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Short communication

Can Pd_3M_1 Nanoparticles be Prepared by a Pyrolysis Method Using Room Temperature Ionic Liquids (RTILs) as the Solvent?

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A serials of Pd_3M_1 composite nanoparticles (namely, Pd_3Au_1, Pd_3Cu_1, and Pd_3Co_1) with a diameter less than 30nm were prepared by a simple method of pyrolysis in the presence of multi-walled carbon nanotubes (MWCNTs), in which room temperatures ionic liquids (RTILs) of Butyl-3-methylimidazolium hexafluorophosphate (denoted as $[BMIM]PF_6$) was employed as the solvent. XRD, TEM and EDS have been employed to characterize the obtained samples. The electrocatalysis of the catalysts toward ethanol oxidation reaction (EOR) were mainly evaluated by using cyclic voltammetry (CV), revealing that the catalysis of the samples toward EOR is in the following declining order: Pd_3Cu_1, Pd_3Co_1, Pd_3Au_1, based on the peak current of EOR. Also, it is found that the catalyst of Pd_3Co_1 displayed the best tolerance to the potential sweeping even after 70th cycles. This initial work may open a very simple and promising way for fabricating composite nanoparticles.

Keywords: Pd_3M_1 composite nanoparticles; pyrolysis; Room temperature ionic liquids; ethanol oxidation reaction (EOR)

1. INTRODUCTION

Although RTILs have been introduced in the pyrolysis process for fabricating nanoparticles in our previous work [1, 2], the preparation of composite nanoparticles by RTILs was rarely reported. The aim of this work is directed to show the possibility of preparing Pd-based composite nanoparticles using the method of pyrolysis in the presence of MWCNTs, in which a kind of RTILs was employed as the solvent.

As a novel medium between "water" and "oil", room temperature ionic liquids (RTILs) have attracted much more attention, mainly due to their excellent features, including low-volatility, non-toxicity, non-flame, higher conductivity compared to the common organic solvents, and higher solubility for organic substances when compared to aqueous solutions [3,4]. However, the application of RTILs in large scale was not much reported mainly due to its high cost compared with the traditional solvent such as acetone. Thus, exploring the new application of RTILs has become into an important task especially in the fundamental research field of chemistry. Although many novel kinds of carbon such as nanofiber [5] and graphene [6] have been developed recently, carbon nanotubes (CNTs) is still a hot topic in the electrocatalysis field when being used as the ideal support for catalyst [7]. To the best of our knowledge, no paper reporting the fabrication of bimetallic composite nanoparticles of Pd_3M_1 onto CNTs by a simple pyrolysis method has been published, though we have immobilized Au [2] particles onto CNTs successfully.

Due to their superior properties compared to the traditional battery, alcohol-based fuel cells have been regarded as the potential power sources in the near future. However, the high cost and limited supply of the catalysts such as Pt used in fuel cells have effectively limited the development of fuel cells at least in some degree. Thus, developing Pt-free catalyst is thought as a main way to resolve above problem. Recently, Pd-based catalysts have been found having satisfied catalysis toward EOR especially in an alkaline medium. Till date, there are two typical methods to prepare Pd-based catalyst, namely, chemical reduction method [8] and electrochemical reaction [9]. Pyrolysis method, owing to its simplicity in manufacturing, has been widely applied in the synthesis field [10]. Howbeit, the method of pyrolysis used for preparing Pd-based nanoparticles was seldom reported in the field of electrochemistry, though the catalysts of Pd-Co [11] and Pd-Au [12] have been prepared recently.

In this work, we fabricated Pd-based composite nanoparticles, i.e., Pd_3M_1 (M=Au, Cu and Co), onto MWCNTs via a simple pyrolysis method in which no other reducing reagents were introduced except for MWCNTs and the used solvent of RTILs. This pyrolysis process described here may open new application field for RTILs. Also, some novel electrochemical properties possessed by the RTILs-assisted prepared nanoparticles are expected to be found in the further investigation.

2. EXPERIMENT

In a typical synthesis, firstly, $PdCl_2$ and $AuCl_3$ (or $Cu(NO_3)_2\cdot 3H_2O$, $Co(NO_3)_2\cdot 6H_2O$) were dissolved into 4 ml $[BMIM]PF_6$ at the molar ratio of Pd to Au=3:1, and then 20 mg MWCNTs were added to above solution leading to 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℃ 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 by dichloromethane, ethanol, and distilled water successively, and dried at ambient temperature to generate the binary composite nanoparticles Pd_3M_1 supported on MWCNTs (denoted as Pd_3M1/WMCNTs). The catalyst of Pd/MWCNTs was prepared by the same process only in the presence of $PdCl_2$ and MWCNTs. It should be mentioned that prior to TEM measurement, all samples were ultrsonicated in ethanol for about 10min, and then the obtained ink of catalyst was dropped on a copper-wed to complete the TEM measurement.

