Real-time size tuning and measuring of silver nanoparticles by cyclic voltammetry and Raman spectroscopy

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ABSTRACT

Noble metal nanoparticles (NM-NPs) have drawn attentions due to their remarkable wide spectrum of applications such as electrocatalysis, energy conversion, surface-enhanced Raman spectroscopy (SERS) and sensing. However, it is challenging to monitor and control the growth of these nanoparticles simultaneously. Here, using silver nanoparticles (AgNPs) as a demonstration, we report a scheme to tune and measure their size and spatial distribution in real-time by supporting them on monolayer graphene through simple cyclic voltammetry (CV) and by Raman scattering measurement. This is accomplished through an accelerated Ostwald ripening process, that takes advantage of the electronic conductivity of graphene, where the size tuning extent is determined by the number of voltammetry cycles. And size measuring is conducted by Raman spectroscopy, exploiting the linear dependent relation between particle size and the width of the Raman G-peak. The presented new strategy potentially can be extended to other metal nanoparticle systems, thus providing an effective solution to a long-standing challenge in nanoscience.

1. Introduction

NM-NPs and NM-NPs-modified electrodes are widely used in catalytic and electro-optic applications. Numerous reported results have confirmed that sizes, shapes, spatial distribution and composition of NM-NPs are essential parameters to realize specific applications [1]. However, it has been a long-standing problem to tune and monitor their sizes simultaneously [2]. On one hand, previous studies have shown that the size of NM-NPs is Ostwald cycling dependent, whose growth is mediated by Ostwald ripening [3]. Although this is a slow process, if it could be accelerated it would be ideal for size tuning due to its simplicity. On the other hand, Raman spectroscopy is sensitive to graphene-nanoparticle interaction [4]. Therefore, it is natural to explore a possible scheme using graphene as substrate to support AgNPs for accelerated Ostwald-ripening to tune the particles, while employing Raman measurements to gauge their size in real time.

Presented here, the AgNPs on graphene undergo iterative oxidation–reduction cycles in an alkaline solution, correspondingly tuning their size and density with the number of applied cycles. Meanwhile, Raman spectroscopy measurements were carried out on the AgNPs-graphene which showed a monotonic change of Raman G-peak width with their sizes and densities. An empirical equation is constructed to quantify the size of AgNPs on graphene through the Raman G-peak width. To the best of our knowledge, this is the first time Raman spectroscopy has been employed to gauge the size of the nanoparticles synthesized on a substrate [5,6]. We believe this provides an avenue to in-situ monitor, precisely control and measure particle sizes at the nanoscale, which is clean, low cost and can be extended to other systems.

2. Material and methods

Monolayer graphene was grown on a copper foil and subsequently transferred to ITO (Indium-Tin-Oxide coated glass plate). 5 nm thick Ag layer was deposited on graphene using e-beam evaporation. AgNPs were formed by annealing at 300 °C for 45 mins with the hydrogen (H\textsubscript{2})/argon (Ar) (10/90 sccm) and then were left to cool down to room temperature (see Fig. S1a). The characterization and monitoring of nanoparticles were conducted through a potentiostat and homemade Raman spectrometer (see supplementary information for details).

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3. Results and discussion

An atomic force microscope (AFM) image of the initial status of AgNPs on graphene (AgNPs/Gr) is shown in Fig. S1 b. It demonstrates uniformly dispersed AgNPs on the graphene surface with heights in the range of 20–30 nm. The X-ray photoelectron spectroscopy (XPS) of AgNPs/Gr is shown in Fig. S1 c indicates the Ag\(^0\) chemical state of AgNPs [7]. The electrochemical characterization of AgNPs/Gr was performed by three-electrode system CV up to 50 cycles in 0.1 M NaOH as shown in Fig. 1a. As discussed in previous studies, the silver and silver oxide particles alternatively form on the electrode surface due to the electro-chemically reversible kinetics [7]. The voltammetry curves of AgNPs/Gr display peak current changes and potential shifts (Fig. 1a inset) in both oxidation and reduction processes. This reflects the size changes of AgNPs with the number of cycles [8].

