Invisible ink-assisted pattern and written surface enhanced Raman scattering substrates for versatile chem-/bio-sensing platforms

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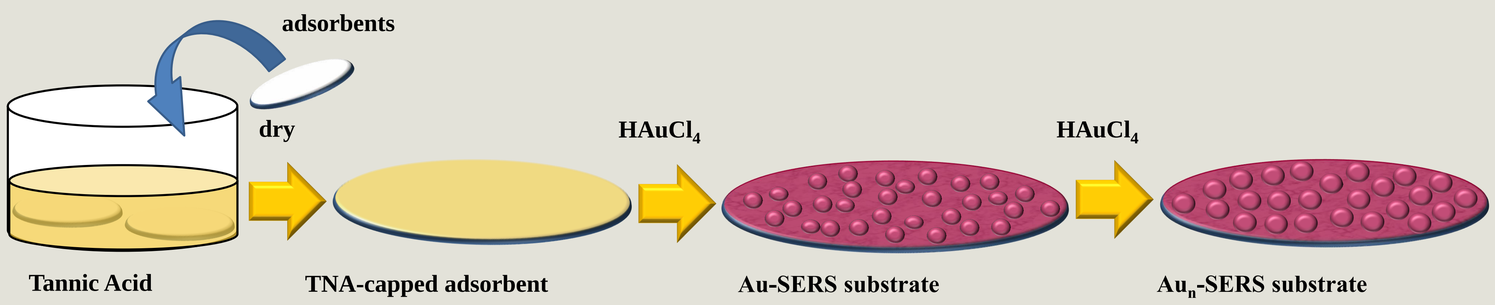
Abstract

In recent years, highly sensitive surface enhanced Raman scattering (SERS) integrated with flexible substrates for labeling-free detection and studying the chemical and biological reactions has drawn more and more attention. In this work, invisible-ink inspired process to fabricate plasmonic Au-based SERS substrates through an on-site redox strategy was developed. The tannic acid (TNA) as green source reductant was capable of sticking in different absorbents or masking of the desirable patterns. Specifically, the surface of the TNA-coated porous absorbent materials could bind gold ions and then denoted electrons due to the polyphenol groups of TNA molecules, leading to assemble aggregation of Au atoms into edged Au nanoparticles. Because of the reaction in the confined area, clustering structure of Au nanoparticles was obtained which were incorporated into the microfiber micro-structures. In the presence of amphiphilic TNA-modified surface properties of hydroxyl/phenol groups and aromatic ring at TNA, this micro-nanostructured SERS substrate exhibited strong SERS enhancement and demonstrated versatile analysis platform by using a single SERS substrate, including: i) chemisorption and physisorption of small molecules at μM-nM concentrations, ii) facile biological detection of the antibiotic/E. coil pharmaceutical, and iii) the accelerated the hydrogenation reaction rate determined by in-situ SERS spectra. Moreover, the strategy based on the TNA invisible ink combined with redox reaction to turn on the crystallization of metal nanoparticles is easy to apply in drawing a beautiful picture and designing the substrate shape as well as approaching a reliably way to synthesize bimetallic Au/Ag SERS substrate, which further promoted the SERS intensity of molecule and pushed the low limit of detection.

Preparation



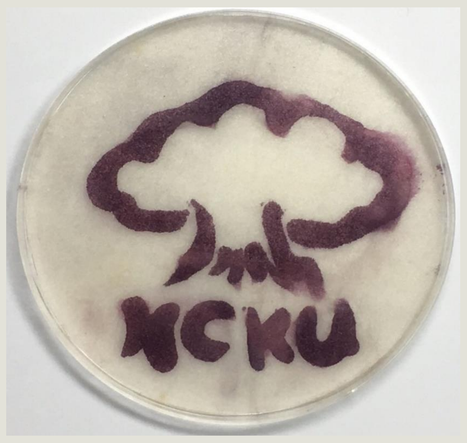


Figure 1: Schematic showing of in-situ formation of Au nanoparticles by soaking of i) the absorbent materials with ii) TNA solution and iii) the subsequent reduction of $HAuCl_4$ solution and the repeated addition of the $HAuCl_4$ solution to prepare Au_n-based SERS substrates

