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Synthesis and Characterization of Hybrid Nanocomposites of Gold Nanostars Encapsulated on Graphene Oxide as Active SERS Nanotags

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ABSTRACT

Hybrid nanocomposites of gold nanostars and graphene oxide exhibit intriguing optical and electrical properties derived from the sharp-tip effect of nanostars and the high conductivity of honeycomb structure from C-sp2 hybridization of graphene-based materials. This work presents a facile way to wrap graphene oxide nano-colloids surrounding the as-prepared gold nanostars via the assistance of linker molecules, 4-aminothiophenol, as effective nanotags. Upon tightly binding to the surface of gold nanostars via gold- thiol interactions, 4-aminothiophenol can modify the surface of gold nanostars positively charged originated from amine groups and thus facilitate the self-assembly of negatively charged graphene oxide to wrap around the surface of gold nanostars. The SEM, TEM images and the shift in the Uv-Vis spectra of the resulting gold nanostars- graphene oxide nanocomposites reveal the successful encapsulation. Besides, the enhanced Raman signal of 4-aminothiophenol highlights the potential of the obtained gold nanostars-graphene oxide hybrids as effective nanotags for applications in surface enhanced Raman scattering sensing and bio-imaging.

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1. Introduction

Surface enhanced Raman scattering (SERS) is widely used as a highly sensitive analytical technique for chemical sensing and bio-imaging.[1] – [3] The signal enhancement can be obtained when Raman active reporter molecules are in close contact with the surface of plasmonic materials such as gold or silver nanoparticles via a so-called localized electromagnetic field (EM) enhancement mechanism. The enhanced EM can be achieved by engineering the geometry of plasmonic nanomaterials. Therefore, numerous structures of metal nanoparticles have been developed to date which exhibit intriguing optical and electrical properties.[4] – [6] Among them, branched nanoparticles which are also known as nanostars or nanourchins have attracted tremendous attention due to their huge EM enhancement derived from the sharp-tip effects.[7] – [9]

In addition, recent reports show that the combination of plasmonic nanoparticles and graphene derived materials including graphene oxide (GO) or reduced graphene oxide (rGO) to form hybrid structures not only possess advantages from each material, but also induce exceptional structural and electrochemical properties which are not observed in individual materials.[10] – [12] For example, Lim et al. found that reduced graphene oxide coated gold nanoshell/nanorods produced an enhanced photothermal effect to kill cancer cells more rapidly than that of the non-coated nanoparticles.[11] The local EM was further enhanced by the conjugation of branched gold nanoparticles with metal films or satellite nanoparticles such as small gold/silver nanoparticles.[13] – [15] Besides, the perfect honeycomb structure of graphene derived materials can also facilitate the charge transfer between the Raman reporters and plasmonic nanomaterials and thereby induce the signal enhancement.

Herein, we developed a method to coat GO colloid surrounding gold nanostars (AuNS) with the assistance of linker molecules. The 4-aminothiolphenol (4-ATP) was chosen as linkers due to its small structure which ensure the close contact of GO and the gold surface. In addition, the 4-ATP can form strong interaction with AuNSs via its thio (-SH) group in one hand and the other hand with GO via its positive amine (-NH2) groups, respectively. Furthermore, the 4-ATP is also reported as Raman active reporters, thus highlighting the potential of the hybrids of AuNS-ATP-GO as active SERS tags for applications in sensing, imaging, and photothermal/chemo-therapy.

2. Materials and Methods

2.1. Materials

All chemicals including tetrachloroauric acid trihydrate ($HAuCl_4.3H_2O$), silver nitrate ($AgNO_3$), ascorbic acid ($C_6H_6O_6$), 4-aminothiophenol, and graphene oxide colloid solution (2mg/mL) were purchased from Sigma Aldrich and used of reagent grades without purification.

2.2. Method

All glasswares were washed intensively with freshly prepared aqua regia solution (HCl: HNO_3 = 3:1 v/v) and rinsed thoroughly with milli-Q water before using.

