*Supplementary Files*

# Charge-Transfer Process in Surface-Enhanced Raman Scattering Based on Energy Level Locations of Rare-Earth $Nd^{3+}$-Doped $TiO_2$ Nanoparticles

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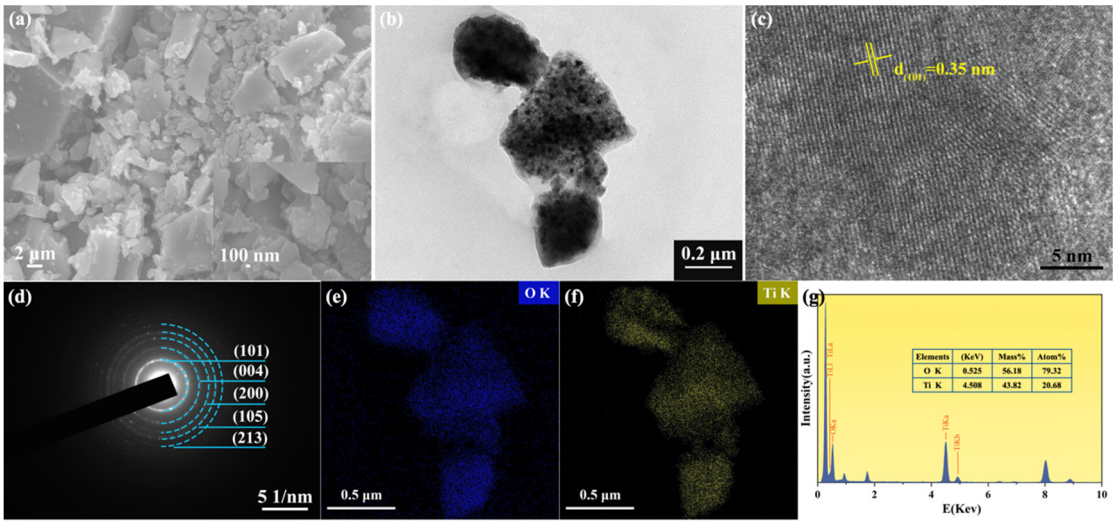


Figure **S1**: Characterization analysis of the $TiO_2$ NPs. (**a**) SEM and (**b**) TEM images; (**c**) HRTEM image showing lattice space; (**d**) SAED pattern mainly showing the (101), (004), (200), (105) ,and (213) crystal faces; the element mapping of (**e**) O, (**f**) Ti, respectively; (**g**) EDS spectrum.

Figure S1 shows the characterization analysis of the $TiO_2$ NPs by SEM and TEM. As shown in Figures S1a and b, it can be seen that the $TiO_2$ NPs are agglomerated in sharp and irregular block shapes. The HRTEM image of $TiO_2$ also shows clear lattice fringes and 0.35 nm interplanar crystal space. These are similar to the Nd-doped samples, indicating that the small amount of doping has little effect on the morphology and crystal structure of the $TiO_2$ NPs. In the SAED pattern (Figure S2d), $TiO_2$ NPs are polycrystalline structures of anatase $TiO_2$ with (101), (004), (200), (105), and (213) concentric diffraction rings, but the diffraction rings of the doped samples are much clearer. The elemental mapping patterns (Figure S2 e and f) and EDS show that the distribution and amount of O and Ti element and unmarked peaks are copper

ions from the copper grid of the sample holder.

**Calculation of enhancement factor (EF)**

To quantitative investigate the enhancement ability, the enhancement factor (EF) for as prepared SERS substrate can be calculated by the following equation:

$$EF = (\frac{I_{SERS}}{I_{Bulk}})(\frac{N_{Bulk}}{N_{SERS}})$$

where $I_{SERS}$ and $I_{Bulk}$ are the Raman intensities of 4-Mpy in the SERS spectra and standard Raman spectra; Where $N_{SERS}$ and $N_{Raman}$ present the numbers of 4-Mpy molecules adsorbed on the SERS substrate and in the bulk condition, respectively.

