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Supporting Information

Article

Ionic Liquid-Modulated Synthesis of Porous Worm-Like Gold with Strong SERS Response and Superior Catalytic Activities

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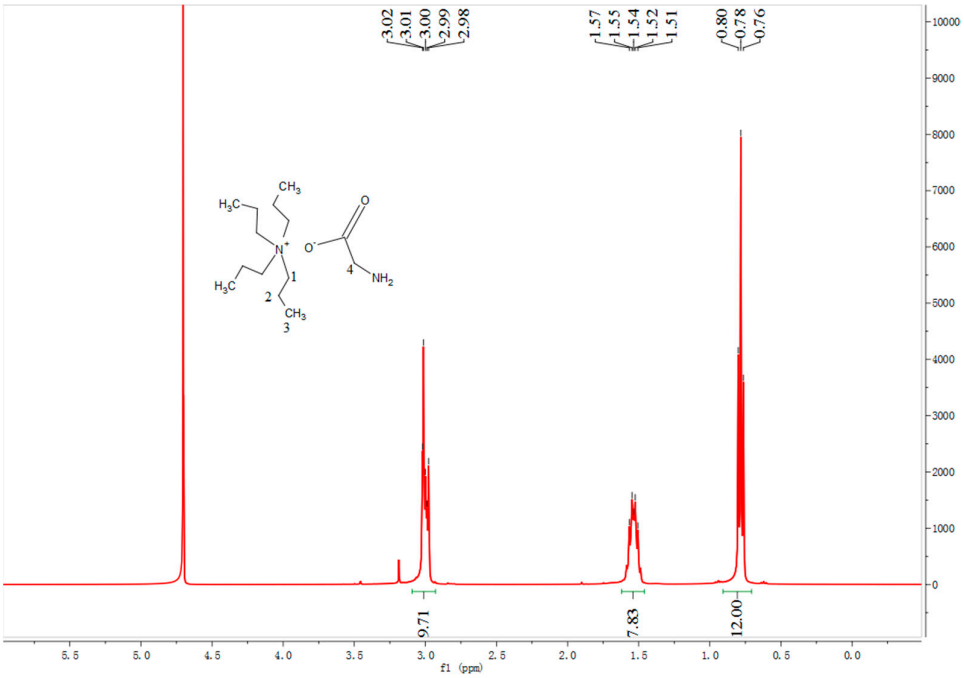

Figure S1. ^{1}H NMR spectra of synthesized ionic liquid [N_{3333}][Gly]. ^{1}H NMR (400 MHz, D_2O) δ 3.09 - 2.93 (m, 10H, H(1) and (4)), 1.62 - 1.46 (m, 8H, H(2)), 0.78 (t, J = 7.3 Hz, 12H, H(3)).

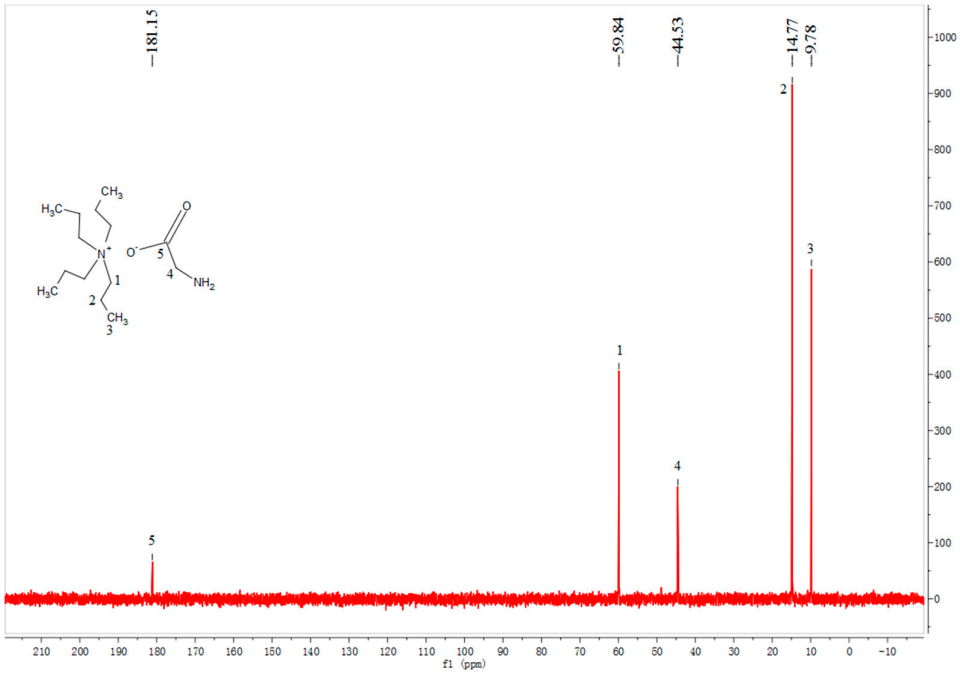

Figure S2. ^{13}C NMR spectra of synthesized ionic liquid [N3333][Gly]. ^{13}C NMR (101 MHz, D_2O) δ 181.15 (s, C(5)), 59.84 (s, C(1)), 44.53 (s, C(4)), 14.77 (s, (2)), 9.78 (s, C(3)).

