

文章编号 : 1000-6281 (2001) 05-0599-04

Electrochemical preparation and AFM characterization of gold nanoparticles on HOPG^{*}

TANG Jing, WU Jian-ming, XIE Zhao-xiong, MAO Bing-wei

(State Key Lab. for Phys. Chem. of Solid Surfaces, Dept. of Chem., Xiamen Univ., Xiamen 361005, China.)

Abstract: We present a study on the electrochemical preparation of Au nanoparticles on HOPG from HAuCl₄ solution characterized by tapping mode AFM. It has been shown that deposition on activated HOPG and non activated HOPG follows progressive and instantaneous nucleation and growth mode, respectively. The size and morphology of the nanoparticles depends on the deposition condition. Au nanoparticles of narrow size distribution of ~ 50 nm can be prepared which has a tendency to arrange into a two dimensional order on homogeneous HOPG (non-activated). The electrocatalytic properties and SERS properties of the Au nanoparticles are briefly discussed.

Key words: AFM; electrodeposition; nanoparticle; Au

中图分类号: TB383; O621.25; TN16 文献标识码: A

Nanosized metal particles (and thin film) show significantly different physical and chemical properties from those of their bulk^[1] and great efforts have been devoted to preparation and characterization of metal nanoparticles. For example, massive Au is much less reactive than noble metal such as Pt, Rh and Pd in homogeneous catalysis and electrocatalysis. However, enhanced reactivity for CO oxidation from a supported Au nanoparticles on TiO₂^[2] has been observed due to the electronic and structural effect of the composite^[3]. Due to its unique properties, gold nanoparticles are also the candidate for single-electron tunneling experiment. To facilitate investigation and application of the properties, preparation of nanoparticles on surface becomes one of the focuses of the field. As the preparation method becomes increasingly sophisticated^[4, 5], electrodeposition remains as an easy, efficient and controllable way for the formation of metal nanoparticles on electrode surfaces^[6]. With electrochemical control, proper composition of electrolytes as well as suitable surface pretreatment, nucleation and growth behavior for the nanoparticle formation may be adjusted.

In this paper, we report electrochemical preparation and AFM characterization of gold nanoparticles on highly oriented pyrolytic graphite (HOPG) of different surface conditions. Results are presented to show the influence of electrode potential, deposition time and surface pretreatment (activated and non-activated). The surface morphology of the deposits is investigated by tapping mode AFM that is useful in the study of weakly attached deposit on substrate surfaces. The electrocatalytic properties and optical properties will also be discussed.

Experimental

Electrochemical experiments were carried out in a conventional three-electrode cell. A saturated calomel electrode (SCE) and a platinum wire were used as the reference electrode and the counter electrode, respectively. The working electrode was a freshly cleaved HOPG. Depending on demand, the

基金项目: 自然科学基金资助项目 (No. 29833060)

This project is financed by National Natural Science Foundation of China (No. 29833060)

HOPG may be electrochemically activated prior to electrodeposition in phosphorous by anodic oxidation in a 0.1 mol/L phosphate buffer (pH = 7.0) solutions^[7]. Electrodeposition was carried out in a freshly prepared 1 mmol/L HAuCl₄ · 4H₂O and 0.1 mol/L HClO₄ solution following a preset potential and time control scheme. Electrocatalytic activities of the nanoparticles were measured in a solution containing 0.2 mol/L ethylene glycol and 0.1 mol/L NaOH. All reagents were of analytical grade and solutions were made of millipore water. Tapping mode AFM characterization of the deposit was performed ex situ on a DI Nanoscope IIIa.

Results and discussion

The initial stage metal deposition behavior depends strongly on the substrate surface state^[8]. Defects of the surface such as steps, kinks often serve as the nucleation sites. Therefore, we started with the activated HOPG surface from which dense active sites for nucleation are expected. AFM characterization shows that HOPG after experiencing 60 min