The ratio of intensities ($I_{SERS}/I_{Bulk}$) can be obtained by 4-Mpy in the SERS spectra and standard Raman spectra (Figure.S2), which is 37.57

The $N_{Bulk}$ is related to the density of the sample ($\rho$ = 1.2 g ·cm$^{-3}$) and the volume of laser irradiation[1]. The volume of laser irradiation can be calculated from 532 laser excitation focus depths (h = 21 μm) and the diameter of laser beam spot (D = 0.72 μm). So, the mass of the 4-Mpy in bulk condition within laser irradiation is 1.03×10$^{-11}$ g. Moreover, the $N_{Bulk}$ can be calculated from the known molar mass of 4-Mpy (79.1 g ·mol$^{-1}$) and Avogadro's constant, which is 7.83×10$^{10}$.

The $N_{SERS}$ can be estimated by concentration and volume of 4-Mpy adsorbed on Nd-$TiO_2$ NPs (10$^{-2}$ M and 10 μL). The amount of molecules is 1×10$^{-7}$ mol and spreads onto a glass slide of 3.14 cm$^2$. The number density of molecules on the surface is 1.91×10$^8$ molecules ·μm$^{-2}$. Thus $N_{SERS}$ = 7.79×10$^7$ on the 0.72 um diameter laser[2]. Therefore, the EF = ($I_{SERS}/I_{bulk}$) × ($N_{Bulk}/N_{SERS}$) =3.79×10$^4$.

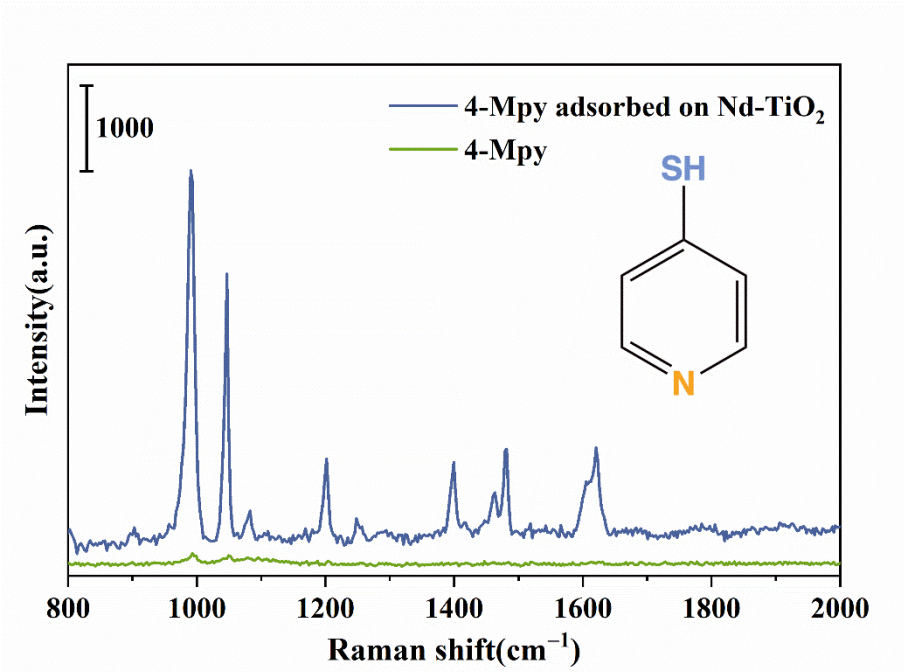


Figure **S2**. SERS spectra of 4-Mpy on Nd-$TiO_2$ NPs substrate (blue line) and in bulk condition (green line).

**References**


1. Li, M.; Gao, Y.; Fan, X.; Wei, Y.; Hao, Q.; Qiu, T. Origin of layer-dependent SERS tunability in 2D transition metal dichalcogenides. *Nanoscale Horizons* **2021**, *6*, 186-191.
2. Park, H.K.; Yoon, J.K.; Kim, K. Novel fabrication of Ag thin film on glass for efficient surface-enhanced Raman scattering. *Langmuir* **2006**, *22*, 1626-1629.