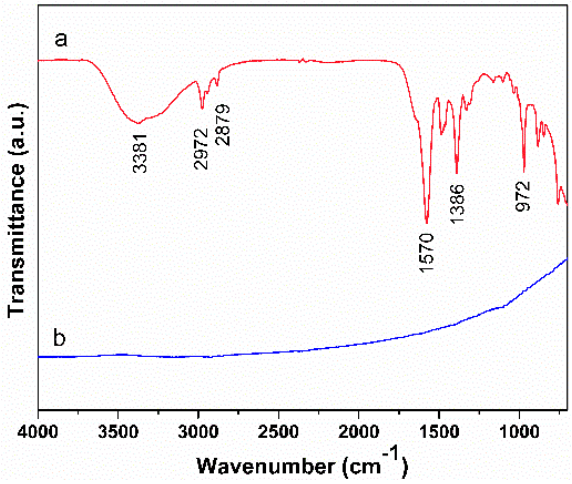

Figure S3. FTIR spectra of (**a**) [N3333][Gly] and (**b**) porous Au worms.

Figure S3 a presents the FTIR spectra of synthesized [N_{3333}][Gly]. The wide peak at 3381 cm^{-1} is attributed to $–NH_2$ asymmetric telescopic vibration. The peaks at 2972 and 2879 cm^{-1} belong to asymmetric and symmetric stretching vibration of $–CH_3$, respectively. The peak at 1570 cm^{-1} is the characteristic absorption of $–COO^-$. The band at 1386 cm^{-1} is assigned to the symmetric variable angle vibration of $–CH_3$. The 972 cm^{-1} is ascribed to the C–N bending vibration in quaternary ammonium ions.

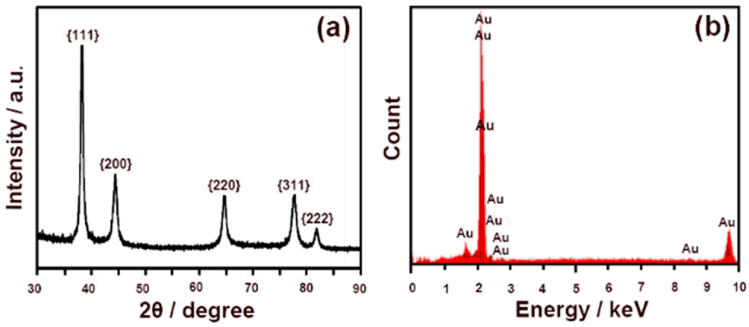

Figure S4. (**a**) XRD pattern and (**b**) EDX spectrum of porous Au worms synthesized in the presence of [N3333][Gly].

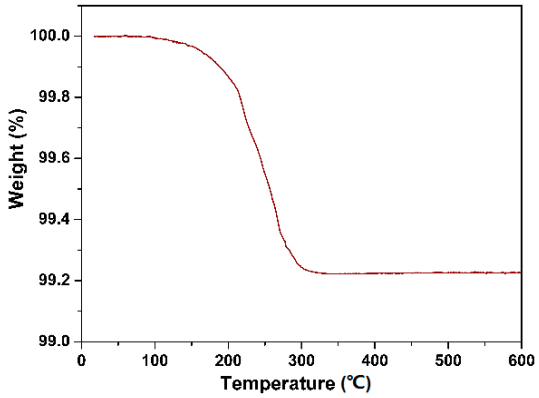

Figure S5. TG curve of porous Au worms.

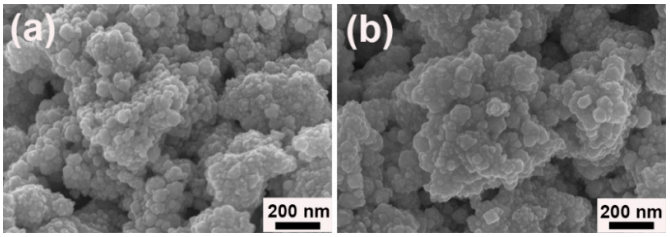

Figure S6. FESEM images of Au samples synthesized with different ascorbic acid concentrations: (**a**) 50 mM, and (**b**) 200 mM.

