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Assembly of Aggregated Colloidal Gold Nanoparticles on Gold Electrodes by In Situ Produced H^+ Ions for SERS Substrates

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We report here a novel method on the assembly of gold nanoparticles (NPs) at the gold electrode surface, which was induced by in situ produced H^+ ions at the surface though the electrooxidation of hydroquinone (QH_2). In situ Raman spectroscopy was employed to monitor the assembly by detecting the signal of adsorbed QH_2. Electrooxidation of other molecules like ascorbic acid (VC) can also be utilized to the assembly of gold NPs at the electrode surface. Surface morphology of the aggregated gold NPs has been characterized by scanning electron microscopy (SEM). The assembled film of aggregated gold NPs can serve as an excellent substrate for surface-enhanced Raman scattering (SERS) using pyridine (Py) or melamine as the probe molecule. As a preliminary application of this strategy, we also assembled films of aggregated colloidal Pt NPs at the gold electrode surface by the electrooxidation of VC.

Keywords: Assembly, gold colloid, aggregation, nanoparticle, hydroquinone, ascorbic acid, SERS

1. INTRODUCTION

Self-assembly of nanoparticles (NPs) provides an interesting route to the preparation of nanostructured thin films with broad applications in biosensors [1-2], optics [3], catalysis [4-6], electronics [7-8], SERS [9], etc. Gold NPs are the building blocks mostly used due to their stable chemical property, good catalytic activity and prominent localized surface plasmonic resonance [10-11]. To date, various methods on the assembly of NPs have been developed such as evaporation [12-16], Langmuir-Blodgett (LB) technique [17], electrophoretic deposition (EPD) [18-19], Layer-by-

Layer (LBL) assembly technique [1, 20], and spontaneous assembly at water-air [21] and water-oil [22] interfaces.

In this paper, a novel electrochemical strategy is proposed to assemble colloidal gold NPs at the gold electrode surface by in situ produced H^+ ions. It is well known that the colloidal gold NPs can be easily prepared by the reduction of gold salts with citrate. The excess citrate can also act as a stabilizer to protect the colloid. Although the prepared gold colloid is very stable for a long period of time due to the electrostatic repulse of the negatively charged NPs, it is very sensitive to changes in pH and in ionic strength [23]. We demonstrate that the colloidal gold NPs could aggregate into a compact film at the electrode surface by in situ produced H^+ ions utilizing the electrooxidation of hydroquinone or ascorbic acid. The assembly principle of colloidal gold NPs, the optimum operation, and the application as SERS substrates under electrochemical conditions are all presented here in detail.

2. EXPERIMENTAL PART

Reagents used were of analytical grade quality including $HAuCl_4{\cdot}4H_2O$, $H_2PtCl_6{\cdot}6H_2O$, trisodium citrate, ascorbic acid (VC), pyridine (Py) and melamine from Sinopharm Chemical Reagent Co., Ltd., as well as hydroquinone (QH_2) from Alfa Aesar. All solutions were freshly prepared with ultrapure water from a water purification system (Millipore Corp., USA).

Gold colloids were synthesized by a known citrate-reduction procedure [24] and used directly for the assembly. Briefly, 100 ml of a 1.0 mM aqueous $HAuCl_4{\cdot}4H_2O$ solution was added into 100 ml of water, which was then boiled. Then 10 ml of 1 wt.% sodium citrate was added and boiled for 20 min. The color of the solution changed from light yellow to purple and finally to deep red. The gold colloid was naturally cooled to room temperature with volume of 200 ml and kept in a refrigerator at 4 °C for later use. Pt NPs were prepared by the reduction of $H_2PtCl_6{\cdot}6H_2O$ aqueous solution with sodium citrate according to a previous report [25]. Briefly, 1 ml of 1 wt.% H_2PtCl_6 aqueous solution was added into 100 ml of water and the solution was heated to boil. Then, 3 ml of 1 wt.% sodium citrate aqueous solution was added rapidly, and the mixture was kept boiling ca. 60 min with a final volume of 50 ml. The Pt sol looked deep brownish black and was kept in the refrigerator at 4 °C for later use after cool.

