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Short communication

Gold (Au) Huge Particles Prepared by a Simple Pyrolysis of $AuCl_3$ Dissolved in Various Solvents in the Presence of MWCNTs

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For the first time, large gold (Au) particles with a diameter greater than 300nm were prepared in the presence of multi-walled carbon nanotubes (MWCNTs), using Au nanoparticles as seeds. This was achieved through a simple pyrolysis process of $AuCl_3$ dissolved in different solvents: room temperature ionic liquids (RTILs) of 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIBF_4$) and distilled water. X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were used to characterize the obtained Au particles; the results showed that Au huge particles with a highly crystalline structure and a diameter of greater than 300nm were fabricated when using RTILs as the solvents, while spherical particles of Au with a diameter close to 500nm were fabricated in distilled water. Cyclic voltammograms (CVs) of ethanol oxidation reaction (EOR) were observed, also for the first time, on the as-prepared large Au particles modified electrode in alkaline solution.

Keywords: pyrolysis; Au huge particles; distilled water; RTILs; MWCNTs; ethanol oxidation reaction (EOR)

1. INTRODUCTION

The purpose of this work is to show the influence of various solvents on the morphologies of huge gold (Au) particles that were fabricated by a simple pyrolysis process in the presence of MWCNTs.

Due to their chemical stability, specific optical and other physical properties, gold nanoparticles are important objects of contemporary chemistry [1]. So far, there are two typical methods to generate Au nanoparticles. The first is a chemical reduction reaction. For example, Seeber [2] reported the Au/Pt bimetallic nanoparticle systems, in which $NaAuCl_4 \cdot 2H_2O$ and $NaBH_4$ were employed as the precursors of Au and the reductive reagent, respectively. Tsakova [3] described the preparation of an Au nanoparticle solution, in which $HAuCl_4$ and sodium citrate were used as the starting materials. The second method is an electrochemical reduction reaction. For instance, S. Yoshihara [4] immobilized Au nanoparticles on a grown and oxygen-terminated (O-terminated) boron-doped diamond (BDD) film electrochemically, in which the deposition solution was 0.1M H_2SO_4 containing 0.3mM of $AuCl_4^-$ solution. Although many works on Au nanoparticles have been published, there are few reports on the preparation of huge particles of Au with a diameter of more than 300nm.

Room temperature ionic liquids (RTILs) have attracted much more attention recently, due to their excellent features, including low-volatility, non-toxicity, non-flame, higher conductivity compared to common organic solvents, and higher solubility for organic substances when compared to aqueous solutions [5,6]. Generally, RTILs are mainly applied in the following fields of chemistry: (1) solvents in organic synthesis [7], (2) electrolytes in electrochemistry [8]. To the best of our knowledge, the application of RTILs in the pyrolysis process has not been widely reported, though numerous papers concerning RTILs are published every year.

Meanwhile, carbon nanotubes (CNTs) have become an important research field, especially since the publication of Iijima's [9] work. Since then, the many advantages of CNTs have been reported in the field of electrochemistry [10]. Of them, being employed as an ideal substrate in order to modify the electrode surface was thought as the main contribution of CNTs [11]. Therefore, immobilizing metal nanoparticles (especially, platinum, gold and other transition metals) onto CNTs, has become an important task for electrochemistry researchers. As addressed previously, chemical reaction and electrochemical methods are the main ways to prepare Au particles onto the surface of carbon nanotubes (CNTs). To our knowledge, no paper reporting the fabrication of Au onto CNTs by a simple pyrolysis method has been published, though we have immobilized Pt [12] nanoparticles onto CNTs successfully.

In this work, we fabricated huge Au particles onto MWCNTs through a simple pyrolysis process in which no other reducing reagents were introduced except for MWCNTs and the used solvents. Results showed that huge Au particles with a diameter of more than 300nm were prepared. Moreover, for the first time, cyclic voltammograms (CVs) of ethanol oxidation reaction (EOR) were observed on the as-prepared huge Au particles modified carbon electrode.

2. EXPERIMENT

2.1 Chemicals and materials

Multi-walled carbon nanotubes (MWCNTs, outer diameter: 10-20nm, length: 0.5-500μm) were purchased from Shenzhen Nanotech Port Co., Ltd (China). RTILs of EMIBF4 with a purity of more than 99% were obtained from Hangzhou Chemer Chemical CO., Ltd (China). A glassy carbon (GC)

(Ø =2mm) electrode and a graphite (Ø =2mm) electrode purchased from Tianjin Aida Co., Ltd (China) were used as the working electrodes. All chemicals were used as received without further purification.