Results and discussion

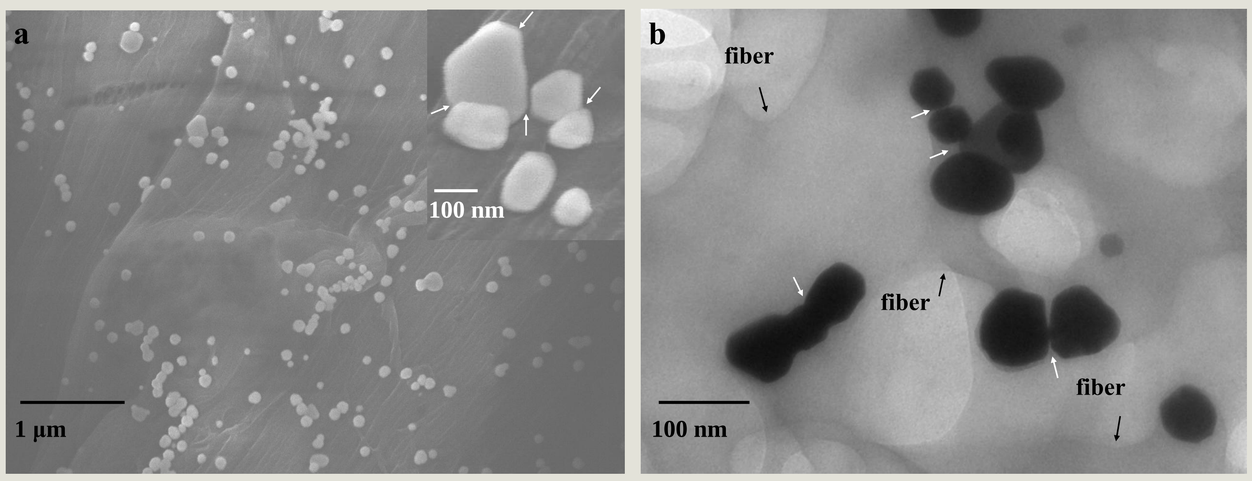


Figure 2: a) SEM image and b) TEM Image of Au_3-SERS substrate.

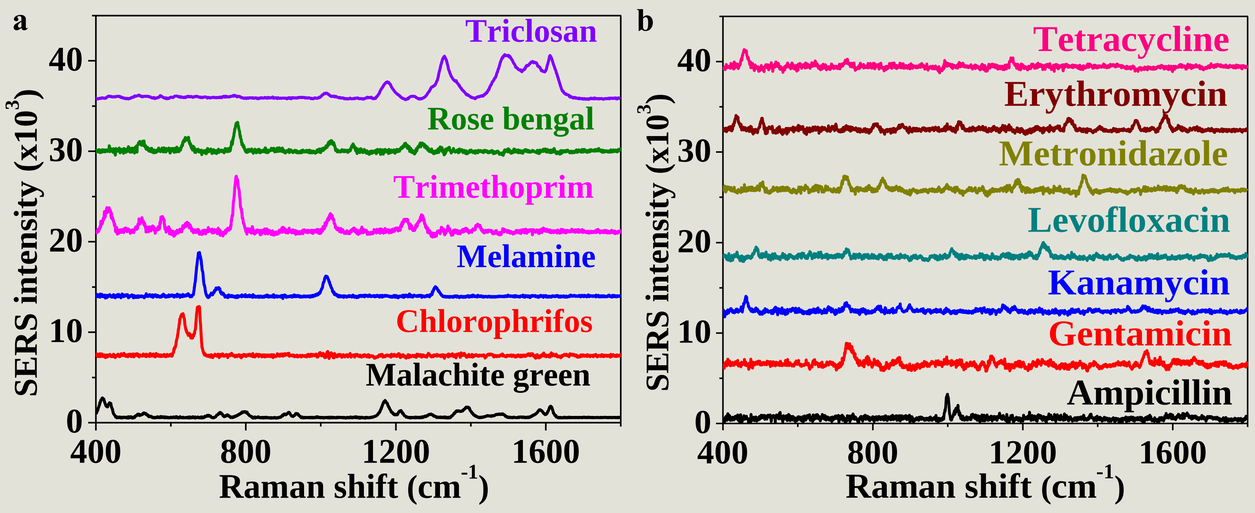
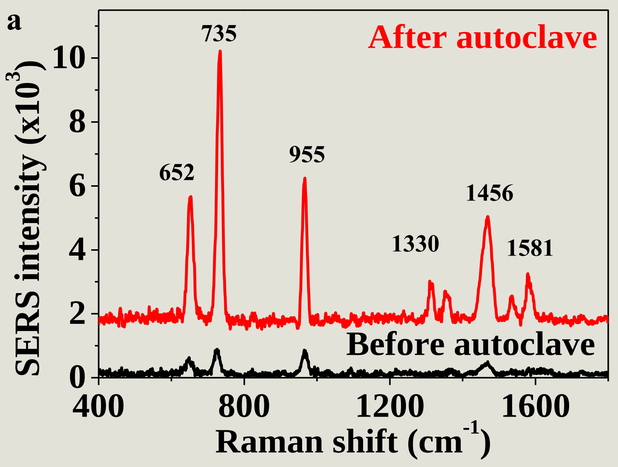


