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# Self-assembly Synthesis of High-density Platinum Nanoparticles on Chemically Reduced Graphene Sheets

Wenbo Li, Dongyuan Zhai, Hao Qiu, Huan Pang, Lijia Pan,* and Yi Shi*
*National Laboratory of Microstructures (Nanjing), Key Laboratory of Advanced Photonic and Electronic Materials of Jiangsu Province, School of Electronic Science and Engineering, Nanjing University, Nanjing 210093, P. R. China*

(Received October 12, 2010; CL-100872; E-mail: ljpan@nju.edu.cn, yshi@nju.edu.cn)

Self-assembly was used to synthesize high-density Pt nanoparticles on chemically reduced graphene sheets (CRGSs). By employing 1-pyrenemethylamine (Py-$CH_2NH_2$) as the interlinker to form a self-assembled layer on the surface of graphene nanosheets via $\pi$–$\pi$ stacking, high-density Pt nanoparticles on CRGSs were obtained. The uniform and high-density Pt nanoparticle/CRGS composite may have potential in the fields of catalysis, surface-enhanced Raman spectra, and fuel cells.

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Graphene has attracted considerable attention since its discovery by Novoselov et al. in 2004.[1] The two-dimensional material exhibits many unique properties, such as high intrinsic electronic mobility at room temperature,[2] high mechanical strength,[3] large surface area, and thermal stability.[4] These properties provide potential applications in many fields, such as nanoelectronics, sensors, batteries, and catalysis.[5] Recently, graphene has gained interest as a catalyst carrier, having the advantages of excellent electrical conductivity and large surface area. Many efforts have been devoted to synthesizing noble metal nanoparticles on graphene. For example, Xu et al. synthesized Pt, Au, and Pd nanoparticles on graphene,[6] and Li et al. obtained a Pt/graphene composite using ethylene glycol as a reducing agent to directly reduce hexachloroplatinic(IV) acid and graphite oxide (GO).[7] This work has demonstrated that the Pt/graphene composite has good catalytic activity for the oxidation of methanol, which can be used in direct methanol fuel cells. However, Pt nanoparticles directly loaded on graphene have limited density and stability because of chemical inertia and the atomic smooth surface of graphene. Chemically reduced graphene sheets (CRGSs) are often used as the carrier, which have many unreduced groups and defects on the surface that can provide interaction sites for nanoparticles. However, the density, dispersion, and structural stability of the metal nanoparticles on graphene are limited by the quantity and random distribution of oxygen-containing groups and defects on the CRGS surface. To obtain high-density and highly dispersed Pt-loaded graphene composite, we introduced active amine group to load Pt nanoparticles by using 1-pyrenemethylamine (Py-$CH_2NH_2$) as the interlinker on the graphene surface, which can form a self-assembly layer on the surface of graphene via $\pi$–$\pi$ stacking interactions between the pyrene group and the graphene substrate.[8] The alkylamine tail group provides nucleation centers for the nanoparticles to anchor and grow on the surface, which can bind to a Pt nanoparticle through the lone pair of electrons on the nitrogen atom and also be helpful to enhance the stability of Pt on graphene sheets.[9] The schematic of the self-assembly structure is shown in Figure 1.

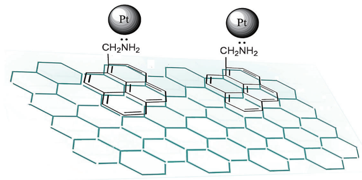

**Figure 1.** Schematic for the Pt nanoparticles loaded on graphene through using 1-pyrenemethylamine, a self-assembly molecule, as the interlinker.

A typical synthesis procedure is described as follows. First, GO was synthesized by Hummers' method,[10] and CRGSs were prepared by hydrazine reduction of GO[11] at 95 °C for 1 h. The synthesized CRGSs were then washed and freeze-dried. Next, 8 mg of CRGS were dispersed in 80 mL of ethylene glycol by ultrasonic agitation, followed by the addition of 12 mL of 0.001 M ethylene glycol solution of 1-pyrenemethylamine hydrochloride (95%, Aldrich). The solution was stirred for 30 min. Then, 0.8 mL of 0.048 M ethylene glycol solution of hexachloroplatinic(IV) acid was added to the mixture, followed by the addition of 0.1 M aqueous solution of sodium hydroxide to adjust the pH value to approximately 8–9. The mixture was place in an oil bath (ca. 160°) for 2 h under mild stirring. Finally, the product was washed with deionized (DI) water and ethanol. The composite was analyzed by transmission electron microscopy (TEM, JEOL JEM-2100), scanning electron microscopy (SEM, Hitachi S4800), and X-ray diffraction (XRD, Shimadzu XRD-6000, Cu K$\alpha$ radiation).

Figure 2 shows the morphologies of the as-synthesized Pt nanoparticles anchored on CRGS. As shown in Figure 2a, the Pt nanoparticles are uniformly dispersed on the CRGSs. The CRGSs are very thin because of the low contrast of the sample on the TEM image. It is clearly observed that the density of the particles is high, and the surface of the CRGSs has been covered by discretely dispersed Pt nanoparticles. The Pt content loading on the CRGSs was measured to be 27.5 wt % by inductively coupled plasma-atomic emission spectrometry (ICP-AES). As shown in Figures 2b and 2c, the Pt nanoparticles have diameters between 2 and 5 nm. The high-resolution TEM image in the inset of Figure 2a shows the oriented and ordered lattice fringes for Pt nanoparticles, the lattice fringe with a distance of 0.22 nm coincided with the (111) plane of Pt nanoparticles.