Electrochemical experiments were carried out with a CHI 660C electrochemical workstation (Chenhua Instruments, Shanghai, China). A self-designed spectroscopic cell was used, which was made from Teflon with a quartz window. A pure gold disk (1 mm diameter), a platinum wire in ring (12 cm at length and 1 mm in diameter) were employed as the working and counter electrode, respectively. A $Pt_{80}Ir_{20}$ (wt. %) wire (0.1 mm diameter) or a saturated mercurous sulfate electrode (SMSE) electrode was used as the reference electrode. Prior to use, the working electrode was successively polished with 1200 grit carbimet paper and alumina powder down to 0.05 μm, and then ultrasonically cleaned with ultrapure water. Typically, the assembly of colloidal NPs was performed as follows: putting the polished gold electrode in 15 ml of Au or Pt colloid containing 0.06 M QH_2 or 0.12 M VC, and applying a constant potential of 1.2 V versus the Pt-Ir wire for 50 s to produce H^+ in situ at the surface via the oxidation of QH_2 or VC. The potential step was repeated up to 10 times to obtain a compact film of colloidal NPs. The assembled film was cleaned with ultrapure water before further use. For comparison, the potential step was also carried out in the absence of colloids or QH_2.

The UV-Vis spectrum and size of the Au colloid were characterized with a Thermo Nicolet Evolution 500 UV-vis spectrophotometer and a transmission electron microscopy (TEM) (JEOL-1230), respectively. The morphology of aggregated gold NPs was characterized by a Hitachi S-4800 field-emission scanning electron microscopy (SEM) with an electron beam voltage of 5 kV.

SERS spectra were measured with a Renishaw RM 1000 model confocal microscopy Raman spectrometer. The excitation laser was 785 nm with 5.5 mW, 2.0 mW, or 0.33 mW power at the sample. A 50× long-working-length objective was used and the collection time was 10 s.

3. RESULTS AND DISCUSSION

The UV-vis spectrum of gold NPs in Fig. 1a shows an absorption band centered at 523 nm, and the diameter of gold NPs was estimated around 20 nm with the equation $\lambda = 0.4271\ D + 514.5$ (D refers to the diameter of gold NPs) [1], consistent with the TEM result in Fig. 1b.