2.2 Pyrolysis of $AuCl_3$ to form Au huge particles onto MWCNTs

Firstly, 2 ml distilled water (or EMIBF4) solvent containing 5×10^{-3} M $AuCl_3$ and 10 mg MWCNTs were mixed together to yield a suspension solution; this resultant solution was ultrasonicated for 30 min. Secondly, the obtained suspension solution was placed in a homemade autoclave at room temperature; the well-sealed autoclave was then transferred to a box-type furnace. Lastly, the temperature of the box-type furnace was increased to 200 ^{0}C within 20 min, and was kept at that temperature for 3 h to fulfill the pyrolysis process. The resultant solution was filtered, and the obtained samples were washed thoroughly with redistilled water, and dried at ambient temperatures to generate the large Au particles coated MWCNTs (denoted as Au/MWCNTs).

2.3 Preparation of Au/MWCNTs-coated electrode

Prior to each experiment, the working electrode of a glassy carbon (GC) (or a graphite electrode) electrode with a diameter of 2 mm was successively polished with 1 and 0.06 μm alumina powder on a microcloth wetted with doubly distilled water, resulting in a electrode with a mirror-like surface. For the preparation of an Au/MWCNTs-coated electrode, 4.6mg of the resultant Au/MWCNTs materials was added to a 1ml aqueous solution of sodium lauryl sulfate (SDS) (the content of SDS is 1.5mg/ml). The mixture was then treated for 30 min with ultrasonication to form a uniform suspension, after which 5 μL of this mixture was dropped onto the surface of a well-treated electrode. Finally, the resultant Au/MWCNTs-modified electrode was dried with hot air prior to the following electrochemical experiments.

2.4 Characterization

X-ray diffraction (XRD) analysis of the catalyst was carried out on a Bruker D8 ADVANCE X-ray diffractometer equipped with a Cu Kα source (λ= 0.154 nm) at 40 kV and 30 mA. The 2θ angular region between 10 and 90°was explored at a scan rate of 1°/step. The obtained samples were characterized using scanning electron microscopy (SEM, S-4800, HITACHI, Japan). EDS spectrum analysis was carried out on an X-ray energy instrument (EDAX, PV-9900, USA). Pyrolysis was implemented in an SRJX-8-13 box-type furnace equipped with a KSY 12-16 furnace temperature controller.

Electrochemical experiments were conducted on a model CHI660B electrochemical workstation (Shanghai Chenhua Apparatus, China). A conventional three-electrode system was employed, in which an Au/MWCNTs-modified electrode and platinum wire (1 cm^2) were used as the working electrode and counter electrode. It should be noted that the reference electrode was a saturated calomel electrode (SCE). All potentials in this paper were reported with respect to SCE. Experiments were carried out at room temperature.

3. RESULTS AND DISCUSSION

3.1 Characterization of the obtained samples

The typical XRD patterns of the obtained samples are shown in Fig.1.

