Supporting Information

Interfacial Self-Assembled Functional Nanoparticle Array: A Facile Surface-Enhanced Raman Scattering Sensor for Specific Detection of Trace Analytes

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Three dimensional finite difference time domain (3D-FDTD) simulations. The 3D-FDTD simulations were used to theoretically illustrate the electromagnetic near-field distribution of gold nanoparticles at the liquid/liquid interface. All calculations were performed with FDTD Solutions (Lumerical Solutions, version 8.5). Details of the FDTD algorithm can be found in ref. S1. The calculation model is shown in Figure S1A. An isolated gold nanoparticle or a nanoparticle dimer localized at the water/DMC interface was selected as the objective of the surface plasmon resonance study. The optical constant of Au was according to the data of Johnson and Christy.[S2] The simulated Au nanoparticles were set to 30 nm in diameter, and the dielectric constants of water and DMC were taken to be 1.77 and 3.09, respectively. The simulation time was set to 1000 fs for ensuring calculation convergence. The cell size was set to 1×1×1 nm^3 due to the limitation of computation resources. Perfect matched layer (PML) boundary conditions were used in the calculation. The incident plane wave propagates along the *y*-axis direction with the polarization along the *z* direction.

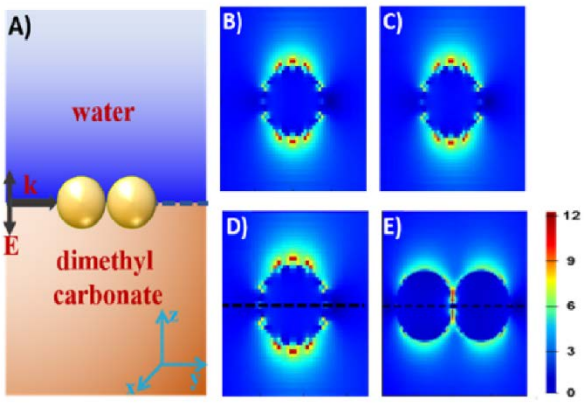

Figure S1. Finite-difference time domain (FDTD) calculations of Au nanoparticles in different environment. (A) Schematic diagram of Au nanoparticles at DMC/water interface with a diameter of 30 nm. Dashed line represents the DMC/water interface. FDTD calculated electric field distribution (|E|) in the y-z plane of a single Au nanoparticle immersed in (B) water, (C) DMC, and (D) at the DMC/water interface. (E) Electromagnetic enhancement of a gold dimer at the DMC/water interface. The electric field was concentrated at the junction between neighboring NPs at the DMC/water interface, indicating the strong inter-particle electronic coupling.

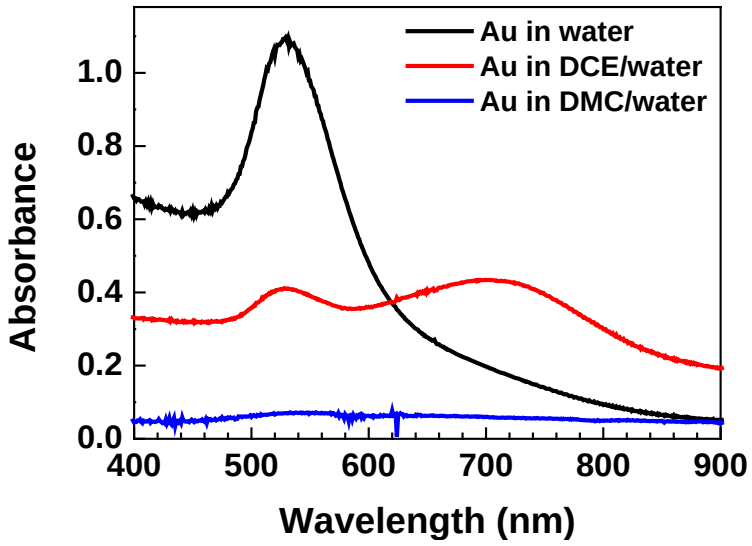

Figure S2. Extinction spectra of Au NPs (black) in aqueous phase before assembly and after assembly at (red) the 1, 2-dichloroethane (DCE)/water interface and (blue) the DMC/water interface.