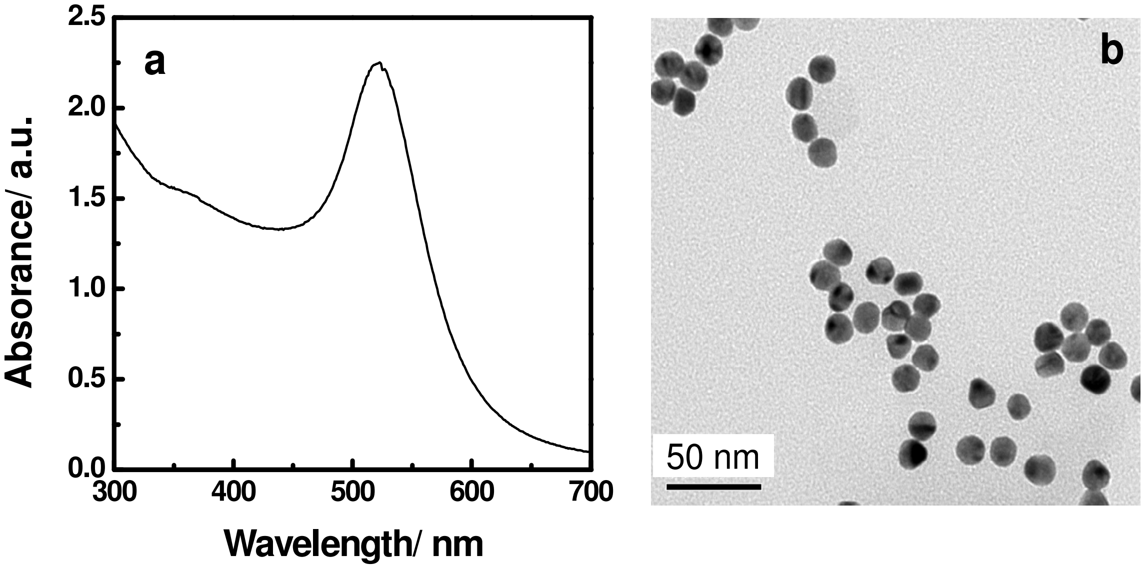


Figure 1. (a) A typical UV-vis absorbance spectrum and (b) TEM image of the prepared gold colloid.

Fig.2. shows the linear sweep voltammograms of the polished Au electrode in the gold colloid with (the solid line) or without (the dished line) QH_2, and the current-time transient at 1.2 V versus the Pt-Ir wire (the red dash-dotted line) for the polished Au electrode in the gold colloid containing QH_2. Apparently, there is a large oxidation current peak around 1.2 V in the presence of QH_2. The oxidative current decreases with time (the red line) at 1.2 V due to the depletion of QH_2 near the surface.

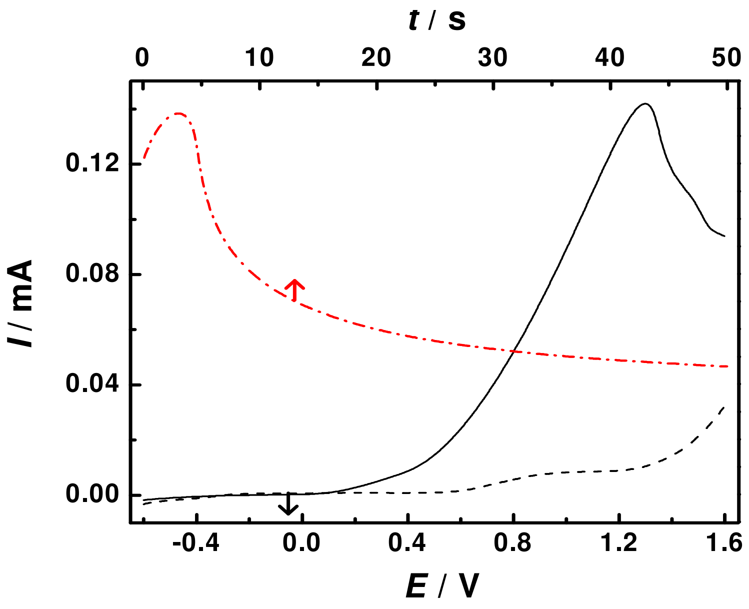
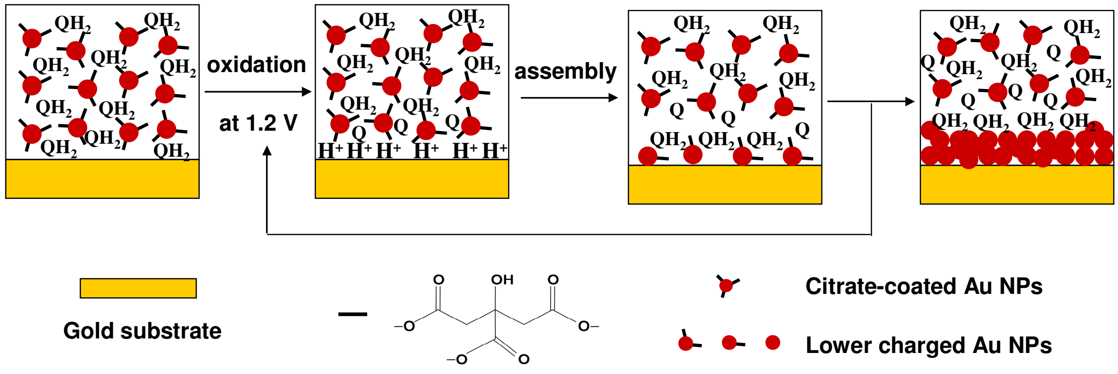


Figure 2. Linear sweep voltammograms of the polished gold electrode in the gold colloid with (the solid line) or without QH_2 (the dashed line), and current-time transient (the red dash-dotted line) for the polished gold in the gold colloid with QH_2 under an applied potential of 1.2 V versus the Pt-Ir wire.

