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Benzylamine-Assisted Noncovalent Exfoliation of Graphite-Protecting Pt Nanoparticles Applied as Catalyst for Methanol Oxidation

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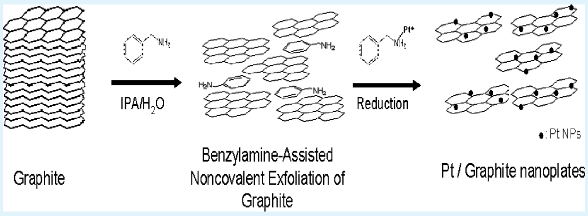
ABSTRACT: A novel method has been developed to physically exfoliate graphite and uniformly disperse Pt nanoparticles on graphite nanoplates without damaging the graphene structures. A stable aqueous suspension of graphite nanoplates was achieved by benzylamine-assisted noncovalent fuctionalization to graphite and characterized by transmission electron microscopy, X-ray diffraction and Raman spectroscopy. A uniform dispersion of Pt nanoparticles was then prepared on the graphite nanoplates, where the benzylamine acts as a stabilizer. These Pt loaded graphite nanoplates were then prepared as an electrode, which significantly increased catalytic activity toward the methanol oxidation reaction, resulting in a 60% increment in mass activity compared to that of E-TEK.



KEYWORDS: benzylamine, noncovalent, exfoliation, graphite, catalyst, oxidation

As a two-dimensional carbon nanomaterial, graphene has attracted great attention because of its outstanding mechanical, thermal, and electronic properties.[1−5] The most commonly used form of graphene is graphite nanoplates, which are composed of a few layers of graphene sheets stacked together. The graphene is usually produced by the exfoliation of graphite via an oxidation reaction, followed by sonication to isolate graphite nanosheets and give aqueous dispersions of graphene oxide (GO).[6−9] However, this method is complicated, and GO is a poor electrical conductor because the disruption in the π-orbital structure on the oxidation process often damages their structure.[10,11] Noncovalent fuctionalization has successfully been carried out for carbon nanotubes[12−17] and is also of interest for the solubility of graphene.[18−21] To address these issues, Coleman et al.[18,19] and others groups[20,21] have developed methods to exfoliate graphite in the liquid phase without oxidation or defect formation using special solvents or surfactants. However, the solvent-exfoliated graphene faces some significant disadvantages. These solvents, such as N-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO) and N,N′-dimethyl-formamide (DMF), need special handling and careful treatment during and after usage.[22−24] Recently, graphene or GO-based materials have been used to serve as catalyst support and could be alternatives to carbon nanotubes and carbon black to act as a carbon support for fuel cells.[25−28]

In this research, it is found that 0.05% benzylamine added in isopropanol (IPA)/H_2O acts as a noncovalent penetrator to very effectively exfoliate graphite without damaging any graphene structures. Meanwhile, benzylamine also functionally acts as a stabilizer to prepare Pt^0 nanoparticles between graphite nanoplates. The synthesis of benzylamine-assisted exfoliation of graphite nanoplates (BGN) supporting Pt nanoparticles (Pt/GN) is shown in Fig 1. First, the BGN was achieved by using IPA/H_2O as a cosolvent and subjected to an ultrasonic condition. Here, the benzylamine containing a benzene ring and an amino group may penetrate inside the layers of graphite and exfoliate them. Then aromatic π electrons can interact with the conjugated π electrons on the graphite surface through $\pi-\pi$ interaction, while the polar amino group interacts with a polar solvent in the meantime. Therefore, benzylamine can be regarded as an amphiphilic molecule to disperse graphite nanoplates in a polar solvent. Similar results are also found in the literature.[29] As benzylamine is positively charged because of the protonation of its amino group, it is expected that the resulting BGN can be decorated with negatively-charged nanoparticles by electrostatic attractive interaction.[30−33]

TEM was used to study the morphology and the states of the graphite nanoplates dispersion. Fig 2a shows that the raw graphite exists mainly as large, dark, and thick flakes with diameter of about 2−5 μm. Under the extended duration of sonication in IPA/H_2O without benzylamine (Figure 2b), solvent-exfoliated graphite nanoplates are observed with diameters of about 1−2 μm. The top view of the graphite nanosheets clearly shows that they are still stacking together. With the addition of benzylamine, the graphite is found to be dispersed into thin graphite nanoplates, which resemble silk veil with a reduced diameter of 100−300 nm (Figure 2c) accompanied by some nanoplates not yet fully exfoliated. The above method describes a convenient procedure to transform graphite into highly exfoliated graphite nanoplates. Raman spectroscopy, which is highly sensitive to the electronic structure and the defect level of the graphene structure, can be compared via the D-band (1350 cm^{-1}) to G-band (1580 cm^{-1}) intensity ratio (I_D/I_G), as shown in Figure 2d. The I_D/I_G value for graphite and BGN are 0.38 and 0.49, respectively, suggesting that the