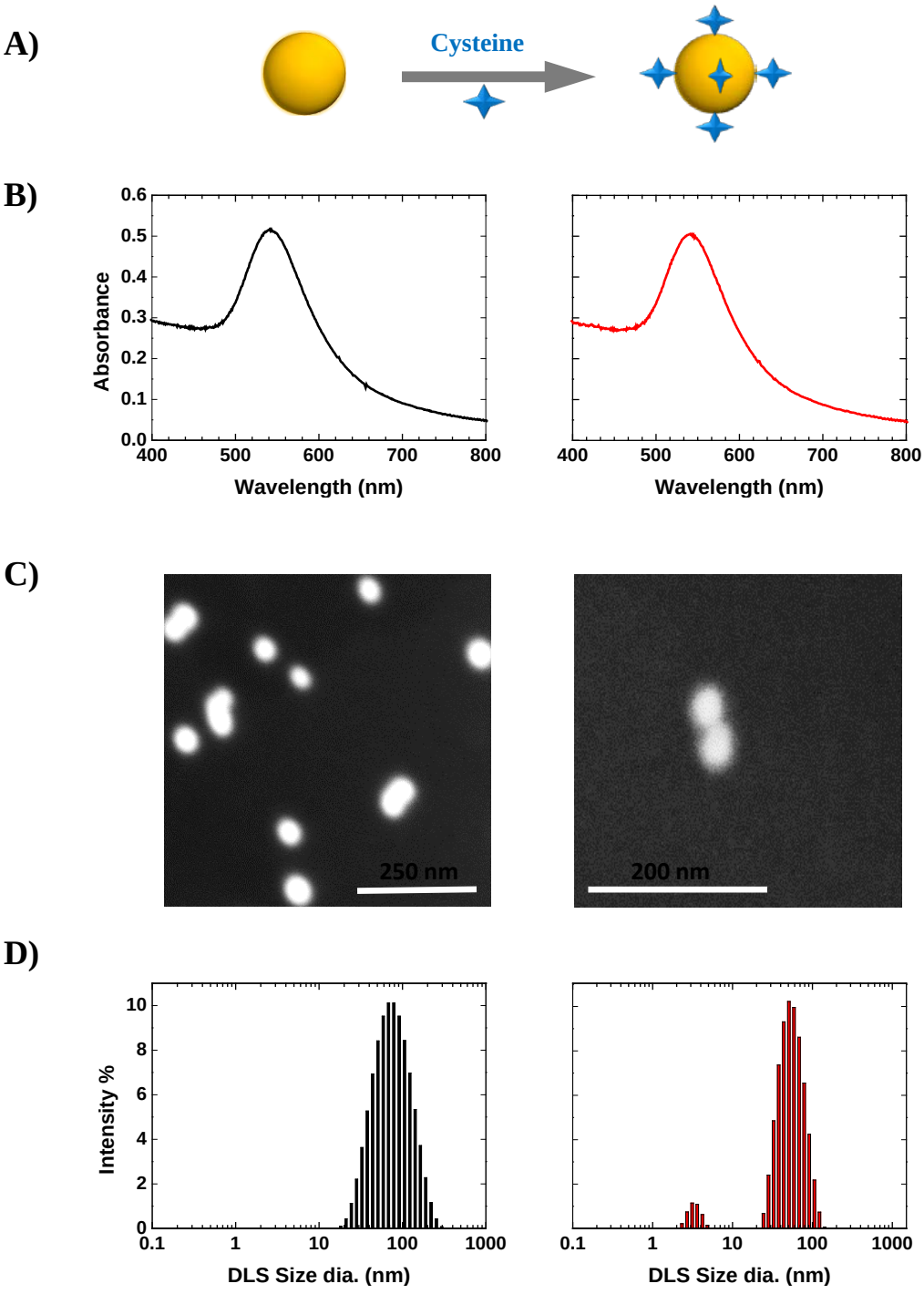

Figure S3. Design, preparation and properties of cysteine modified Au nanoparticles for self-assembly at the liquid/liquid interface. (A) Preparation and schematic structures of cysteine modified Au nanoparticles from the original Au colloid. (B) Extinction spectra, (C) scanning electron microscope, and (D) dynamic light scattering size data obtained from the original and cysteine modified Au nanoparticles as shown in (A).