A conventional three-electrode system was employed, in which a Pd_3M_1/WMCNTs-modified glassy carbon (GC) electrode and platinum wire were used as the working electrode and counter electrode, respectively. It should be noted that the reference electrode was a saturated calomel electrode (SCE) and prior to each measurement, the the electrolyte of 1M KOH+1M CH_3CH_2OH was bubbled by high pure nitrogen gas for at least 30 min to avoid the influence of oxygen dissolved in the solution. All the characterization techniques used in this work have been described in our previous work[2].

3. RESULTS AND DISCUSSION

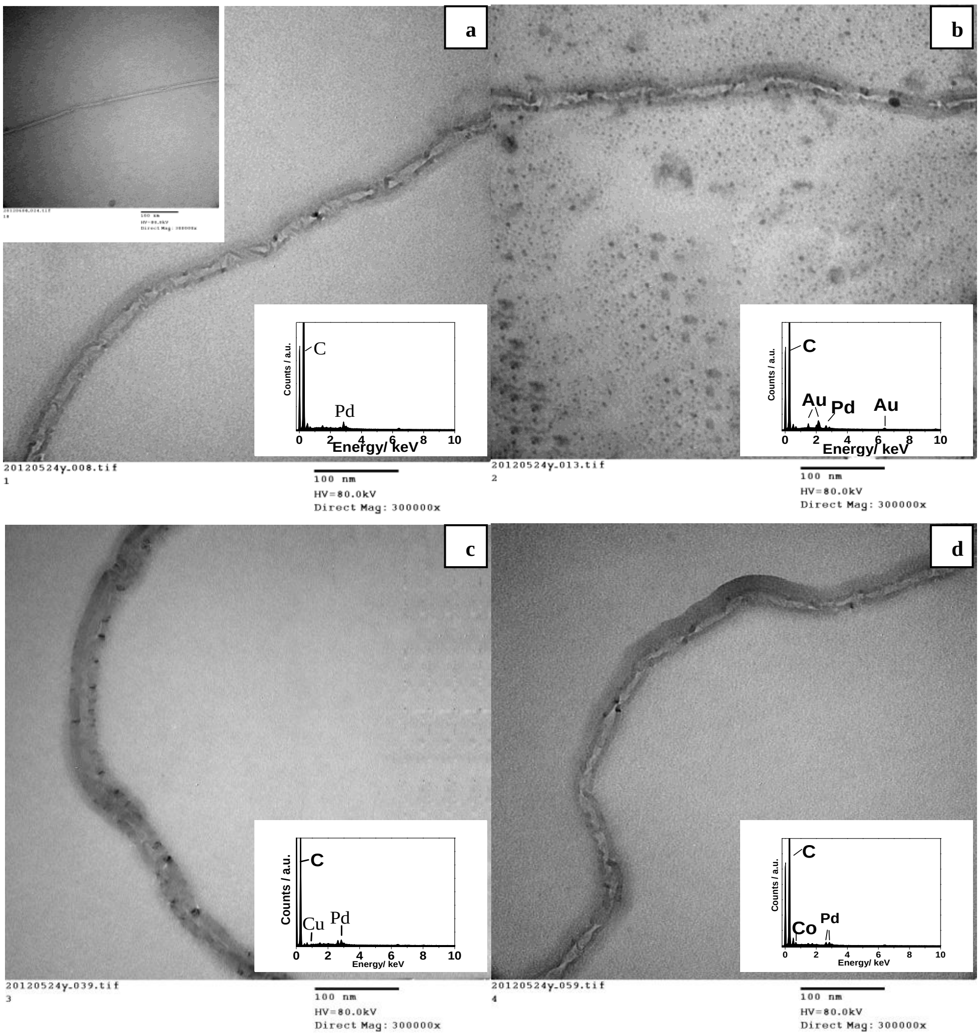

Figure 1. TEM images for the prepared samples. Image **a**: Pd/MWCNTs; image **b**: Pd_3Au_1/MWCNTs; image **c**: Pd_3Cu_1/MWCNTs; image **d**: Pd_3Co_1/MWCNTs. Inset of image **a** is the pure MWCNTs. The inset of each image is the corresponding EDS spectrum

