

Supporting information

Gold Nanoparticles Prepared by Glycinate Ionic Liquid Assisted Multi-Photon Photoreduction

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1. The ^1H NMR data

The ^1H NMR data of the ionic liquid (IL) (2-hydroxyethyl)trimethylammonium glycinate [HETMA][Gly] was shown as follows: ^1H NMR δ /ppm (400 MHz, D_2O): 3.16 (2H, s, CH_2NH_2), 3.18 (9H, s, $(\text{CH}_3)_3\text{N}$), 3.41 - 3.44 (2H, m, $\text{CH}_2\text{CH}_2\text{N}$), 3.95 - 3.98 (2H, m, CH_2OH).

2. Cyclic voltammetry (CV) spectra

CV scans were recorded to study the reaction of the IL and HAuCl_4 as shown in Fig. S1. The concentration of HAuCl_4 and IL was 0.001 and 0.028 M, respectively. The reduction peak shifted from 0.373 to 0.289 V when HAuCl_4 was added into the aqueous solution of IL. The lower potential shift indicated the generation of complex and it was more difficult to be reduced than that of the pristine aqueous solution of HAuCl_4 . Combined with the results from Fig. 1, it was confirmed that the [Gly]-Au(III) complex were formed.

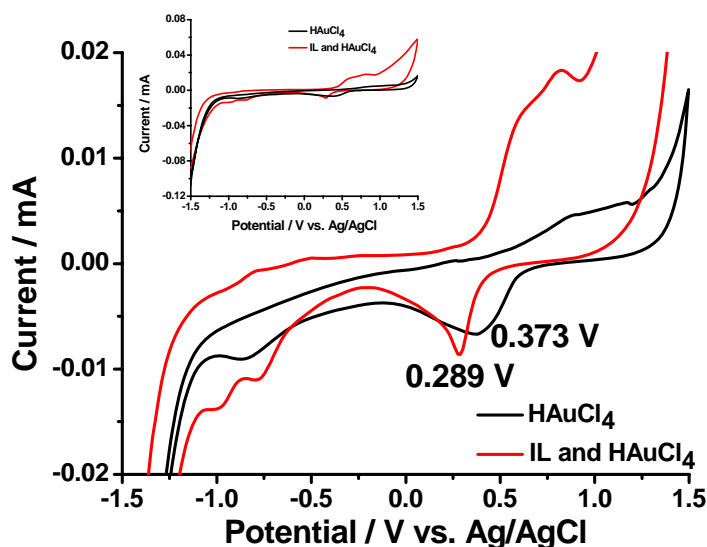


Fig. S1 Magnified CV curves for pristine HAuCl_4 (black) and the solution of HAuCl_4 mixed with IL (IL/ HAuCl_4 = 28) (red), respectively. Inset showed the CV cycles in original range. The solvent used was 0.1 M NaCl aqueous solution. Scan rate: 0.05 V/s.

3. The UV-Vis absorption spectra

We studied the MPR properties of aqueous solution of HAuCl_4 that had the same concentration of 0.02

M to compare with that of the mixed solution of HAuCl_4 and IL. The same experiment process was kept in both cases. The evolution of the UV-Vis absorption spectra during the irradiated (solid line) and non-irradiated (dot lines) processes were shown in Fig. S2. Inset showed the complete absorption of the aqueous solution of HAuCl_4 from 250 to 900 nm with its concentration was 10 times lower than that of the evolution spectra. No surface plasmon resonance peak of AuNPs could be observed even if the sample was irradiated for 10 h, indicating that there was no AuNPs formed during the process without IL.

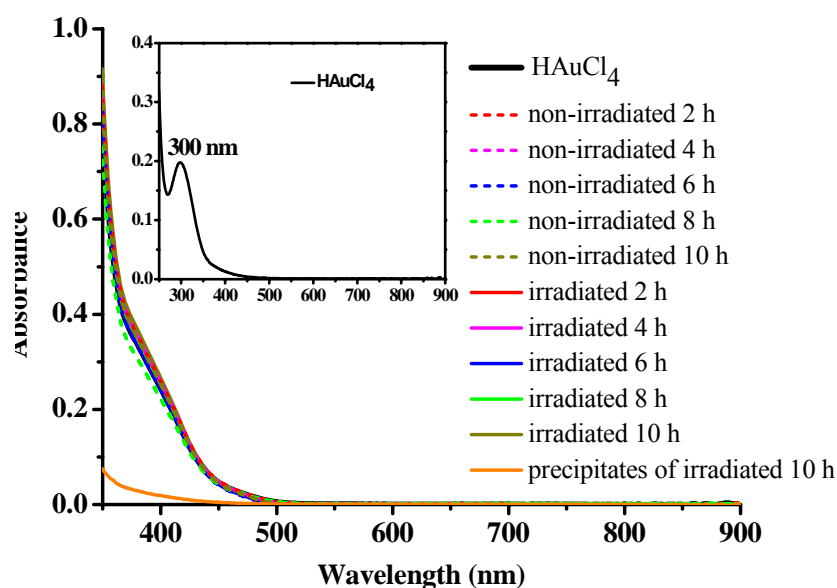


Fig. S2 The evolution of the UV-Vis absorption spectra during the irradiated (solid line) and non-irradiated (dot lines) processes. Inset showed the complete absorption of the aqueous solution of HAuCl_4 from 200 to 900 nm with its concentration was 10 times lower than that of the evolution spectra.