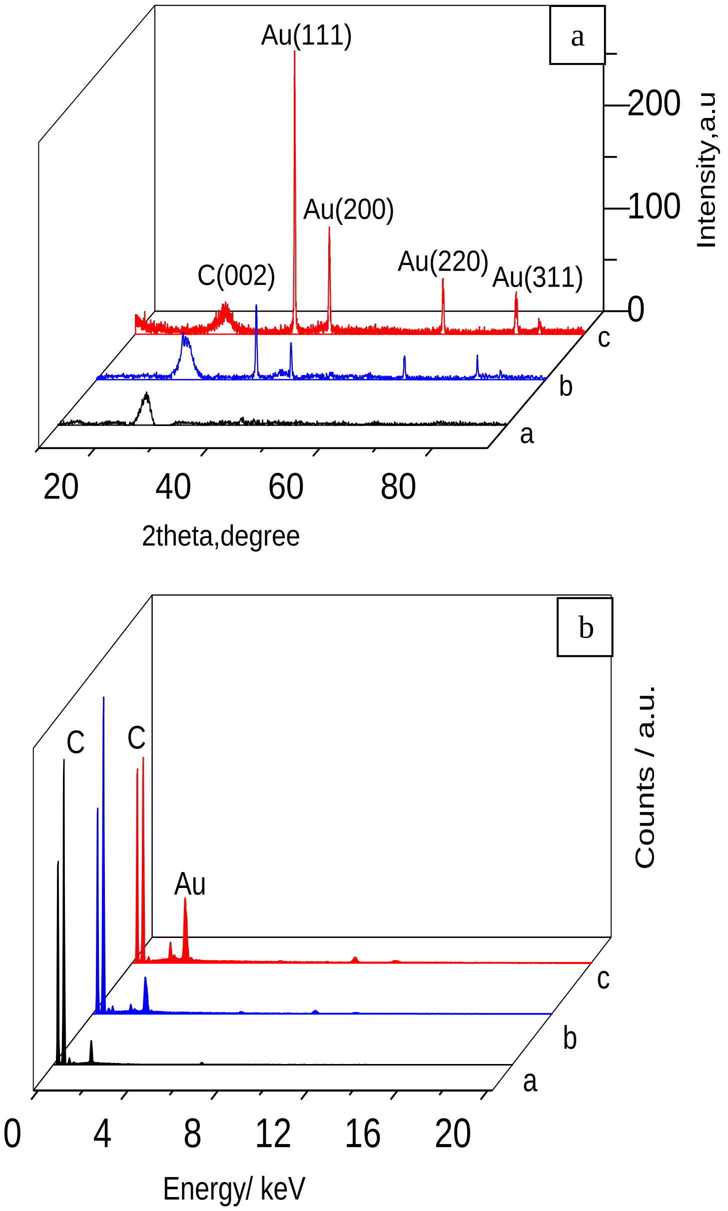


Figure 1. a) XRD patterns for samples prepared in different solvents. Pattern **a**: pure MWCNTs, Pattern b: Au/MWCNTs (in EMIBF4); Pattern c: Au/MWCNTs (in distilled water). b) EDS spectra for samples prepared in different solvents. Pattern a: pure MWCNTs, Pattern b: Au/MWCNTs (in EMIBF4); Pattern c: Au/MWCNTs (in distilled water).

For the pure MWCNTs, as shown by pattern a, the diffraction peak at 2θ of 26.1° is indexed to (002) planes of carbon nanotubes (CNTs), in accordance with the previous report [12]. After the pyrolysis process, the diffraction peaks corresponding to CNTs are still clearly exhibited, suggesting the pyrolysis process did not destroy the crystal structure of the MWCNTs. Additionally, as shown by patterns b and c, some novel peaks were exhibited, and those peaks correspond to the planes (111), (200), (220), (311) located at 38°, 45°, 65°and 78°, respectively. It indicates the characteristic peaks of a single face-centered cubic (fcc) structure of gold (00-002-1095) are shown, which is consistent with the former report [13]. No impurity phases could be detected, indicating the formation of pure and highly crystalline Au. Meanwhile, the crystallinity of Au particles fabricated in distilled water is higher than that generated in RTILs of EMIBF4, based on the higher intensity of diffraction peaks in pattern c when compared to those in pattern b. Since no other diffraction peaks were found, Fig. 1 demonstrates that only Au particles were formed on the surface of MWCNTs.