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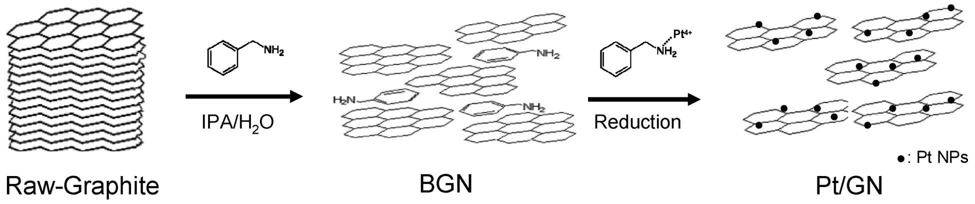

Figure 1. Synthetic procedure of Pt/GN.

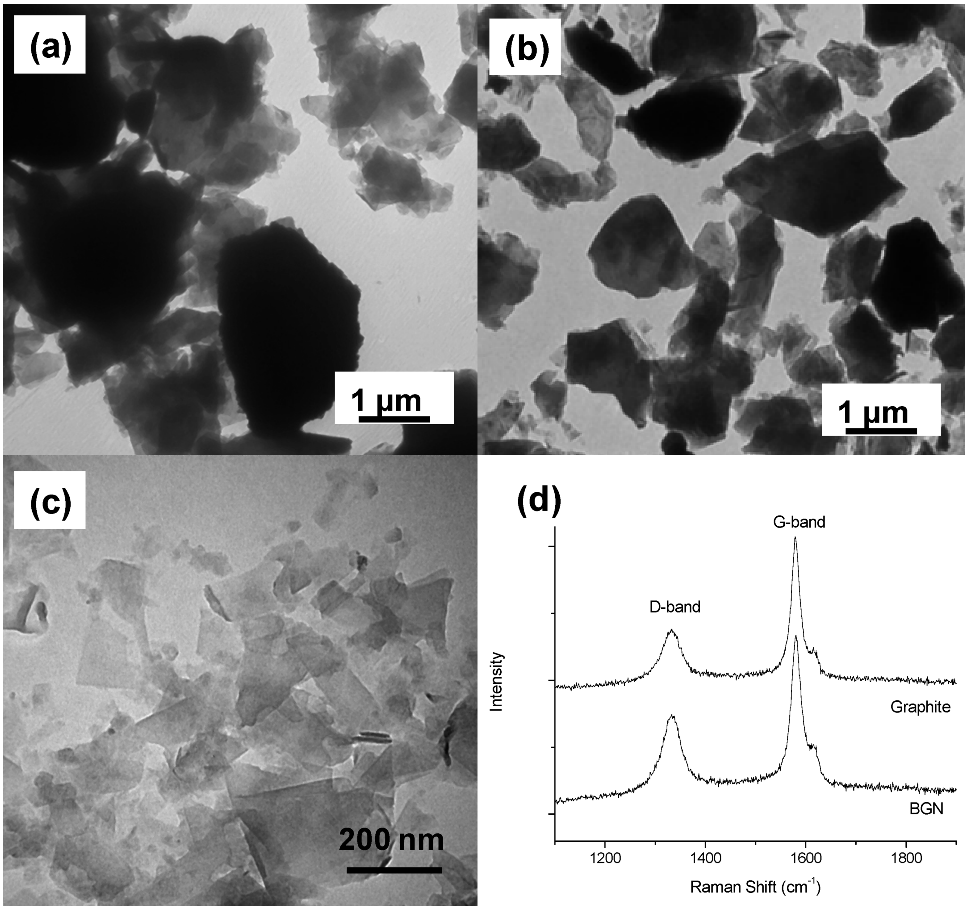

Figure 2. TEM images of (a) graphite, (b) IPA/H_2O exfoliated graphite, and (c) BGN; (d) Raman spectra of graphite and BGN.

extended ultrasonic condition introduces defects associated with new edges.[18]