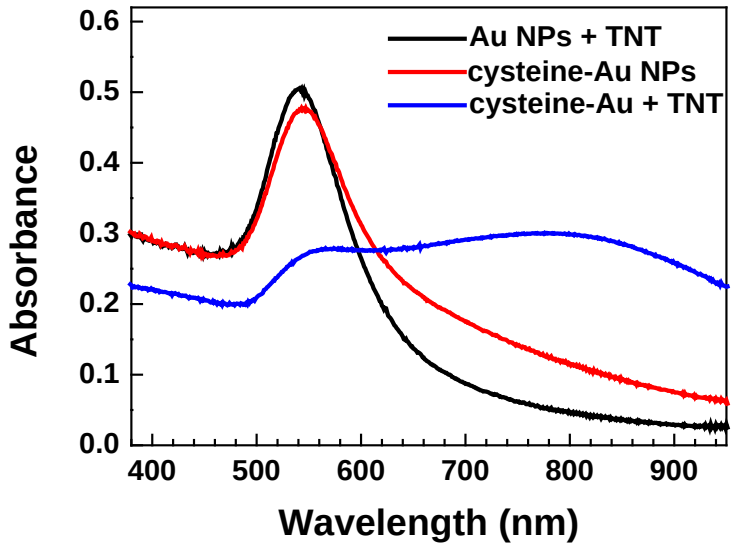

Figure S4. Extinction spectra of Au NPs aqueous dispersion: (black) citrate stabilized Au NPs + TNT; (red) cysteine modified Au nanoparticles; (blue) cysteine modified Au NPs + TNT.

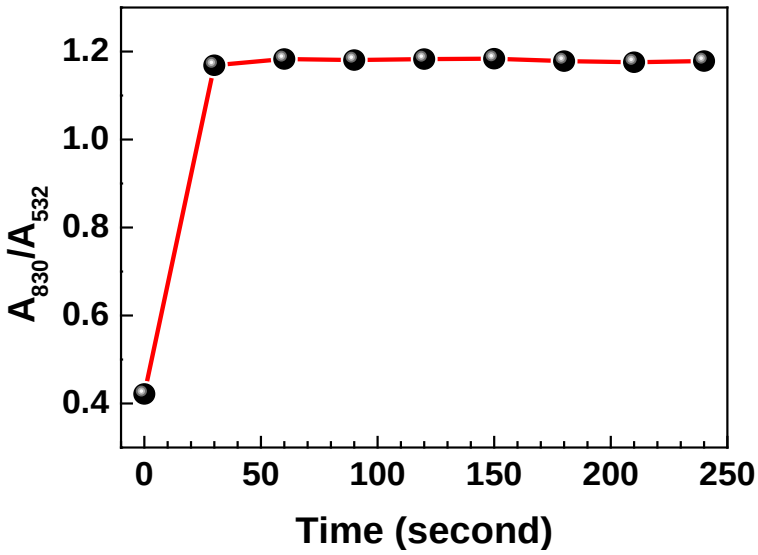

Figure S5. Plot of A_{830}/A_{532} as a function of time to demonstrate the reaction dynamics of cysteine modified Au NPs and TNT.

REFERENCES

S1. Kunz, K. S.; Luebber, R. J. *The Finite Difference Time Domain Method for Electromagnetics*; *CRC press*: *Cleveland*, **1993**.

S2. Johnson, P. B.; Christy, R. W. Optical Constants of the Noble Metals. *Phys. Rev. B* **1972**, 6, 4370-4379.