The XRD pattern of the synthesized Pt/CRGS composite is shown in Figure 3. The peak at the $2\theta = 25.0°$ is attributed to the (002) plane of graphitic carbon,[7] and no signal appears around 10.0° corresponding to the characteristic diffraction peak (002) of GO,[12] which indicates that GO has been reduced. The four strong diffraction peaks at the $2\theta$ of 39.8, 46.3, 67.7, and 81.7° correspond to the characteristic (111), (200), (220), and (311) crystalline planes of the Pt crystal, indicating its face-centered cubic structure. From the XRD data, the size of Pt particles is

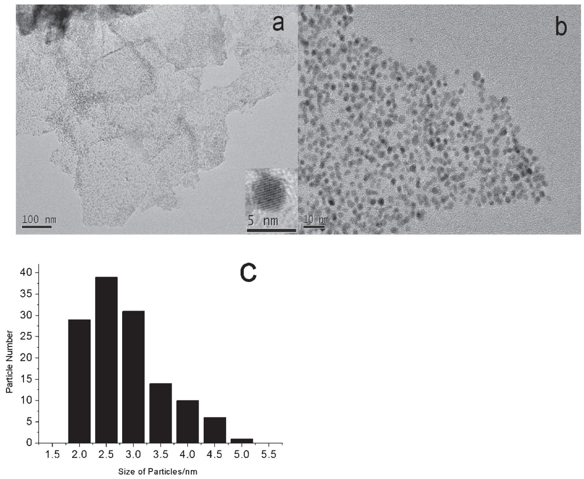

**Figure 2.** (a) TEM image of Pt nanoparticles on CRGS, scale bar: 100 nm; Inset: high-resolution TEM image, scale bar: 5 nm; (b) magnified TEM image shows uniformly dispersed high-density Pt nanoparticles loaded on graphene, scale bar: 10 nm; (c) the size distribution of the Pt nanoparticles.

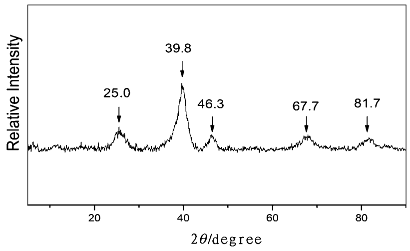

**Figure 3.** XRD patterns of Pt/CRGS composite.

estimated to be around 3 nm by the Debye–Scherrer equation, which is consistent with the result obtained from the TEM observation.

To further affirm the formation of the self-assembly layer and the interlinker role of Py-$CH_2NH_2$, SEM was used to conduct the element mapping of the characteristic element, and Pt/CRGS composite was synthesized without Py-$CH_2NH_2$ for comparison under the same conditions. Figure 4a shows the initial SEM image of a Pt/CRGS composite. As shown in Figure 4b, the imaging of the element C shows the main frame of the sample, which is consistent with Figure 4a. The element mapping of N in Figure 4c shows the position of Py-$CH_2NH_2$ in the composite, although the signal of N can be seen in the whole image, a clear profile can be observed, within which the signal is more intense than that of the circumstance. Accordingly, it is reasonable to deduce that Py-$CH_2NH_2$ has formed a self-assembled layer on the surface of CRGS. Figure 4d shows the TEM image of the comparison sample of Pt/CRGS without Py-$CH_2NH_2$. The area shown in the image is inside a large CRGS, and the dark area indicates the Pt nanoparticles. It is obvious that the density of Pt on CRGS is much less than the composite synthesized using Py-$CH_2NH_2$ as the interlinker. The Pt nanoparticles form domains and cannot form a uniform distribution on CRGS. As shown in Figure S1 in Supporting Information,[13] the size of the particles synthesized under the same conditions is close to that prepared with Py-$CH_2NH_2$, but more Pt nanoparticles link together which indicate that the presence of Py-$CH_2NH_2$ can improve the morphology and distribution of Pt particles.

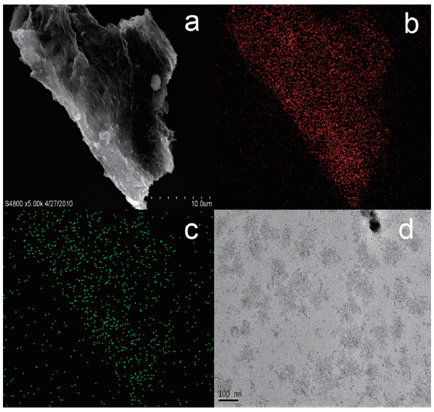

**Figure 4.** (a) SEM image of Pt/CRGS composite; the scale bar is 10 µm, (b) element mapping of C, (c) element mapping of N. (d) TEM image of Pt/CRGS without Py-$CH_2NH_2$, scale bar: 100 nm.

In conclusion, Pt/CRGS composite was synthesized by using Py-$CH_2NH_2$ as the interlinker. Py-$CH_2NH_2$ formed a self-assembled layer on the surface of graphene via $\pi$–$\pi$ stacking interactions between the pyrene group and CRGS. The alkylamine group of the self-assembly molecule provided nucleation centers for the growth of the Pt nanoparticles. High-density and highly dispersed Pt nanoparticles on CRGSs were obtained by this self-assembly synthesis route. The method does not require oxidized groups and defects on the surface to provide interaction sites for nanoparticles; therefore, it can also provide a potential for using wholly pristine graphene to load high-density noble metal nanoparticles.

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13 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.