Fig.1 is the TEM images for the typical samples prepared. For the pure MWCNTs, as shown by the inset of image **a**, no substances were found on the surface of MWCNTs. While after pyrolysis, for all the samples, some black dotts were formed on the surface of MWCNTs. For instance, for the catalyst of Pd/MWCNTs, as seen in image **a**, after pyrolysis, some black particles with a particle size ranging from 19 to 25 nm were found dispersing on the surface of MWCNTs. The localized EDS spectrum, as plotted by the inset of image **a**, strongly indicated that the particles are the Pd particles rather than other substances, being consistent with our previous report [1]. For the sample of Pd_3Au_1, interestingly, spherical particles are seen in the whole image **b**. According to the TEM measurement described, this result can only indicate that the formed particles can not be tightly anchored on the surface of MWCNTs. That is to say, in the ultrasonication procees before TEM detection, the particles immobilized on the surface of MWCNTs were released from the surface of MWCNTs. The localized EDS spectrum, as plotted by the inset in image **b**, indicates that these particles in image **b** have two main elements of Pd and Au, though the atomic ratio of Pd to Au was not 3:1. Interestingly, for the catalyst of Pd_3Cu_1/MWCNTs, as shown by image **c**, particles with a diameter ranging from 21 to 30nm are uniformly dispersed on the surface of MWCNTs.

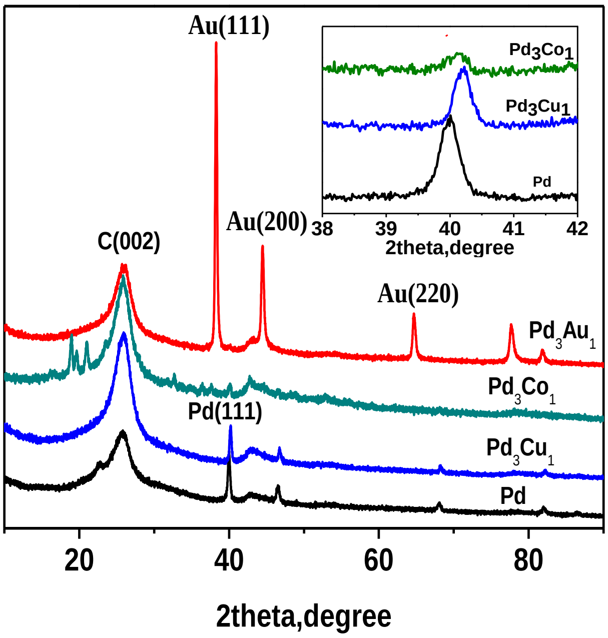

Figure 2. XRD patterns for samples prepared in RTILs of $[BMIM]PF_6$.

The elements of Cu and Pd can be found in the EDS spectrum, though the intensity of the peak corresponding to Cu is much smaller than that of Pd, as illustrated by the inset in image **c**. Also, for the sample of Pd_3Co_1/MWCNTs, carbon nanotubes decorated by some black particles are observed clearly. In this case, the particle size estimated from TEM images is from 23 to 26nm. These TEM images, shown in Fig.1, substantially demonstrated that the composite particles of Pd_3M_1 can be fabricated by this novel method. Before drawing a conclusion, the following points must be mentioned. First, the atomic ratio of Pd to M measured by EDS did not match the desired ratio of 3:1. Second, except for the main peaks corresponding to Pd and M, other elements such as O can also be observed in the EDS spectrum, therefore, the composite nanoparticles should be noted as quasi-bimetallic particles of Pd_3M_1 instead of pure Pd_3M_1.