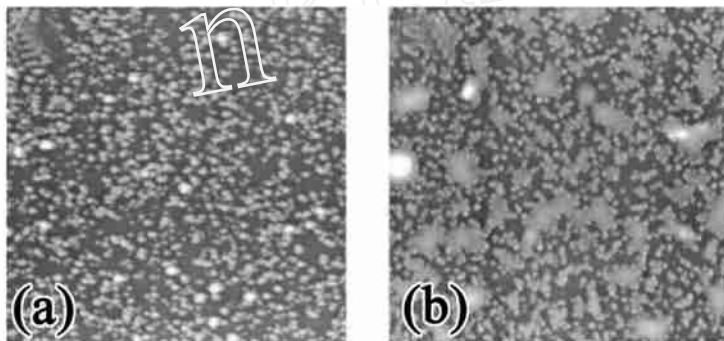


Fig. 1 AFM images of electrodeposited gold nanoparticles on activated HOPG surface potential change follows the sequence of (a) 0V 10s, - 0.3 V 60s, 0V ~ 30s and (b) 0V 10s, - 0.3 V 10s, 0V ~ 100s. Scan size 3 μ m \times 3 μ m.

oxidation at 1.2 V in 0.1 mol/L phosphoric acid is atomically rough but maintains its smoothness within the scale of about 10 nm in a reasonably large area, which provides a suitable surface for electrodeposition and subsequent characterization by AFM. Fig. 1 (a) is the AFM images showing the electrodeposited Au nanoparticles on the activated HOPG surface following a potential step sequence. Note that the open circuit potential of the system is around +0.9 V and there is no particular reason for the first negative potential step to 0V in this set of experiments. While stepping back from -0.3 V to 0 V allows further growth of the nuclei in a slower speed. Densely distributed but isolated nanoparticles of 70 ~ 80 nm were observed presumably on the defect sites of the HOPG surface. The time influence on the nucleation and growth is shown by Fig. 1(b). Sizes of the large and the small island are about 50 nm and 400 nm, respectively. From the size distribution shown in Fig. 1(a) and (b), a progressive nucleation and growth mode at -0.3 V is suggested. Particle aggregation in Fig. 1(b) is likely due to the overlap of particles after prolonged growth at 0 V.

Formation of more uniform Au nanoparticles is desirable on non-activated HOPG. Instantaneous nucleation and growth mode is expected on the almost defect-free surface of HOPG. As is shown in Fig. 2 (a) and (b), only part of the HOPG surface were covered with nanoparticles of ~75 nm. It should be noted that stepping into either +0.3 V or -0.3 V already fall into the diffusion-controlled regime of potential where the growth rate of the nuclei maintains the same. Thus, the deposition potential influences mainly the density of the particles. The formed nanoparticles have a similar narrow size distribution for both Fig. 2 (a) and (b) compared with those on activated HOPG surfaces shown in Fig. 1 (a) and (b). Some brighter or bigger particles were seen on top of the densely packed first layer of the Au nanoparticles. This was because

as the time increased the partially covered surface provided a new starting point for further nucleation of Au on the as formed Au nanoparticles. In either case, there was a tendency for the particles to arrange into order. Interestingly, particles can be arranged in a long line on some parts of the surface as shown in Fig. 2(b).

There are experimental evidences and theoretical

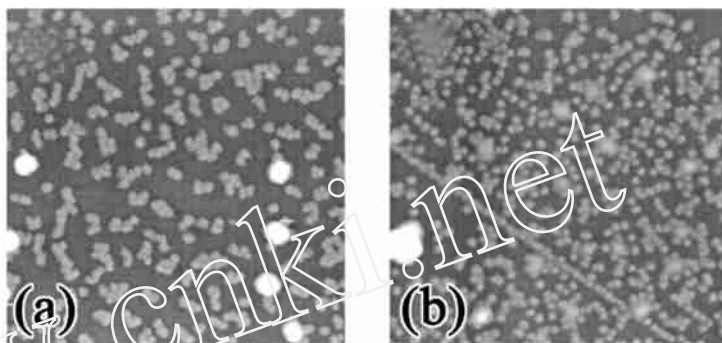


Fig. 2 AFM images of electrodeposited gold nanoparticles on nonactivated HOPG surface at (a) 0.3 V for 10 s and (b) - 0.3 V for 60 s. Scan size $3\mu\text{m} \times 3\mu\text{m}$.