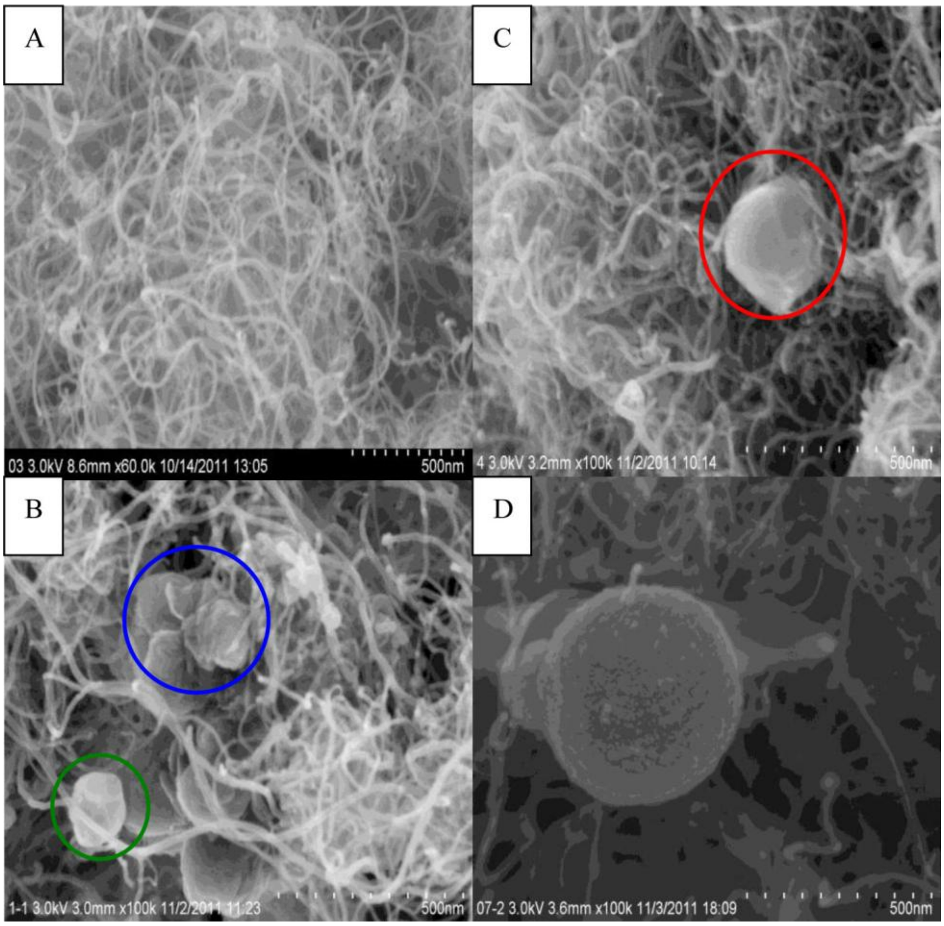


Figure 2. SEM images for the samples appearing in the pyrolysis process. Image A: pure MWCNTs; image B: the precursors having MWCNTs and $AuCl_3$; image C: Au huge particles prepared in EMIBF4; image D: Au huge particles prepared in distilled water.

The average particle size was estimated using the Debye-Scherer formula, $t = 0.89\lambda / (\beta\cos\theta_B)$, where λ is the X-ray wavelength (1.5406Å), θ_B is the Bragg diffraction angle, and β is the peak width at half-maximum. The average sizes of Au particles prepared in distilled water and those in EMIBF4, were 7.1 nm and 3.5 nm, respectively, as calculated from the Debye-Scherer formula on the (111) peak. Unfortunately, these calculated sizes were *rather smaller than* those seen by SEM, as shown in Fig.2, suggesting that aggregation or other processes took place in the growth of Au particles. EDS spectra for the samples were also measured as illustrated by Fig. b in Fig.1. One peak corresponding to C element can clearly be seen for the pure MWCNTs. Regarding the as-prepared samples, excepting C element, the peaks corresponding to Au were evident, as shown by lines **b** and **c** in Fig. b. It indicated that after pyrolysis, only elementary Au was obtained since no other elements were detected. For the case using EMIBF4 as the solvent, the weight percentages before and after the pyrolysis of C and Au elements in samples were 84.5% and 82.1%, 1.9% and 10.0%, respectively. However, for the pyrolysis process using distilled water as the solvent, the weight percent before and after pyrolysis of C and Au were 76.0% and 74.1%, 9.5% and 19.9%, respectively. That is to say, after the pyrolysis process, carbon in MWCNTs was consumed, and more Au was generated. It may be implied that MWCNTs were used as the reductive reagents in the pyrolysis process.