Further, the scanning electron microscope (SEM) images show the evolution of size and density of AgNPs/Gr with increasing number of potential cycles (Fig. 1b-j). The average particle sizes were extracted...
from the images with statistical analysis and are shown in Fig. 11, which indicates the monotonic size increase from 25 nm to 400 nm in 50 potential cycles. Meanwhile, the particle density decreases sharply during the first few cycles, then descends gradually. Fig. 1k shows the AgNPs on ITO and on graphene after same potential cycles, the boundary is clearly visible. It is noticeable that both the size and density distribution of AgNPs stay almost the same on ITO glass compared with the ones on graphene. This highlights the essential role of graphene in tuning the size of nanoparticles. As a tentative explanation, the monolayer graphene creates an ideal electron transfer channel [9] compared to ITO, which dramatically accelerates the Ostwald ripening process.

To further confirm the tuning mechanism, EC-AFM was employed to investigate the potential cycles-dependent coarsening of the graphene supported AgNPs (schematic illustration in Fig. 2a). Fig. 2b-j show topographical images with corresponding number of cycles. After potential cycling, the smaller sized nanoparticles rearrange and shrink, while the larger ones grow with the price paid by the losses of smaller ones. This can be catalogued as Ostwald ripening [3], a schematic mechanism is shown in Fig. 2k. Small-sized nanoparticle has a higher free energy due to the surface curvature [10]. Since the difference in surface energy of nanoparticles, silver ions move from small-sized nanoparticles with high energy through the electrolyte, and electrons are transferred through the conducting substrate to reach electrical equilibrium [3]. When performing cyclic scanning, it promotes the formation of silver ions and the re-deposition onto the large-sized nanoparticles [7]. As the total amount of silver in the system doesn’t change, small particles aggregated into larger nanoparticle results in decreases of particle density. A typical nanoparticle coarsening usually takes from hours to days [11]. However, taking advantage of the graphene-formed superior conductive channel, potential cycling dramatically accelerates the Ostwald ripening, which makes possible AgNPs size tuning in a few minutes.

We suggest that this accelerated Ostwald ripening strategy may be exploited in other graphene-nanoparticle materials. Since the excellent electrical conductivity of graphene provides an ideal electrochemical ripening environment and could be used for tuning of the morphology of loaded nanoparticles for various applications.

Fig. 3a shows the Raman spectra of AgNPs on monolayer graphene with different number of potential cycles. We focus on the behavior of the Raman G-peak. AgNPs with different sizes give different extent of Raman enhancement. The irregular shape of AgNPs leads to the large Raman enhancement due to the existence of coupled resonance hot spots (see Fig. S6). The broadening of the Raman G-peak can be attributed to the interaction between AgNPs and graphene, which induces a change in the graphene electronic structure [12]. One possible mechanism is the nanoparticle produced localized stress, as some kind of defect compare to the pristine graphene, which in turn leads to the change of G peak [13]. Because of the quantum confinement effect, $\Gamma_G$ increases with increasing defect density [14]. Experimentally, the broadening of $\Gamma_G$ with increasing roughness of the contacted metal has also been reported [15], which explains the sensitive response of $\Gamma_G$ to the interface metal nanostructure.

The relationship between $\Gamma_G$ and the average diameter of the AgNPs is linear as derived from careful data fitting as shown in Fig. 3b and is represented as the following equation:

$$\text{Diameter}(\Gamma_G) = -21.23\Gamma_G + 1071.87$$

The extrapolation of the function to $d = 0$ intercepts $\Gamma_G = 50.49$, which is close to the value measured from monolayer graphene with initial silver film deposition (as shown in Fig. S7). This indicates that this relation can be safely used for diameter quantification from 30 nm to 400 nm. The particle density is inversely related to their diameter and it can be estimated from the value of $\Gamma_G$ according to the equation:

$$\text{density}(\Gamma_G) = \frac{33.53}{50.27 - \Gamma_G}$$

Again, as we expected, this provides a new strategy for easy size quantification in the nanoscale.

4. Conclusions

In summary, we developed a novel method for effectively tuning the size and spatial distribution of AgNPs on graphene in real time. The use of monolayer graphene as substrate is the key to the success of this method. It not only makes possible to use Raman spectroscopy to gauge the size of the nanoparticles, being totally independent of models, through the scaling of its interaction with the nanoparticles, but also realized the fast tuning of particles by accelerated Ostwald ripening process due to its extraordinary electronic conductivity. The linear relation of nanoparticle size and width of the Raman G-peak, together with the simple correlation between growth and number of voltammetry cycles make this an attractive method to tune the nanoparticle size. From the success shown with AgNPs, we can confidently expect this method to be extended to other NM-NPs.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Author contributions

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Appendix A. Supplementary data

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