calculations that small as well as large metal clusters can rearrange on the surface through diffusion of metal atoms at the peripherals of the clusters^[9]. For the present work, we have no definite explanation for the morphology of the nanoparticles on surface yet, but we speculate that the driving force for this tendency is likely due to the weak adhesion energy of the gold deposit and fast diffusion of the gold atoms within the particles on homogeneous HOPG surface. Arvia and coworkers reported in a recent paper that the shape of the gold islands were determined by the anisotropic diffusion, which is of three-dimensional central core and large quasi two-dimensional branching^[6]. This is obviously not the present case. Diffusion in the present work is isotropic and as a result, round shaped nanoparticles are formed. The diffusion is more favorable at more positive potential because of the higher tendency for atoms to move forth and back and thus higher degree of two-dimensional aggregation at 0.3V, Fig. 2 (a). It is, however, hard to explain why Au nanoparticles persist their shape even when they are very close to each other. It seems the activation energy for the interdiffusion of atoms from different nanoparticles are very high. It should be noted that adhesion of the Au deposit is so weak that it is only possible to characterize the nanoparticles using tapping mode AFM which loses the chance of in-situ monitoring.

Among the four surface morphologies, only the one shown in Fig. 1 (b) shows surface enhanced Raman signal (SERS). The main feature of the morphology is the coexistence of large (400 nm) and small (50 nm) Au islands that are in contact with each other somehow. It is expected that such a morphology would generate strong electromagnetic coupling and thus surface enhanced Raman signal^[10].

To study the electrocatalytic behavior of Au nanoparticles on HOPG, cyclic voltammometric measurements were performed using the electrooxidation of ethylene glycol as the probe. Ethylene glycol is a potential candidate for fuel cell of common interest whose electrooxidation behavior on Au(hkl) has been studied^[11]. In the solution of 0.2 mol/L $(\text{CH}_2\text{OH})_2$ + 0.1 mol/L NaOH, the onset of the ethylene glycol electro-oxidation was found to be at 0.27 V on a massive Au electrode, Fig. 3 (solid line 1). Whereas on the Au nanoparticle modified HOPG electrode (Fig. 1(b)), there is about 50 mV lowering of the oxidation potential and more than 20 times enhancement in electrocatalytic current density, Fig. 2 (dotted line 2). The enhanced electrocatalytic property of the Au nanoparticles is believed to be related to the surface effect and small size effect of the nano-sized gold particle^[12].

Conclusion

We have shown that Au nanoparticles on HOPG can be prepared by electrodeposition. The size and morphology of the nanoparticles on HOPG strongly depends on the original HOPG surface condition and the deposition condition. Fast diffusion on the homogeneous HOPG surface provides a tendency for the nanoparticles to rearrange into order, yet the high activation energy for the interdiffusion of

atoms between different nanoparticles prevent the nanoparticle from being coalesced. The present study demonstrates that preparation of metal nanoparticles of different size and morphology on surface is desirable by electrodeposition. Systematic studies are under progress.

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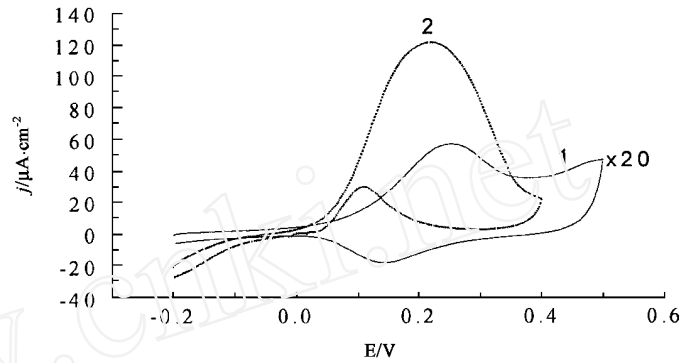


Fig. 3 Cyclic voltammogram of massive Au electrode (solid line 1) and gold nanoparticles electrodeposited on nonactivated HOPG electrode (dotted line 2) in 0.2 mol/L ethylene glycol and 0.1 mol/L NaOH solution. The current density is converted with respect to the geometric area of the electrode surface. Sweep rate: 50 mV/s.

金纳米粒子的电化学制备和 AFM 表征

汤 徽, 吴剑鸣, 谢兆雄, 毛秉伟*

(固体表面物理化学国家重点实验室, 厦门大学化学系, 厦门 361005)

摘 要: 本文以高序石墨为基底, 氯金酸溶液为支持电解质, 以对表面破坏力小的轻敲模式原子力显微镜为观察手段, 研究基底的表面状态及电沉积条件对形成的纳米颗粒尺寸和形态的影响, 并简要讨论所形成的金纳米粒子的表面 Raman 增强效应对乙二醇氧化的电催化效应。

关键词: AFM; 电沉积; 纳米粒子; Au