Fig.2 is the SEM images of the obtained samples. It can be seen that for the pure MWCNTs shown in image A, no substances were found on its surface. For the precursors containing MWCNTs and $AuCl_3$, some layered particles are displayed, as shown by the blue-circled part in image B. It was revealed by the localized EDS that the layered particles were $AuCl_3$ as opposed to other substances. Interestingly, after pyrolysis process in EMIBF4, as shown by image C, huge particles with well-defined structures were observed, proven to be elementary Au by the localized EDS. The morphology of the huge Au particles is very similar to the reported Au nanoparticles by Li [1]. The diameter of large Au particles is close to 300nm based on an SEM image, rather larger than the reported one [1,14]. After the pyrolysis process in distilled water, as shown by image D, huge spherical particles were exhibited on the surface of MWCNTs, the morphology of which is rather different from that of the reported Au nanoparticles [14]. Also, it was detected by localized EDS that the huge spherical particles were Au particles. The diameter of the large Au particles was close to 500nm based on the SEM images. Thus, based on the XRD patterns and SEM images, it can be concluded that the huge Au particle obtained in RTILs is a single crystal since it has the well-defined structure, and those prepared in distilled water are polycrystals rather than single crystals. Thus, it is indicated that the formation mechanism of huge Au particles in RTILs of EMIBF4 is very different from that occurring in distilled water when employing the pyrolysis method. To the best of our knowledge, there is no report on the preparation of such huge Au particles, especially by a pyrolysis process.

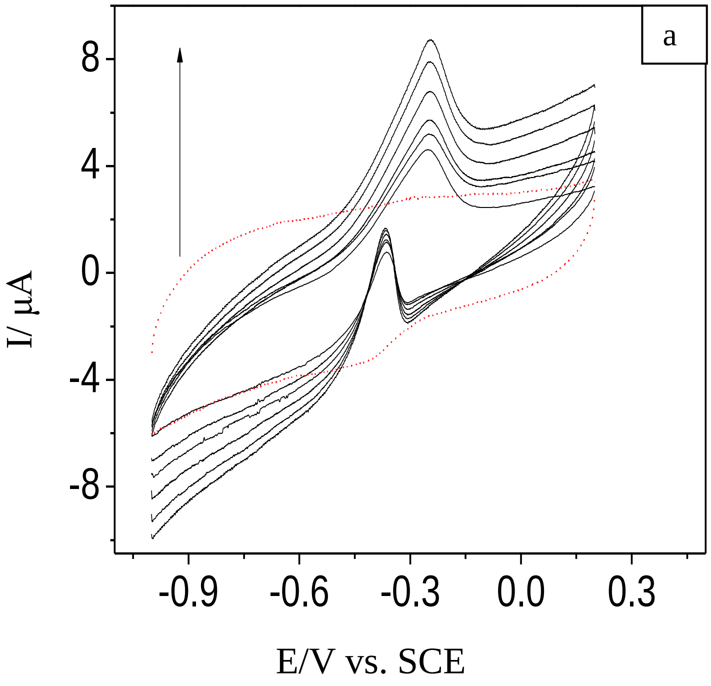
An unavoidable question came into being. What is the reductive reagent in above pyrolysis process? Theoretically, there must be some substance to release its electrons to Au^{3+} to yield Au atoms, leading to Au particles. Numerous attempts told us that Au particles could not be prepared in the absence of MWCNTs in the above pyrolysis methods. That is to say, MWCNTs were employed as the reducing reagents. This result is strongly supported by the weight percent data obtained from EDS as addressed above, i.e., after pyrolysis process, the weight content of carbon was lowered and that of Au was enhanced.

How do these huge Au particles form during pyrolysis? Close inspection revealed that some small nanoparticles have existed in the precursors, as shown by the green-circled part in image B of

Fig.2. The localized EDS revealed that the green-circled part in image B shows pure Au nanoparticles. It is probable that in the pyrolysis process, small Au nanoparticles were used as the seeds upon which the Au crystal growth could progress, leading to larger particles. It is reported that low charges and asymmetrically distributed charges are the key factors causing nanoparticle aggregation [15]. EMIBF4, which has a lower dielectric constant [16] compared to water, can decrease the surface charge of formerly existed nanoparticles of Au due to the change in polarity of the solvent. Therefore, similar to the case described by Li [14], the newly formed Au atoms can migrate from the solution of EMIBF4 to the EMIBF4/Au (formerly existed) interface in sequence, which is also analogous to the nanoparticle self-assembly at the toluene/water or hexane/water interface in ethanol-mediated methanol [17,18]. As a result, huge Au particles were generated. When using distilled water as the solvent, the newly formed Au nanoparticles trapped at the water/Au interface have a strong dipolar field, which can distort the interface shape and cause a strong lateral capillary attraction between nanoparticles [19]. Due to the stronger capillary attraction between adjacent nanoparticles, and compared to the case when using RTILs as the solvents, the aggregation rate was increased, giving rise to a random assembly. Consequently, large spherical Au particles decorated by many small dots were generated. That is to say, the growth rate of an Au crystal in water is higher than that in EMIBF4, which can give birth to Au particles with various morphologies.