Synthesis of gold nanoparticles (AuNPs) as seeds: AuNPs of abt. 13 nm in diameter were synthesized based on the citrate method. Briefly, 1.520 mL of $HAuCl_4$ (10 mM) was added into an Erlenmeyer flask containing milli-Q water. The solution was vigorously magnetic stirred and quickly heated to boiling. Subsequently, sodium citrate (10 mg/mL) was rapidly added into the solution under vigorous stirring. The color of the solution gradually changed from colorless to deep red in about 30 minutes of stirring as a sign of the formation of AuNPs. After that, the heater was removed and the solution was kept under gentle stirring until it cooled down to room temperature. Afterward, milli-Q water was added to the resulting suspension to adjust the concentration of AuNPs in the solution at 0.125 mM respect to Au content. The obtained nanoparticles were then kept in refrigerator at 4 ºC for further use.

Synthesis of gold nanostars (AuNS) coated 4-aminothiophenol (AuNS-ATP): Briefly, 2700 µL of $HAuCl_4$ (10 mM), 750 µL of $AgNO_3$ (10 mM), 450 µL of HCl (1.0 M), and 1500 µL of AuNPs seeds were added into a beaker containing 45 mL of milli-Q. The mixture was magnetically stirred for 5 min at 700 rpm. Subsequently, 2250 µL of ascorbic acid (10 mg/mL) was rapidly added to the solution under vigorous stirring. The solution was kept stirring for a further 1 min. To stabilize the as-prepared nanostars, 700 µL of 4-aminothiophenol 4-ATP (0.1 M) was added drop-wisely to the above suspension and followed by stirring for another 5 min and finally left undisturbed overnight. The 4-ATP modified gold nanostars were then kept in the fridge for further use.

Wrapping of graphene oxide colloids around 4-ATP modified gold nanostars (AuNS-ATP-GO): Graphene oxide (2 mg/mL) colloids were prepared by sonication for 3h in water prior to use. Briefly, 2 mL of 4-ATP modified gold nanostars were purified by two times of centrifugation at 5000 rpm in 5 min and washed with milli-Q water to remove all excess amounts of unbound 4-ATP before wrapping step. Afterward, 20 µL of well dispersed graphene oxide colloid solution (2 mg/mL) was added to the above nanoparticles suspension. The nanoparticle suspension was then vortexed rapidly for a few seconds and then gently shaken for 2h to allow graphene oxide sheets to wrap around the nanoparticles. The purification step was conducted by 2 times of centrifugation at 5000 rpm in 3 min and washing with milli-Q water to remove all excess amounts of free graphene oxide sheets in the suspension.

2.3. Characterization

The morphology of as-synthesized nanoparticles was characterized by field emission secondary electron microscope (FESEM-6340F) and transmission electron microscope (TEM-JEOL 2010). The extinction spectra of obtained nanoparticles were characterized by UV-Vis-NIR spectrophotometer (Perkin).

3. Results and Discussion

In this report, the AuNS were synthesized via a seed mediated growth approach in which gold nanoparticles (AuNPs) were prepared by citrate method and serve as seeds to facilitate the growth of AuNS. The TEM image of the AuNPs seeds with spherical shape and uniform size distribution of abt. 13 nm in diameter is shown in Figure 1. Since the AuNS was produced without addition of any surfactants or polymers in the growth solution, therefore, 4-ATP molecules not only take the role of a linker to facilitate the GO encapsulation process but also help protect the freshly-prepared AuNS from aggregation. Figure 2 displays the SEM and TEM images of AuNS after being stabilized by 4-ATP molecules. The highly dispersed AuNS exhibits a number of sharp tips extruding from a solid core of abt. 50 nm in diameter.

After incubation with GO colloids for 2 hours, the GO shells of abt. 1~5 nm in thickness are observed around the 4-ATP modified AuNS, indicating the successful encapsulation of GO around the surface of AuNS, as shown in Figure 3.