The XRD patterns of the obtained samples are shown in Fig.2. The diffraction peak at 2θ of 26.1° is indexed to (002) planes of carbon nanotubes (CNTs), being in accordance with the previous report [1]. 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. The typical diffraction peaks in XRD pattern for Pd/MWCNTs corresponds to reported XRD pattern of Pd very well [1]. Interestingly, no phases of palladium oxides or hydroxides were found in the XRD pattern. It indicated that after the pyrolysis, only elementary Pd was prepared by the present method. As a result, only Pd nanoparticles were immobilized on the surface of MWCNTs. But for the sample of Pd_3Au_1, peaks corresponding to the planes (111), (200), (220), (311) located at 38°, 45°, 65°and 78°, respectively, were displayed clearly. It indicates that 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]. Interestingly, no phase of Pd was detected in this XRD pattern though Pd can be measured by EDS, probably it is due to the fact that the formed Pd particles have been covered by the newly-formed Au particles. Evidently, under the same conditions, the reduction abilities of the ions of Pd and Au are different from each other due to their various standard potentials. While, for the catalyst of Pd_3Co_1, except for the diffraction peak of carbon, no obvious peaks were found, probably indicating that the formed particles were amorphous in nature or crystalline only in very small region [14]. For the sample of Pd_3Cu_1/MWCNTs, the diffraction peaks at around 40°, 46°, 68°, and 82° can be assigned to the Pd(111), (200), (220), and (311), respectively[1]. Thus, the catalyst of Pd_3Cu_1 displays a typical face-centered cubic (fcc) pattern, similar to that of Pd very well. Close inspection, as magnified by the inset of Fig.2, revealed that the diffraction peak of Pd_3Cu_1 at around 40° shifted to a higher angle compared to that of Pd. Those shifts indicate that the Pd lattice was contracted by replacing fcc Pd atoms with Cu, thus, probably the catalyst of Pd_3Cu_1 was substitutional solid solutions. While for the catalsyt of Pd_3Co_1, the diffraction peak at 40° is too broad, though a shift to a higher angle comapred to the pure Pd was also observed.

Cyclic voltammograms (CVs) of EOR on the as-prepared catalysts coated GC electrode are illustrated in Fig.3. Compared to the peak currents displayed on the Pd/MWCNTs modified GC electrode, lowered peak currents are observed on the catalyst of Pd_3Au_1 and Pd_3Co_1. To one’s surprise, dramatically enhanced peak currents are displayed on the Pd_3Cu_1/MWCNTs-coated GC electrode. The peak current in the forward potential scan on Pd_3Cu_1 is almost 2 times larger than that on the Pd catalyst. The onset potential at the catalyst of Pd_3Cu_1 for the positive-direction peak is about 50mV negative than that on the Pd/MWCNTs coated GC electrode. It strongly indicated that Pd_3Cu_1 shows the best electrocatalytic activity toward EOR among all the prepared catalysts. To our knowledge, no paper addressing the catalysis of bimetallic Pd-Cu particles toward EOR was published.

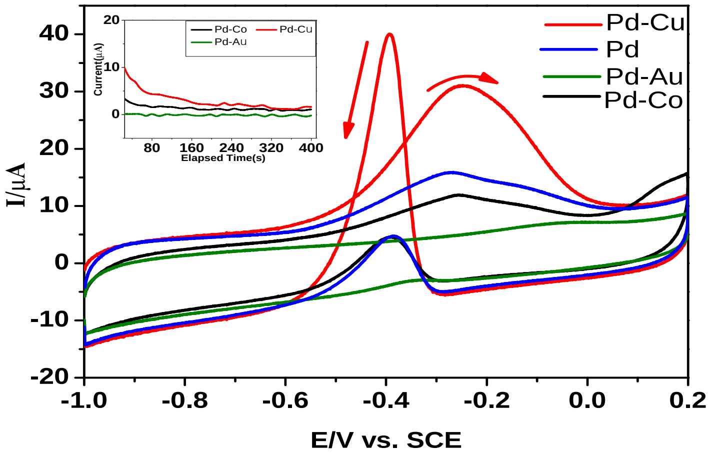

Figure 3. Cyclic voltammograms (CVs) obtained on the Pd_3M_1/MWCNTs-coated GC electrode in 1M KOH+1M ethanol at a scan rate of 50mV/s. Inset is the current-time curves obtained at the applied potential of -0.3V.