3.2 Electrocatalysis of Au/MWCNTs towards EOR

Seeber [2] has presented the CVs of a methanol oxidation reaction (MOR) measured on an Au nanoparticle modified glassy carbon electrode, in which a pair of *normal* redox peaks was observed. Also, Strbac [20] showed the CVs of an ethanol oxidation reaction (EOR) on Au (111) in 0.5M H_2SO_4, where a pair of *abnormal* redox peaks was displayed. Except for the work reported by Lamy [21], to the best of our knowledge, CVs of EOR in alkaline solution on an Au modified electrode were seldom reported.



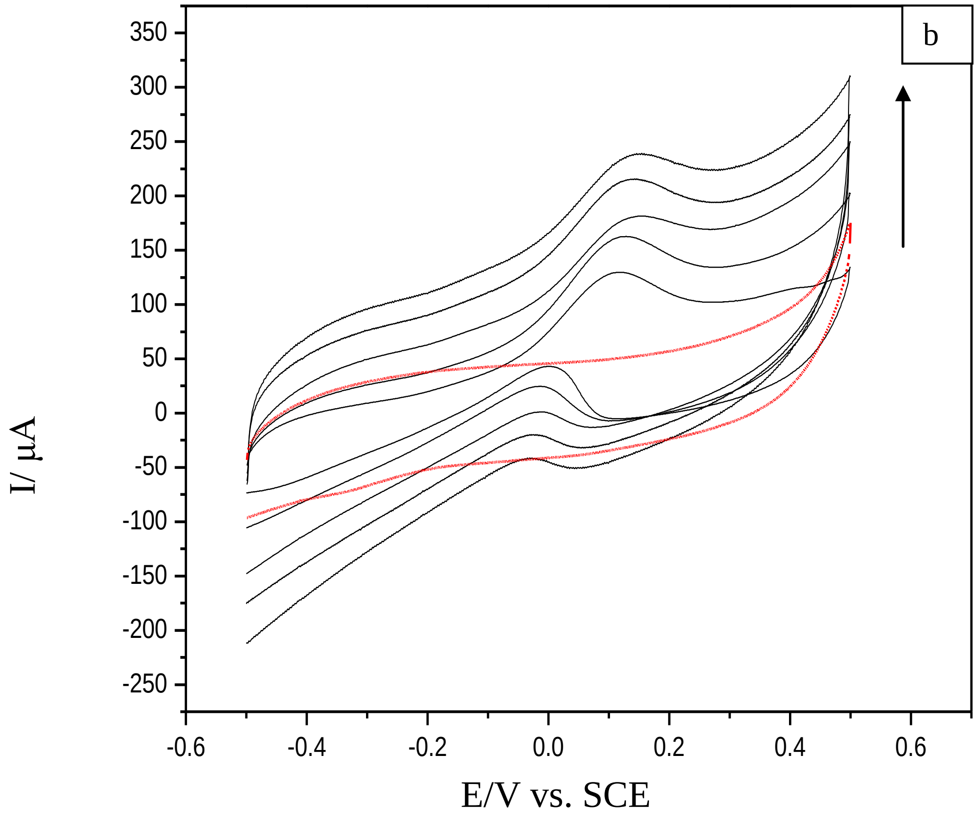


Figure 3. Cyclic voltammograms (CVs) obtained on Au/MWCNTs-coated electrode. In Fig.(a), Au/MWCNTs catalysts were prepared using EMIBF4 as the solvent. In Fig.(b), Au/MWCNTs catalysts were prepared using distilled water as the solvent. For red dotted line: in 1MKOH solution; solid line: in 1M KOH having 1M ethanol solution. Fig (a) and Fig (b) were measured on a glassy carbon electrode and a graphite electrode, respectively. Scan rate of the red lines is 50mV/s. Scan rates for the solid lines in Fig.(a) are 50, 80, 100, 150, 200 and 250 mV/s, respectively. Scan rates for the solid lines in Fig.(b) are 20, 50, 100,150 and 200 mV/s, respectively.