Scheme 1 illustrates the proposed principle for the assembly of gold NPs at the electrode surface by in situ produced H^+ ions. The citrate-protected gold colloid is very stable due to the electrostatic repulsion of negatively charged ligands of citrate, even in the presence of QH_2. At 1.2 V versus the Pt-Ir wire, QH_2 can be easily oxidized into benzoquinone (Q), releasing H^+ ions $QH_2 \rightarrow Q + 2\,H^+ + 2\,e^-$.



Scheme 1. Schematic illustration for the assembly of gold NPs at the gold electrode by in situ produced H^+ ions via the electrooxidation of QH_2.

The in situ produced H^+ at the surface can induce the aggregation of gold NPs by decreasing their charge, because the group of $-COO^-$ in the ligand of citrate is partially transformed into acidic forms (–COOH) by combining the in situ produced hydrogen ions (the three-step pK_a values of citric acid are 3.13, 4.76 and 6.40, respectively, at 25 °C). Thus the colloidal gold NPs near the electrode surface become unstable and aggregate there due to their decreased electrostatic repulse and increased interactions of van der Waals force and hydrogen bonds. By repeating the potential step for several times, we can get a compact film of aggregated gold NPs.

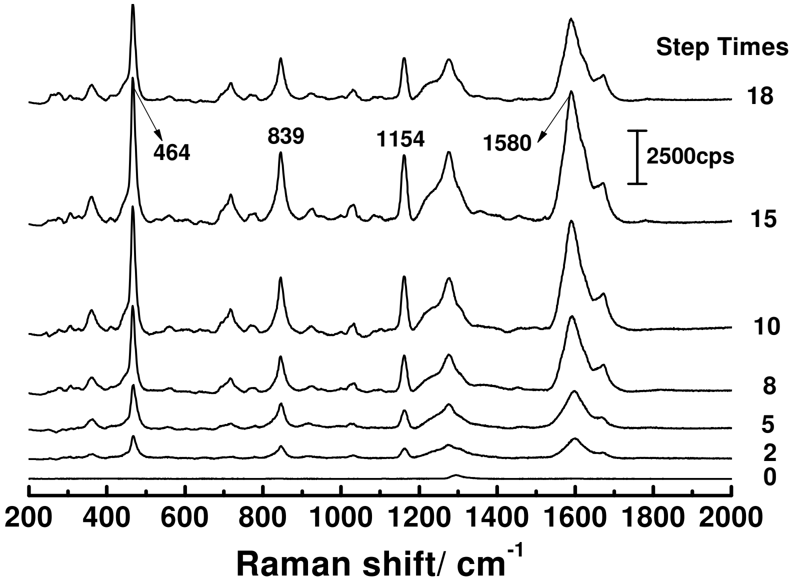


Figure 3. Selective in situ Raman spectra of adsorbed QH_2 for different potential step times. Laser power at the surface: 5.5 mW.

The assembly process was monitored by taking SERS spectra after each potential step. Raman peaks in Fig. 3 around 464 cm^{-1}, 839 cm^{-1}, 1154 cm^{-1}, and 1580 cm^{-1} are assigned to the ring planar deformation, ring breathing, C-H in plane bending, and ring C-C stretching modes of QH_2, respectively [26-27], indicating that the adsorption of QH_2 was stronger than Q. As shown in Fig. 3, the signals of QH_2 became stronger rapidly up to ten times of potential step, which was chosen as an optimum operation for the assembly of gold NPs at the surface. This signal enhancement phenomenon can be explained by the SERS mechanism [28]. With the increase of potential step times, more and more gold NPs aggregated onto the electrode surface, which leads to denser aggregates of NPs and shorter interparticle spacing allowing enhanced electromagnetic coupling of the NPs.