Figure 3: a) SERS measurements of the 0.1 mM of poison molecular with Au_3-SERS substrates. b) SERS measurements of the 100 ppm of antibiotic.



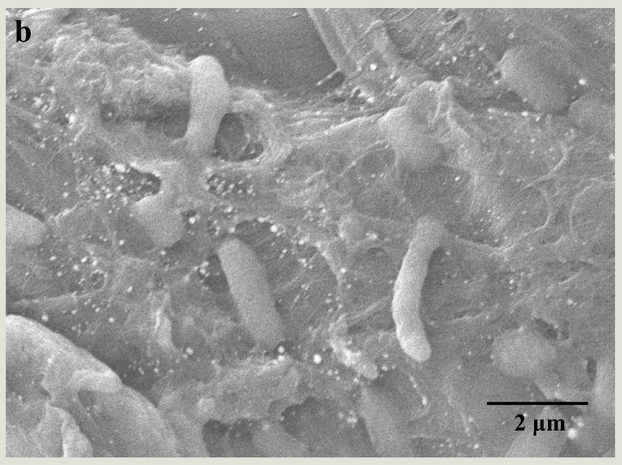
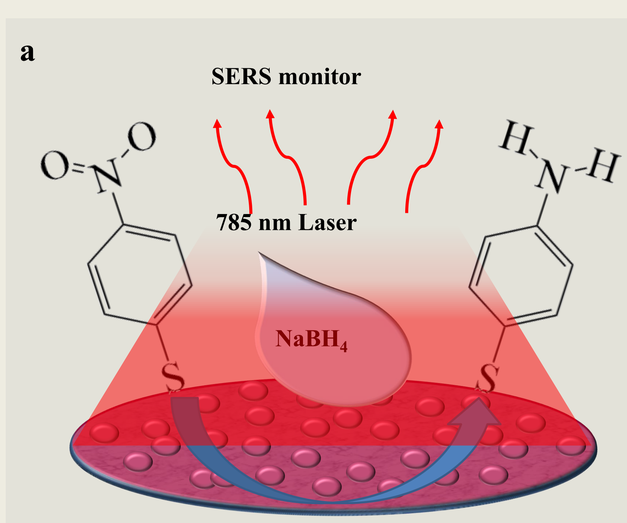
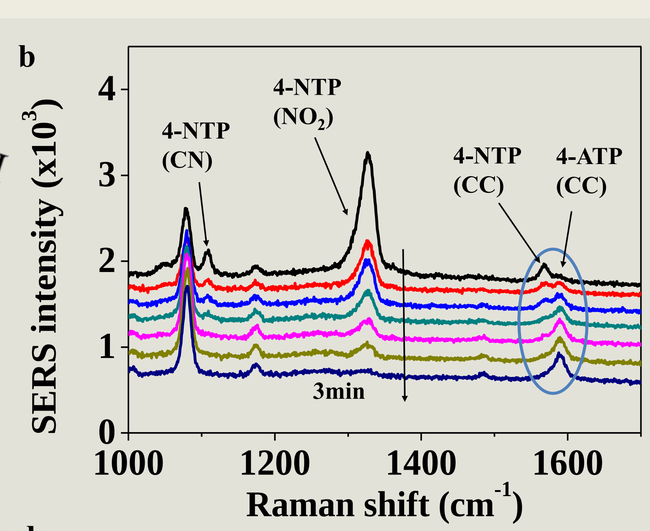
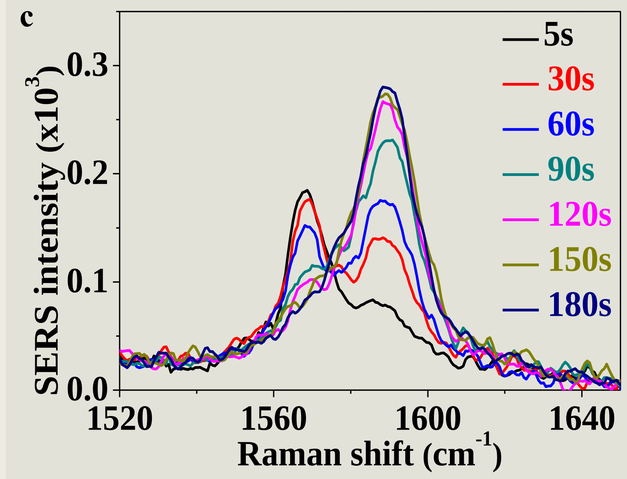