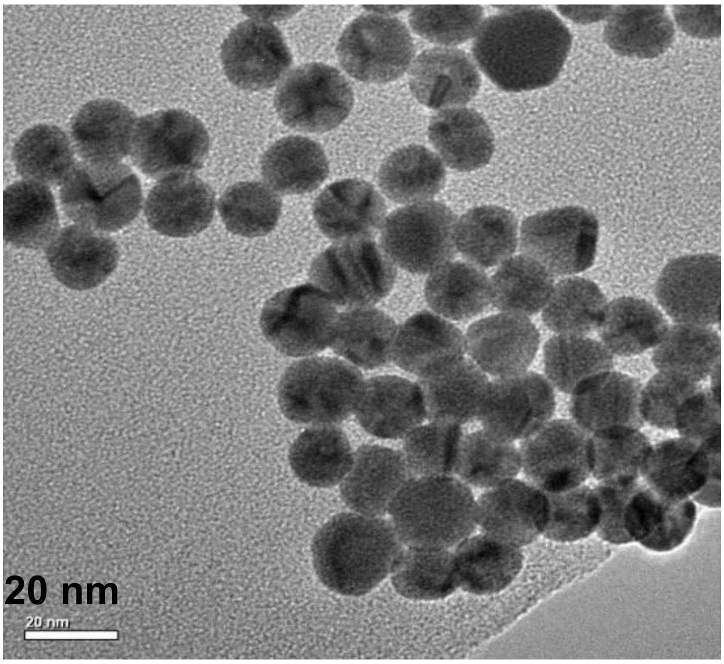

Figure 1. *TEM image of as-synthesized AuNPs.*

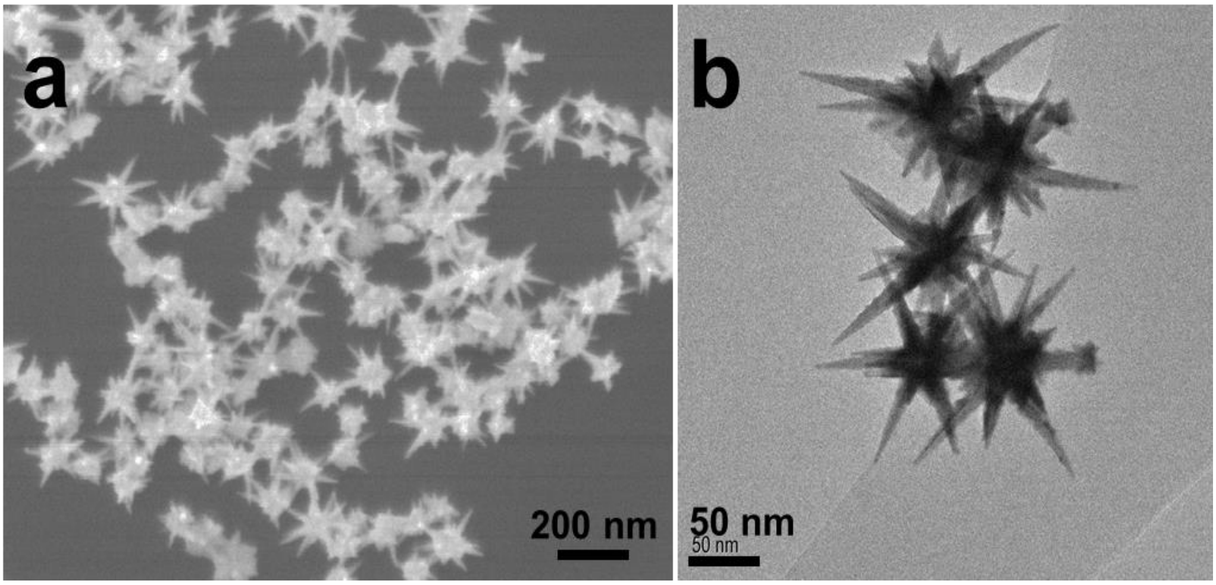

Figure 2. *(a) SEM and (b) TEM image of 4-ATP modified gold nanostars.*

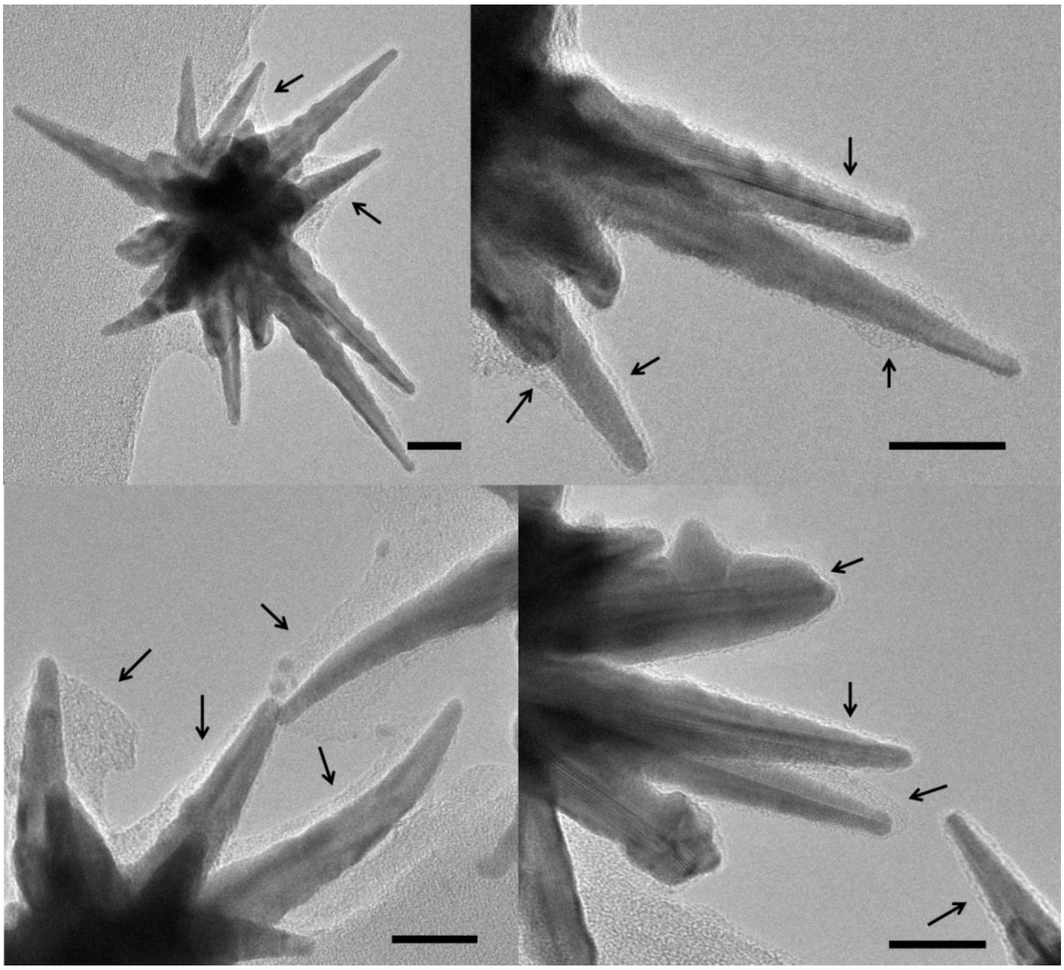

Figure 3. *TEM images of AuNS-ATP-GO nanoparticles. The black arrows show the graphene oxide shells wrapped around the nanoparticles. All scale bars are 20 nm.*

The extinction spectra of 4-ATP modified AuNS before and after incubation with GO colloids are also exhibited in Figure 4. The extinction spectrum of the AuNS shifts to the visible-NIR region which is attributed to their branched structures. Notably, the extinction spectrum of the AuNS-ATP-GO nanoparticles reveals a blue-shift of abt. 1 nm with a stronger background signal compared to that of the 4-ATP modified AuNS. The shift in the LSPR spectra is attributed to the sensitivity to the change in the refractive index of plasmonic nanomaterials.[16] Besides, the wrapping of GO around the tips of AuNS also results in a reduction in the sharpness of these tips and thus leading to a blue shift in the resulting LSPR spectra.[1], [7], [17] This result again demonstrates the successful wrapping of GO colloids surrounding the surface of AuNS.

In fact, the low molecular weight combined with the strong interaction of Au and thiol groups enables the rapid self-assembly of 4-ATP molecules onto the surface of the as-synthesized AuNS. Besides, the exposure of amine –NH2 groups at the other end of 4-ATP molecules can render the surface of AuNS positively charged. Therefore, it allows negatively charged GO to wrap around the surface of 4-ATP modified AuNS due to the attractive electrostatic force.[18] In addition, the π-π interactions from the phenol rings in 4-ATP and the honeycomb structure of GO can also assist the facile adsorption of GO colloids surrounding AuNS.

