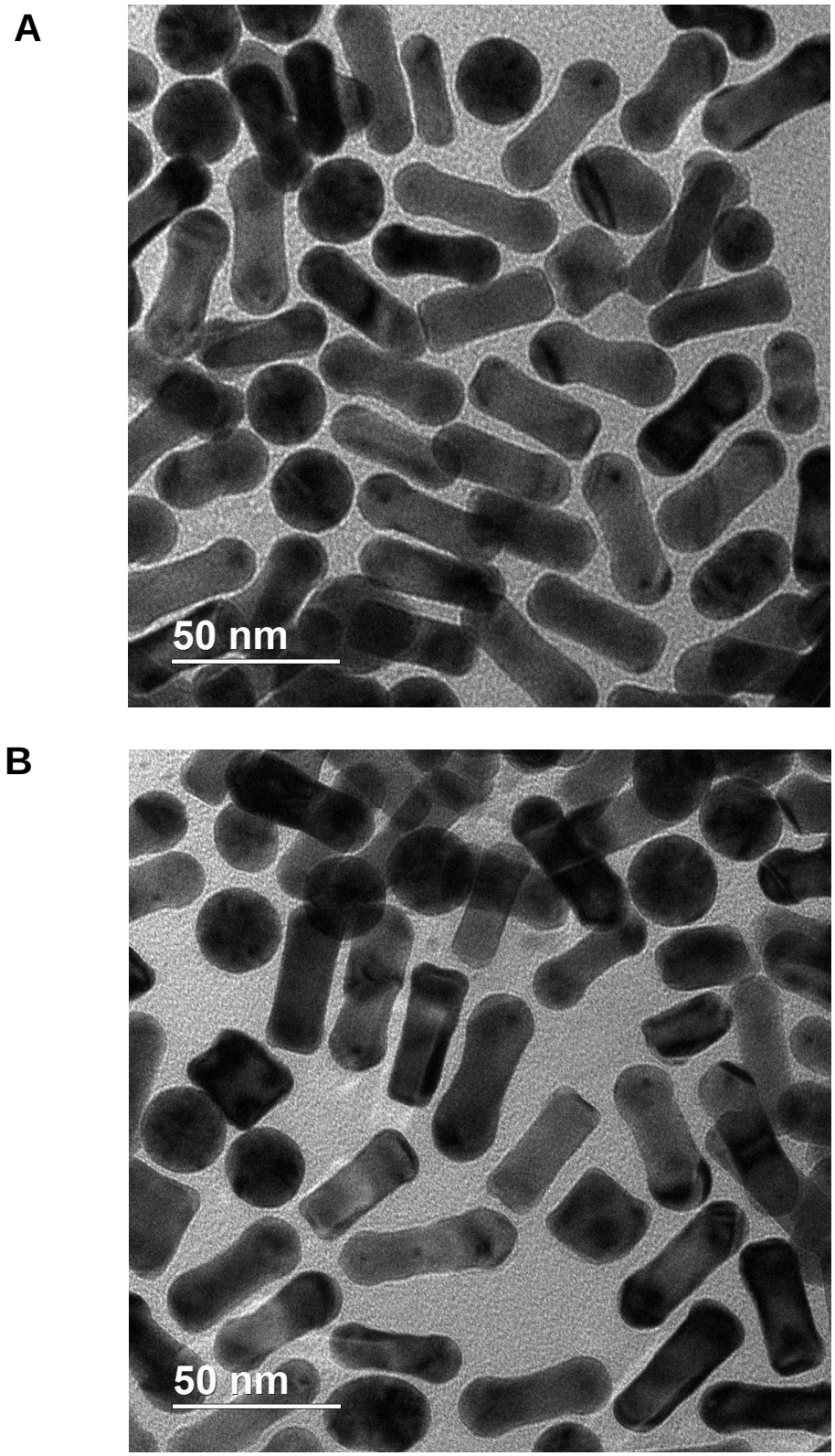


**Figure S17:** TEM images of structurally modified bimetallic Au-Pd nanorods after femtosecond pulsed laser irradiation **A)** before and **B)** after the PEC testing. PEC measurements were performed at -0.4 V *vs*. RHE under 1 sun illumination for 12 h using the experimental apparatus shown in **Figure 4A** in the manuscript.

## References

(1) Nazemi, M.; El-Sayed, M. A. Plasmon-enhanced photo (electro) chemical nitrogen fixation under ambient conditions using visible light responsive hybrid hollow Au-$Ag_2O$ nanocages. *Nano Energy* **2019**, *63*, 103886.