Figure 4: SERS measurements of a) 10^8 CFU/mL O157:H7 before and after autoclaved (160 ^oC, 2hr) to achieve complete killing. b) SEM image of O157:H7 stay on the fiber of Au_3-SERS substrate.







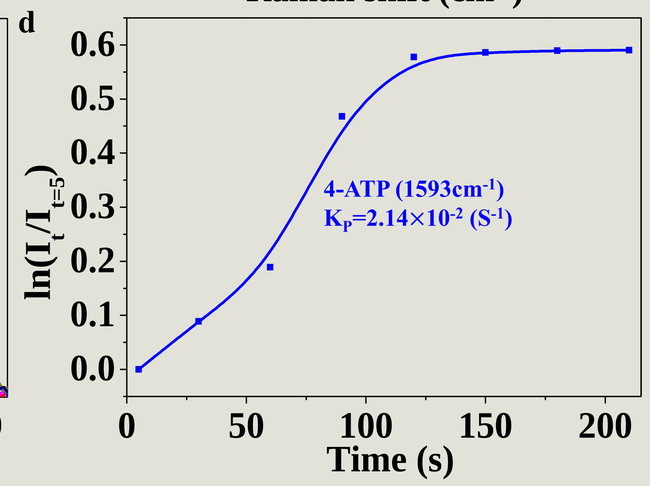


Figure 5: a) Schematic illustration of the SERS monitor for the conversion of 4-NTP to 4-ATP on the surface of Au_3-SERS substrate upon the addition of 10 mM $NaBH_4$. Time-dependent SERS spectra of the conversion from 4-NTP to 4-ATP at b) 1000-1800 cm^{-1} and c) 1520-1640 cm^{-1}. d) the $In(I_{1593(1/cm)}/I_0)$ plot time for the kinetic constant of Au_3-SERS substrate. The fit line from the experimental data of Figure 5c represented a pseudo-first order equation.

Conclusion

In summary, green TNA molecule was used as an invisible ink having demonstrated to approach large-scale, writable, adsorbent material-independent reduction of $HAuCl_4$, allowing to restrictedly formation of Au nanoparticles. The resulting nano-golds and amphiphilic TNA in the filter paper performed intense SERS intensity and reproducible signal in the detection toward label-free analysis of various organic dyes, environmental pollution, food additive, antibiotic, and microbes. It is straightforward to reach the SERS under μM-nM concentration of diversity compounds, and signal generation was minor interference in different water sources. Au_3-based SERS substrate showed the potential way for exploring the metabolism of bacterial cells and microorganism/antibiotics interaction in a control risk of abuse invade our daily. Because of its edge- and clustering-structure of Au nanoparticles, the same SERS substrate showed a heterogeneous catalysis in hydrogenation with a large k_P value of 2.14×10^{-2} s^{-1}. Finally, we readily extend the TNA invisible ink and chemical turn-on reduction synthesis in nano-crystallization strategy to prepare AuAg-based SERS substrate which has successfully pushed the LOD down to sub-nM concentration level.

Acknowledgements

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