The 4-ATP is widely used as an active Raman reporter. Our preliminary SERS spectrum of the AuNS-ATP-GO displayed distinct peaks of 4-ATP, as provided in Figure 5. The enhanced SERS signal demonstrates the potential applications of the AuNS-ATP-GO as active Raman nanotags.[19] – [20]

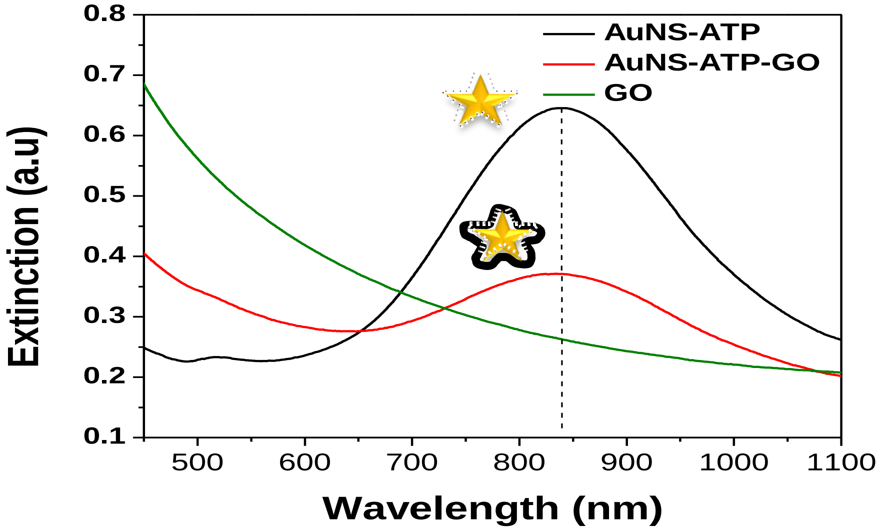

Figure 4. *Extinction spectra of GO, 4—ATP modified AuNS (AuNS-ATP), and AuNS-ATP-GO nanocomposites.*

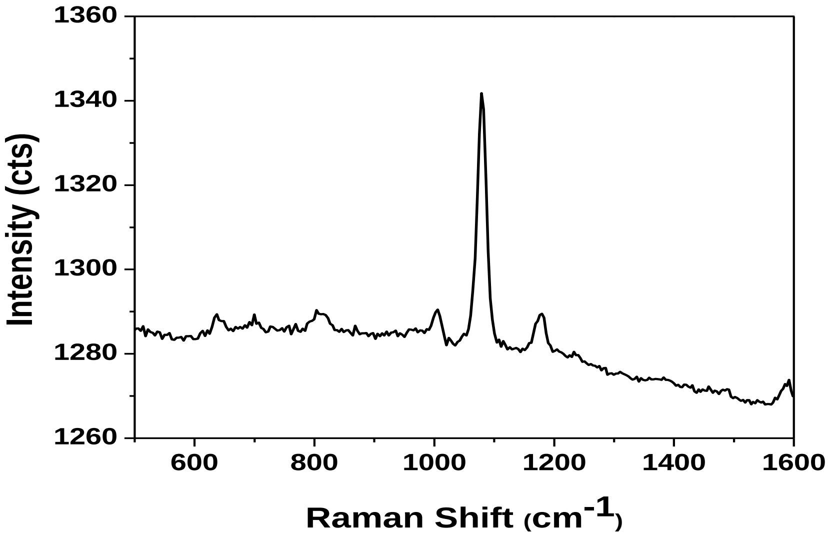

Figure 5. *Raman spectrum of 4-aminothiophenol modified gold nanostars (AuNS-ATP). The spectrum was recorded at the integration time 0.5s, the accumulation time 20, and the laser power 60 mW.*

4. Conclusions

In this work, the hybrid nanocomposites of AuNS and GO were successfully prepared with the assistance of linker molecules, 4-ATP. The AuNS with numerous sharp tips extending from the surface of spherical core nanoparticles and the absorption spectra in the visible region were prepared based on a seed mediated growth approach. The 4-ATP molecules can rapidly self-assembled on the surface of the as-synthesized AuNS via the strong interaction of gold –thiol groups. The exposure of amine groups from the other ends of 4-ATP allows the AuNS to be positively charged and thereby facilitating the wrapping of negatively charged GO surrounding. Besides, the π-π interactions originating from the phenol rings in 4-ATP and GO can also promote the adsorption of GO on the AuNS surface. Furthermore, the enhanced Raman signals of 4-ATP suggest the potential of the AuNS-

ATP-GO hybrids to work as effective SERS nanotags in immunoassay sensing and imaging applications.

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