In Fig.3, as shown by the red-dotted lines, no oxidation peaks can be found on the Au/MWCNTs-coated electrode in the 1 M KOH solution. While oxidation peaks were exhibited clearly on the Au/MWCNTs-modified electrode in the 1 M KOH solution containing 1M ethanol, as shown by the solid lines, which implies the pyrolysis-prepared large Au particles have catalysis towards EOR. It can be seen from Fig. a that the onset potential for EOR on the Au/MWCNTs-modified GC electrode is at around -0.4V, in which the Au/MWCNTs catalysts were prepared using EMIBF4 as the solvent. However, in Fig. b, the onset potential is close to 0.1V, in which Au/MWCNTs catalysts were prepared using distilled water as the solvent. Meanwhile, for both Fig. a and b, the oxidation peak current occurring in the positive-direction potential scan is linear to the square root of the scan rate, indicating that EOR on the as-prepared electrodes are determined by the diffusion process. Also, one can see that the oxidation peak currents observed in Fig. b are larger than those in Fig. a at the same scan rate, probably due to the higher crystallinity of Au particles fabricated in distilled water compared to the huge Au particles prepared in EMIBF4, as shown by their XRD patterns in Fig.1. It may also be due to the larger surface of the huge spherical Au particles when compared with the huge Au particles fabricated in the presence of EMIBF4, as seen by SEM images in Fig.2. The shape of CVs for EOR shown in Fig.3 is very similar to that of CVs of EOR on Au [20] substrate, i.e., an anomalous oxidation peak appeared during the negative-direction potential scan. In ref.20, the CVs of EOR was obtained in 0.5M H_2SO_4 rather than in an alkaline solution. Lamy [21] displayed CVs of EOR that were recorded on Au electrode in 0.1M NaOH. It should be mentioned that in Lamy's work, a pair of normal redox peaks corresponding to EOR was exhibited, no anomalous oxidation peak in the negative-direction potential scan was observed. That is to say, the shape of CVs for EOR shown here is rather different from that of the one previously reported [21].

Actually, the mechanism of EOR in an alkaline solution remains unclear. For example, Lamy [21] has revealed that acetate is the only detectable product of EOR in alkaline solution via the following reaction, i.e., $CH_3\text{-}CH_2OH + 4OH^- \longrightarrow CH_3\text{-}COOH + 3H_2O + 4e^-$, and in the positive-direction potential scan, Au oxide will form, and in the negative-direction potential scan, the oxidation of ethanol will be accompanied by the reduction of surface Au oxide. Recently, Attard [22] reported the cyclic voltammetric (CV) behavior of EOR in alkaline on gold adsorbed on Pt{hkl} electrodes, and pointed out that the ethanol oxidation reaction (EOR) in an alkaline medium is very structure sensitive for submonolayer gold coverage. In other words, EOR on Au in an alkaline solution can be easily affected by the micro-crystal structure of the gold electrode used. Based on the above references [21,22], it is probable that in the positive direction potential scan, oxide of Au was formed, which covered some active sites of the Au surface and hindered the oxidation of ethanol. And in the negative-going potential sweep, similar to the case on Pd substrate [23], the following reaction occurred:

$$Au_2O_3 + 3H_2O + 6e^- \rightarrow 2Au + 6OH^-.$$

Hence, EOR could still occur on the released Au active sites in the negative-going potential sweep. What kinds of reactions have occurred on the large Au particles modified electrodes in the potential scanning? How does the crystal structure of huge Au particles influence the EOR? More studies should be done to further this work. However, we do present CVs of EOR on Au huge particles in this communication, though we cannot present a satisfactory interpretation on the mechanism of EOR on Au in an alkaline solution with our present techniques. More works are in progress in our lab.

4. CONCLUSION

Large Au particles coated MWCNTs, prepared by a pyrolysis process of $AuCl_3$ that was dissolved in various solvents. XRD, SEM and EDS as well, all strongly demonstrated that Au/MWCNTs were generated by our proposed novel method, in which no other reductive reagents were introduced. Further studies revealed that MWCNTs played an important role in the above pyrolysis process, and were used as a reductive reagent to reduce Au^{3+} to yield Au atoms. The obtained

CVs indicated that our developed huge Au particles have catalysis towards EOR, though the exact mechanism of EOR cannot be presented in this work.

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