In this study, Pt nanoparticles deposited on graphite nanoplates (Pt/GN) were prepared from Pt^{4+} using benzylamine as a protector. After hydrogen reduction at 400 °C for four hours, the Pt nanoparticles were formed and well-dispersed on the surface of the graphene nanoplates, as shown in the TEM images (Figure 3a). The particle size of Pt nanoparticles is small and uniform, with sizes of 4.9±2.1 nm on the graphite nanoplates. Without benzylamine (Pt/GN-x), the Pt nanoparticles on the IPA/H_2O exfoliated graphite nanoplates agglomerate with diameters of 12.2±4.4 nm, as shown in Figure 3b. From this result, it is clear that benzylamine effectively protects Pt nanoparticles on graphite nanoplates during reduction at 400 °C. XRD analysis was used to further investigate the change in size of Pt nanoparticles on the carbon support, as shown in Figure 3c. The diffraction peak at 54.3° is attributed to the (004) reflection of the graphite structure, while the peaks at 39.6, 46.1, 67.3, and 81.2° correspond to the Pt (111), Pt (200), Pt (220), and Pt (311) planes of a face-centered cubic (FCC) lattice, respectively. The Pt/GN using benzylamine as stabilizer produces significantly broader peaks of Pt (111) and Pt (200) than those prepared without benzylamine. This indicates that Pt/GN is much smaller on graphite nanoplates when benzylamine is added as a stabilizer. The obtained grain sizes of the Pt/GN and Pt/GN-x samples are 5.8 and 13.2 nm, respectively, which are parallel to those obtained by TEM. For the cyclic voltammograms (CV) of the Pt/C catalyst under N_2 saturated 0.1 M $HClO_4$ aqueous solution (Figure 3d), the electrochemical active surface area (EAS) was 58.9 and 66.6 $m^2\ g^{-1}$ for Pt/GN and commercial 20 wt % Pt/XC-72 catalyst (E-TEK), respectively. The lower EAS value of Pt/GN can be attributed to the larger particle size than E-TEK.

In this study, the Pt^0/GN has shown a powerful catalytic ability toward methanol oxidation as Pt^0/GN was used to

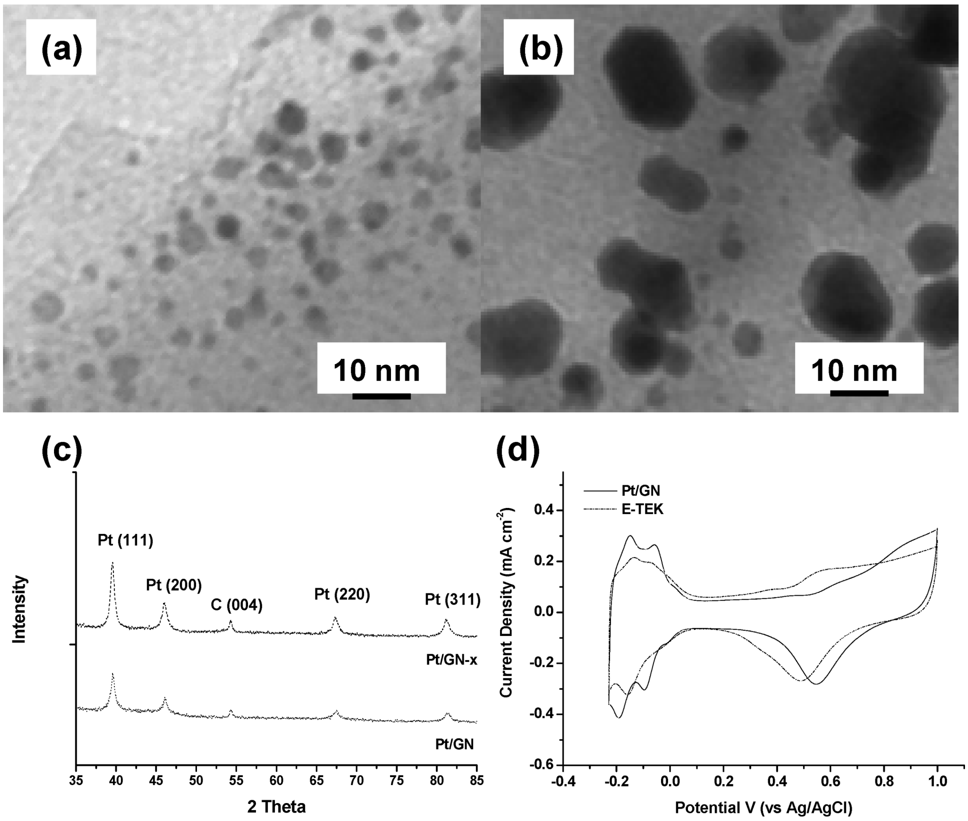

Figure 3. TEM images of (a) Pt/GN, (b) Pt/GN-x; (c) XRD patterns of the graphite, Pt/GN-x, and Pt/GN; (d) the CV curves of Pt/GN and E-TEK at a scan rate of 20 mV s^{-1} in 0.1 M $HClO_{4(aq)}$ solution.