Fig. 4 shows the surface morphology of the electrode under different conditions. Only sporadic spots of aggregated gold NPs appeared on the electrode surface either by electrophoretic deposition of the gold colloid in the absence of QH_2 (Fig. 4a) or by the redox of gold substrate in the absence of gold colloid (Fig. 4b). The scattered gold spheres in Fig. 4b came from the reduction of the oxidized gold substrate by the QH_2. However, contributions from these processes were negligible comparing with the much stronger action of the in situ produced H^+ ions.

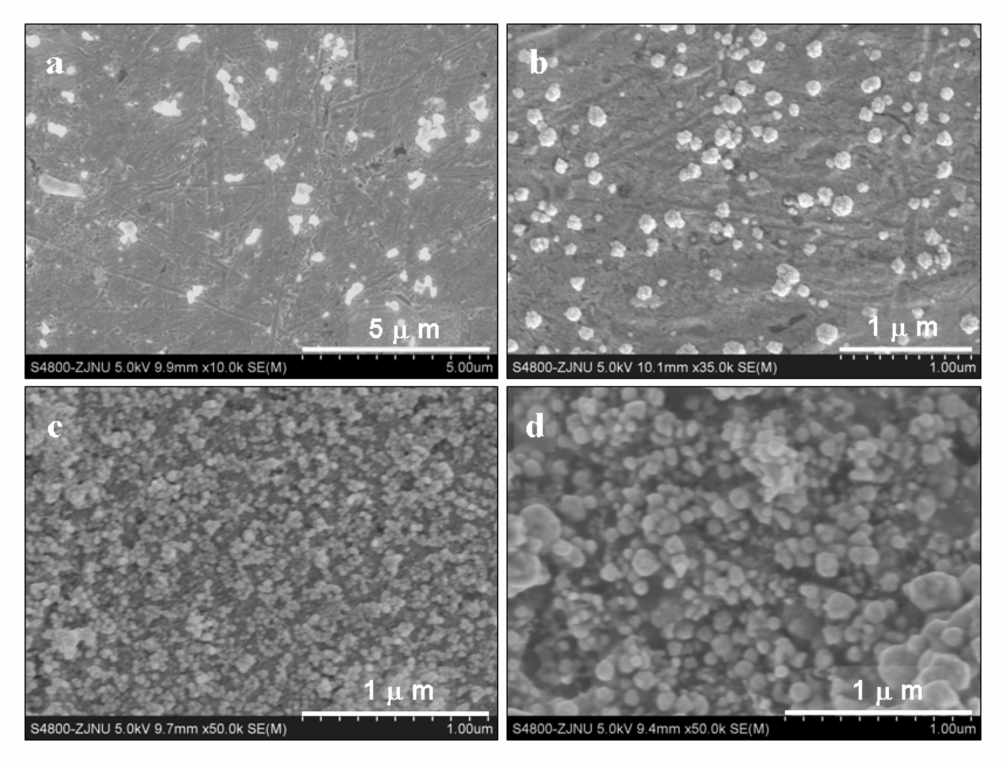


Figure 4. Surface morphology of the gold electrode in the (a) gold colloid only, (b) 0.06 M QH_2 solution only, (c) gold colloid + 0.06 M QH_2, and (d) gold colloid + 0.12 M VC after applying 10 times of potential step of 1.2 V (versus the Pt-Ir wire) with a duration of 50 s.

This conclusion was supported by the morphology of the assembled film in the presence of QH_2 and gold colloid (Fig. 4c), where the gold NPs aggregated together into a compact film. QH_2 can be replaced by other molecules like VC to obtain the assembled film of aggregated gold NPs (Fig. 4d). VC has larger solubility, stronger reduction ability than QH_2 and hence produced more H^+ ions while was electrochemically oxidized. That is the reason why the gold NPs aggregated and coalesced into larger particles while using VC.