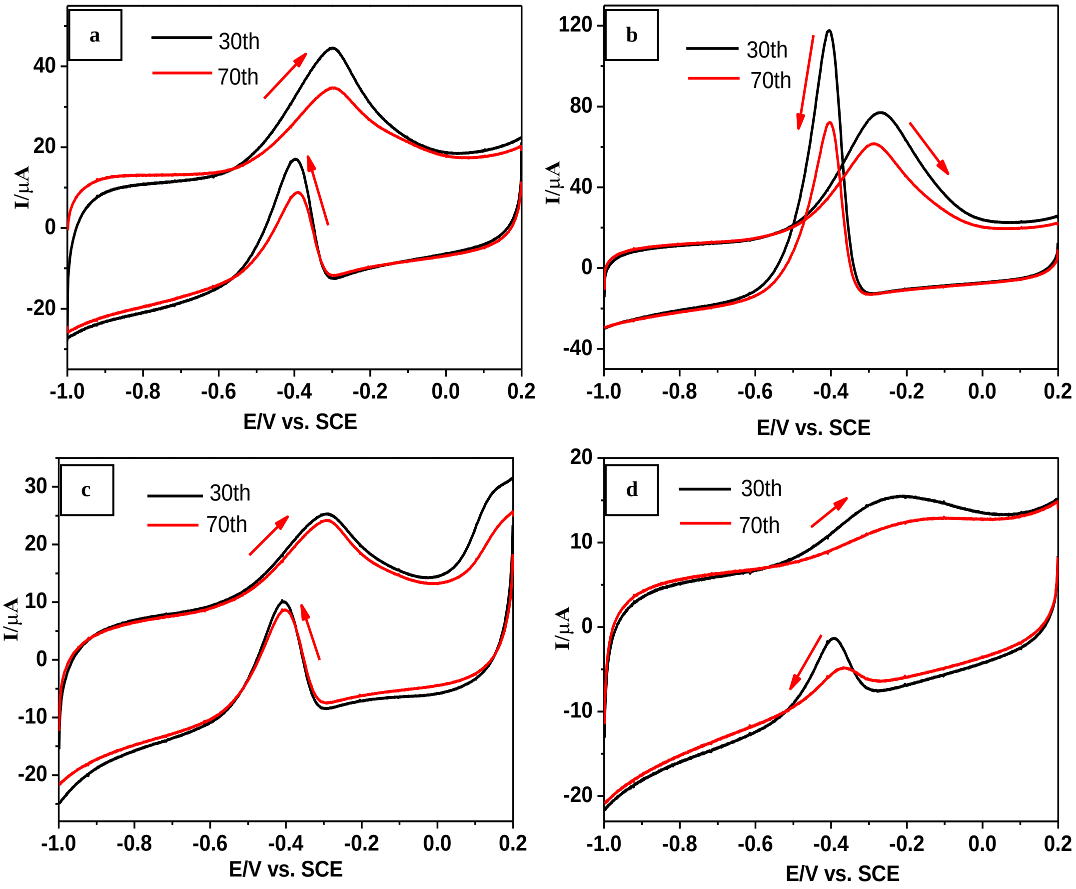

Figure 4. CVs obtained on the Pd_3M_1/MWCNTs-coated GC electrode in 1M KOH+1M ethanol at 30 and 70 cycles. Scan rate is 50mV/s. Fig.**a**, **b**, **c** and **d** were obtained on the Pd, Pd_3Cu_1, Pd_3Co_1 and Pd_3Au_1/MWCNTs modified GC electrode, respectively.

The electrocatalytic stability test for Pd_3Cu_1/MWCNTs, Pd_3Co_1/MWCNTs and Pd_3Au_1/MWCNTs catalysts for EOR were also carried out by the chronoamperometry technique at a potential of -0.3V (vs. SCE) in a deaerated 1M KOH+1M ethanol solution, and the corresponding results are shown in the inset of Fig. 3. It is evident that the Pd_3Cu_1 catalyst exhibites a higher initial current compared to the other catalysts, and the highest steady-state ploarization current was also displayed on it even after 400s duration.

In Fig.4, CVs at various potential cycles are presented, i.e, the black and red curves correspond to the 30th and 70th cycles, respectively. It can be seen that with the increase of potential cycles, all the peak currents are attenuated to some extent, indicating that the surface of the catalysts were more or less poisoned due to the adsorbed intermidiates formed in the oxidation process of ethanol[15]. Interestingly, for the catalyst of Pd_3Co_1/MWCNTs, the peak current at 70th cycles was not much lowered compared to that at 30th cycles. It greatly demonstrated that the catalyst of Pd_3Co_1 has a better tolerance to the poisoning by the intermediate products of EOR.

4. CONCLUSION

For the first time, three kinds of Pd based catalyst Pd_3M_1 were fabricated by a facile method of pyrolysis using RTILs as the solvent. TEM results indicated that nanoparticles with a particle size ranging from 20 nm to 30nm can be well anchored on the outer surface of MWCNTs. CVs of EOR revealed that among the samples Pd_3Cu_1 showed the largest peak current. Interestingly, after 70th cycles, the peak current of EOR displayed on the catalyst of Pd_3Co_1 was not much attenuated, suggesting that Pd_3Co_1 has the best tolerance to the poisoning caused by the intermediates appearing in the process of EOR. Developing a novel method for fabricating nanoparticles is the main contribution of this pioneering work. More detailed research will be released in the further work.

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