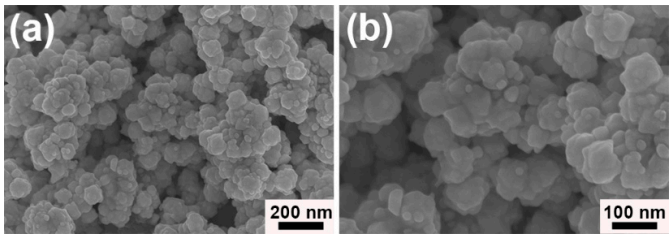

Figure S7. FESEM images of Au samples synthesized in the presence of [N3333][Gly] under vigorous stirring.

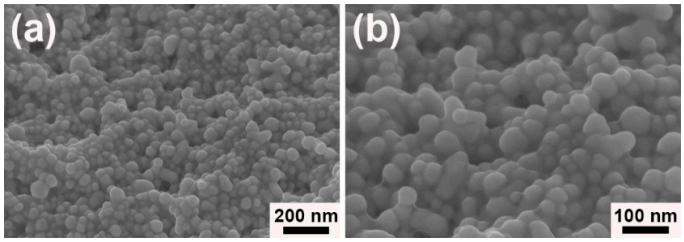

Figure S8. FESEM images of the Au samples synthesized in the absence of [N3333][Gly].

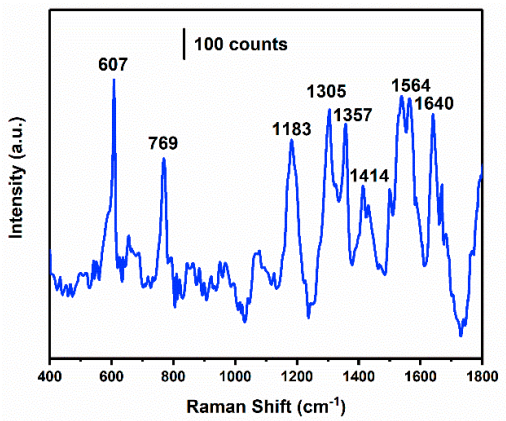

Figure S9. The normal Raman spectrum of pure solid R6G.

The Calculation of SERS Enhancement factor (EF):

The EF was defined as follows [1,2]

$$EF = (I_{SERS}/N_{ads}) / (I_{bulk}/N_{bulk}) \quad \text{(S1)}$$

where I_{SERS} and I_{bulk} denote the Raman intensity of R6G in SERS and normal Raman spectrum, respectively. For the calculation of EF values, the peak intensity at 1358 cm^{-1} was used. N_{ads} and N_{bulk} are the number of R6G molecules adsorbed on the SERS substrates and number of bulk molecules within the SERS detecting spot, respectively.

N_{ads} could be calculated using the following equation [1]:

$$N_{ads} = N_d A_{laser} A_N/\sigma \quad \text{(S2)}$$

where N_d is the number density of porous worm-like Au, A_{laser} is the area of the focal spot of laser, A_N is the footprint area of Au product, and σ is the surface area occupied by an adsorbed R6G molecule on full coverage of Au, which is about 4 nm^2 [1,2]. Due to the complex geometry, it is difficult to calculate the accurate surface area of porous Au worms. It is assumed that porous worm-like Au has a compact flat surface. In addition, the spot diameter of the laser beam is about 1 μm in our experiment. Thus, the total number of N_{ads} within the laser spot was calculated to be about 1.96×10^5. N_{bulk} is the molecule number of the solid R6G in the laser illumination volume. The penetration depth of laser spot was about 2 μm and the solid R6G density was 1.26 g/cm^3 [1]. Then, N_{bulk} of R6G was calculated to be 2.49×10^9. Finally, according to the equation (S1), the EF was calculated to be 3.5×10^6.

References

1. Wang, W.; Han, Y.; Gao, M.; Wang, Y. Facile synthesis of two-dimensional highly branched gold nanostructures in aqueous solutions of cationic gemini surfactant. *CrystEngComm.* **2013**, *15*, 2648–2656.
2. Sun, N.; Yao, K.; Wang, C.; Zhao, C.; Lu, W.; Zhao, S.; Wang, H.; Wang, J. Synthesis of various gold hierarchical architectures assisted by functionalized ionic liquids in aqueous solutions and their efficient SERS responses. *J. Colloid Interface Sci.* **2018**, *531*, 194–203.