Chosen pyridine (Py) as the probe molecule, the assembled films of aggregated gold NPs by the oxidation of QH_2 or VC showed strong SERS activity. It can be seen from Fig. 5 that the symmetric ring-breathing mode (ν_1) at 1014 cm^{-1} for the adsorbed Py on the film shifted to 1008 cm^{-1} as the potential changed from –0.2 V to –1.2 V versus SMSE, which is consistent with previous reports [29]. The peak intensity at 1014 cm^{-1} was also potential dependent and reached a maximum about 4300 counts per second (cps) at −1.0 V for the assembled film prepared using the electrooxidation of QH_2.

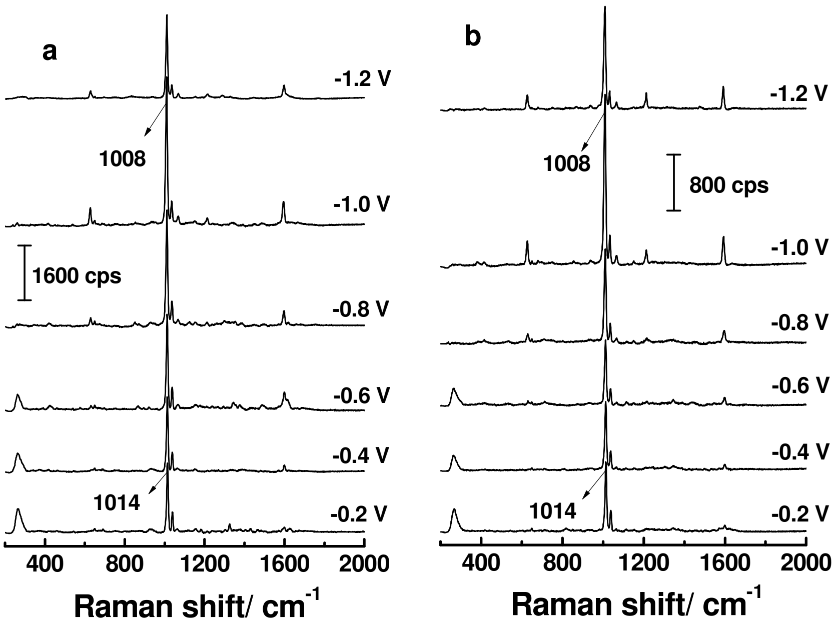


Figure 5. SERS spectra of Py in a solution of 0.01 M Py + 0.1 M KCl for the assembled films of the aggregated NPs prepared by the oxidation of (a) QH_2 or (b)VC. Laser power on the surface: 0.33 mW.