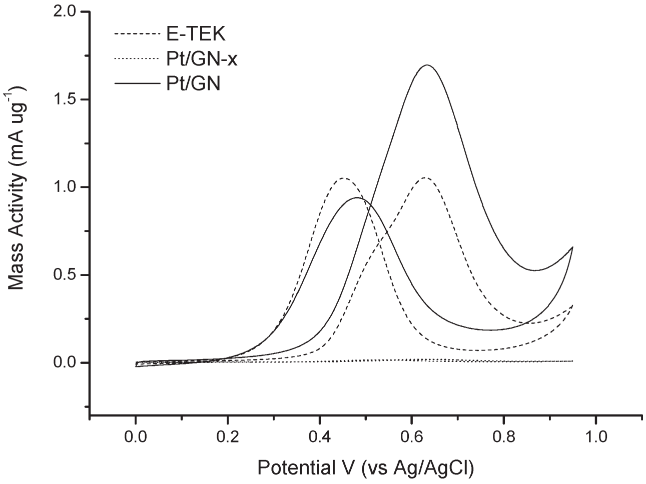

Figure 4. CV curves of E-TEK, Pt/GN-x, and Pt/GN at a scan rate of 20 mV s^{-1} in 1.0 M MeOH+0.5 M H_2SO_4.

prepare an electrode. The performance of the methanol oxidation reaction was measured by a glassy-carbon rotating disk electrode system. Voltammetric curves under N_2 saturated 0.5 M H_2SO_4 and 1.0 M MeOH aqueous solution at room temperature are shown in Figure 4, where the amount of Pt catalyst for Pt/GN-x, Pt/GN and Pt/XC-72 (E-TEK) were 1.2, 2.8, and 2.0 μg, respectively. The maximum mass activity (I_{max}) during methanol oxidation were measured from voltammetric curves and found to be 0.02 mA μg^{-1} for Pt/GN-x, 1.70 mA μg^{-1} for Pt/GN and 1.05 mA μg^{-1} for Pt/XC-72 electrode. The low value in I_{max} for Pt/GN-x is due to its large Pt particle size. The I_{max} for Pt/GN was 60% higher than that of E-TEK even with a little larger particle size. The significant increment is most likely related to the strong interaction between Pt and graphene, induced by the modulation in the electronic structure of the Pt clusters.[26]

In conclusion, benzylamine-assisted noncovalent exfoliated graphite nanoplates have been successfully prepared using benzylamine as a dispersant in an IPA/H_2O solution. Small and uniformly dispersed Pt nanoparticles (4.9±2.1 nm) were then anchored on the surface of exfoliated graphite nanoplates, where benzylamine acts as the stabilizer. Pt/GN shows powerful catalytic activity toward the methanol oxidation reaction as it was prepared into an electrode, resulting in a 60% enhancement of mass activity compared to that of E-TEK.

■ EXPERIMENTAL SECTION

Benzylamine-Assisted Noncovalent Exfoliated Graphite Nanoplates. To prepare exfoliated graphite nanoplates (GN), 30 mg of graphite powder (99.9 % pure, catalog no. 28286-3, Aldrich) and 0.10 g of benzylamine were dispersed in an isopropyl alcohol (IPA)/water solution (10 ml/10 ml) by sonication for various periods from 1 h to 120 h. Then a well-dispersed benzylamine-assisted noncovalent exfoliated graphite nanoplates (BGN) in IPA/water were obtained. In this work, we used one sonication bath, which had a power output of 23 W.

Loading of Pt Nanoparticles on Graphite Nanoplates. A solution containing 10.0 g of IPA and 10.0 g of deionized water had 30 mg of graphite nanosheets and 0.0420 g of benzylamine added (the molar ratio of benzyl amine to Pt was 10:1), and was stirred for 1 h. Then, 0.47 mL of Pt solution (0.082 M) was added into the benzylamine-assisted graphite nanoplates exfoliation suspension and stirred for 3 h at room temperature. After filtration and drying the sample in a vacuum at 70 °C overnight, the sample was then heated at 400 °C in a quartz-tube furnace with flowing argon and hydrogen gas (1:1) for 4 h. For comparison purposes, we also synthesized Pt particles on IPA/H_2O exfoliated graphite nanoplates without using benzylamine (Pt/GN-x), the results of which are presented in the discussion section.

Characterization. Transmission electron microscopy (TEM) was conducted using a Hitachi H-7500 microscope operating at 120 kV. X-ray powder diffraction (XRD) was performed on a Rigaku RINT2100 X-ray diffractometer with $\mathrm{Cu-K_\alpha}$ radiation operated at 40 kV and 30 mA. A micro Raman spectrometer from Renishaw with a He−Ne laser source with a wavelength of 633 nm was used to determine the structure of graphite. A CHI-608A potentiostat/galvanostat and a conventional three-electrode test cell were used for electrochemical measurement. The CV test was performed on the working electrode by cycling the voltage between −0.25 and 0.95 V versus Ag/AgCl electrode in 0.1 M $HClO_4$ solution. The scan rate was 20 mV s^{-1}.

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