4. The photos for the aqueous solution of HAuCl_4

The kinetic process has also been recorded by taking photos with 2 h interval (Fig. S3). In this Figure, a) – f) corresponded to 0 - 10 h, and g) corresponded to the diluted precipitates of reaction for 10 h. In each photograph, the right solution was the one irradiated by fs laser and the left sample was that stayed in dark for comparison. For both of the two cuvettes, color changes could not be observed in Fig. S3 (g) except the colour of water. All the results demonstrated that it was difficult to reduce the aqueous solution of HAuCl_4 by MPR without [HETMA][Gly]. Therefore, it was accepted that aside from the

role of capping agent, IL also acted as an assistant reducing agent in this study, which was ascribed to the complex effect between Au(III) and [Gly] anion.

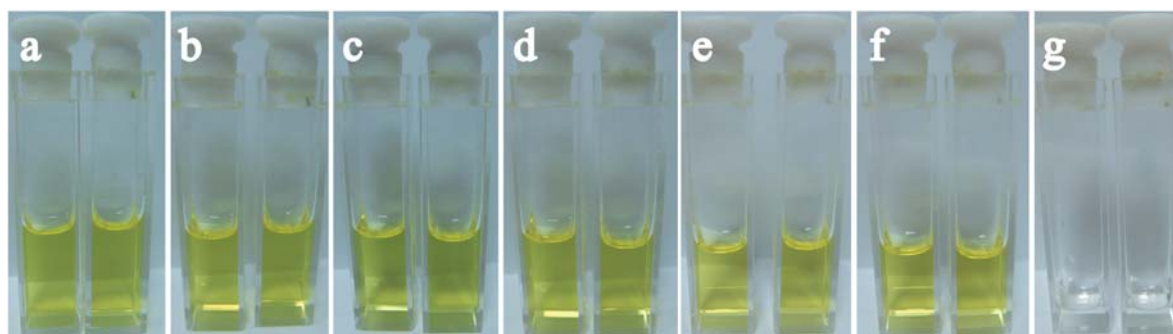


Fig. S3 Evolution of solution color during the reaction processes for the sample of aqueous solution of HAuCl_4 . Photographs were recorded at different reactive time: (a) 0 h, (b) 2 h, (c) 4 h, (d) 6 h, (e) 8 h, (f) 10 h, (g) the diluted precipitates after 10 h. The left and right cuvettes corresponded to the non-irradiated and irradiated solution, respectively.

5. The SAED pattern of the precipitates

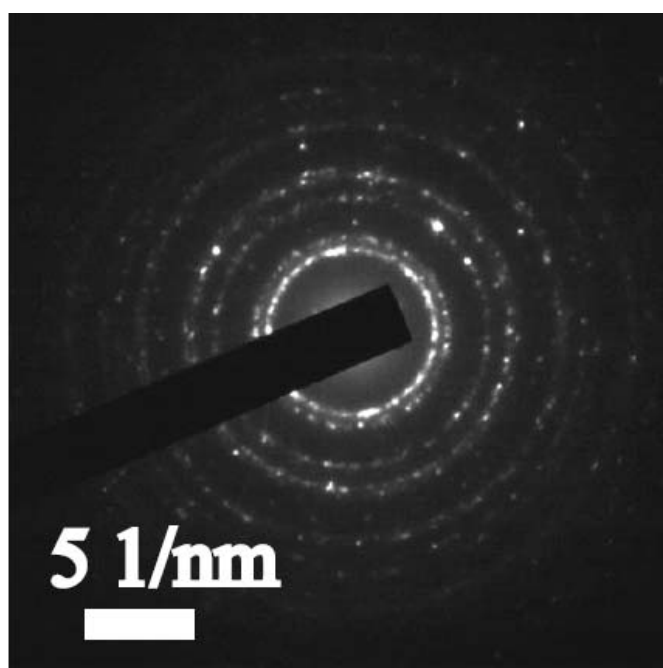


Fig. S4 The SAED pattern of the precipitates of irradiated 10 h.

The SAED pattern shown in Fig. S4 was from the precipitates of AuNPs prepared by irradiating for 10 h, which indicated the gold AuNPs possessed $\{111\}$, $\{200\}$, $\{220\}$ and $\{311\}$ facets.

6. Zeta potential of the AuNPs

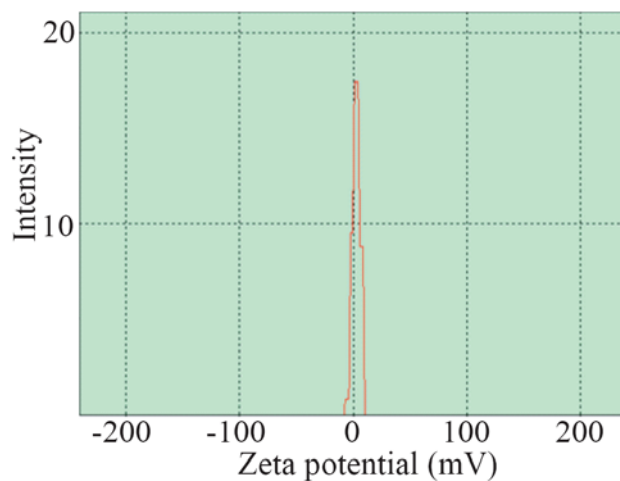


Fig. S5 Zeta potential of the AuNPs obtained after irradiated for 10 h.

For zeta potential analysis, the AuNPs irradiated 10 h were used. The solution of AuNPs was first separated by centrifugation and then followed by washing with ultrapure water. The whole process was repeated 3 times to remove extra ions adsorbed on the surface of the AuNPs. The potential spectrum was shown in Fig. S5. This extremely low value of 2.1 mV suggested weak electrostatic repulsive force between AuNPs, which facilitated their aggregation and contributed the formation of flowerlike AuNPs.