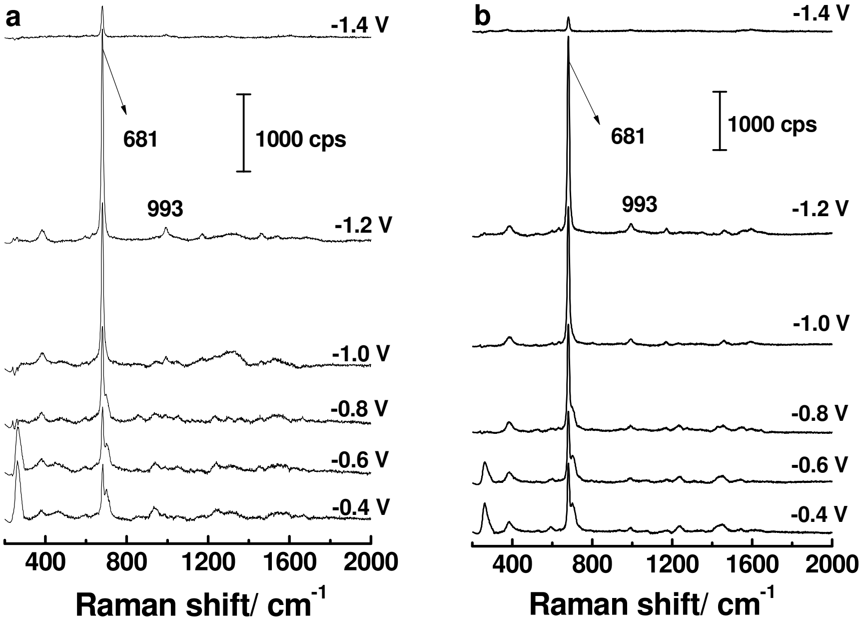


Figure 6. SERS spectra of melamine in a solution of 0.01 M melamine + 0.1 M KCl for the assembled films of aggregated gold NPs by the oxidation of (a) QH_2 or (b) VC. Laser power at the surface: 2 mW.

We also examined the use of the present SERS substrates for melamine detection to evaluate their possible applications in human health and food safety issues. Fig. 6 shows the SERS spectra of melamine on the films of aggregated gold NPs by the oxidation of QH_2 or VC as the potential changed from –0.4 V to –1.4 V versus SMSE. The most intense Raman peak of melamine was at 682 cm^{-1}, which is assigned to the ring breathing mode 2 involving an in-plane deformation of the triazine ring. The medium-strong Raman peak at 987 cm^{-1} is the ring breathing mode 1 of the triazine ring [30]. The peak intensity at 682 cm^{-1} was also potential depended and reached the maximum at −1.2 V.

Moreover, as an extension we successfully applied this strategy to make assembly films of aggregated Pt NPs at the gold electrode surface by the electrooxidation of VC (Fig. 7). Interestingly, we got compact films of sphere-like aggregates of Pt NPs at the electrode surface by the in situ produced H^+ ions.

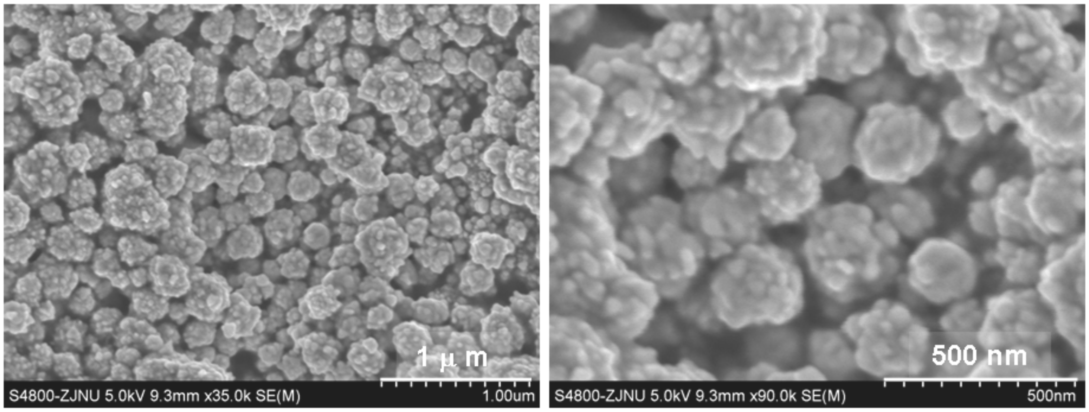


Figure 7. SEM images with different enlargements for the film of aggregated Pt NPs at the gold electrode surface by the electrooxidation of VC in the Pt colloid + 0.12 M VC after applying 10 times of potential step of 1.2 V versus the Pt-Ir wire with a duration of 50 s.

4. CONCLUSIONS

We have described a novel method for the assembly of Au NPs at the surface of gold electrode. Compactly assembled films of aggregated Au NPs at the electrode surface can be facilely obtained by in situ produced H^+ ions via the electrooxidation of QH_2 or VC. The produced H^+ ions can destabilize the gold colloid near the surface by decreasing the electrostatic repulse of the citrate-protected gold NPs. Contributions to the assembly both from the electrophoretic deposition and from the redox of gold substrate are negligible comparing with the much stronger action of the in situ produced H^+ ions. The assembled films show high SERS activity and can serve as excellent SERS substrates. This strategy can be applied to the assembly of other colloids like platinum NPs.

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