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Chemically converting graphene oxide to graphene with organic base

for Suzuki reaction

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Graphical Abstract

Highlights

- Chemically converted graphene (CCG) was made by deoxygenation of graphene oxide with organic bases.
- The dissociation constant of organic bases determines the structure of CCGs.
- Pd/CCG catalyst shows high reactivity and good recyclability for Suzuki reaction.

Abstract: Chemically converted graphene has been synthesized via the reduction of graphene oxide by using organic bases, including 1,8-diazoicyclo (5, 4, 0) undecene-7, triethylamine and 1,4-diazobicyclo (2, 2, 2) octane, as the reducing agent. The chemical characteristics of these organic bases, especially the dissociation constants (pKa), have great influence on the structure and properties of the resultant CCG. Remarkably, the reaction between graphene oxide and some organic bases such as 1,8-diazoicyclo (5, 4, 0) undecene-7 can modify the surface properties of chemically converted graphene for anchoring Pd nanoparticles. The resultant recyclable catalyst exhibits high conversion of 97.2 % for yielding biphenyl from coupling bromobenzene and phenylboronic acid. Even after the 5th run, the conversion of bromobenzene can still be as high as 94.2 %, indicating excellent recyclability of this catalyst. **Keywords:** A. Nanostructures; B. Chemical synthesis; C. Catalytic properties

1. Introduction

Graphene, an one-atom thick sheet made of hexagonally arrayed *sp*²-carbon atoms, has received great interests across the world due to its unique 2D structure and extraordinary physiochemical properties[1-6]. To meet the surging demand of myriad applications, various methods such as micromechanical exfoliation of graphite [7], chemical vapor deposition (CVD) [8, 9], epitaxial growth on electrically insulating surface [10] have been developed for the synthesis of high-quality graphene in terms of different principle. However, these methods usually yield very low quantity of the graphene by using specific equipment. Chemical oxidation/exfoliation of graphite in solution remains so far the most promising route towards mass production of graphene oxides (GO) in virtue of the high throughput, low processing cost and the feasibility for chemical functionalization [11, 12]. Treated by various reducing agents, including the hydrazine [11, 13], sodium borohydride [14], alcohols [15], vitamin C [16], reducing sugar [17], or even inorganic bases such as NaOH and KOH [18, 19], chemically converted graphene (CCG) can be further obtained in large quantities via the deoxygenation of GO in solution. Nevertheless, efficient synthesis of CCG is still a big challenge towards its practical applications in many areas such as catalysis.

In this work, we report a facile solution method for the synthesis of CCG by the reaction of GO with organic bases as the reducing agent at low temperature. Organic bases with various molecular structures and properties, including 1,8-diazoicyclo (5, 4, 0) undecene-7 (denoted as DBU) [20], triethylamine (denoted as TEA) [21] and 1,4-diazobicyclo (2, 2, 2) octane (denoted as DABCO) [22] are chosen because they are able to provide feasible alkaline environment for the deoxygenation of GO in solution. The structure and properties of the resultant CCGs are found largely depended on chemical characteristics of organic bases, especially the dissociation constants (pKa) value.

Specifically, the reaction between GO and DBU can simultaneously modify the surface properties of CCG with N-(3-aminopropyl)-caprolactam (NAPC) [23], the hydrolysis product of DBU, for chemical binding Pd nanoparticles, giving rise to an efficient and recyclable catalyst for Suzuki cross-coupling reaction. In Pd/CCG catalysts, the strong interaction between Pd nanoparticles and CCG could reduce the Pd leaching for better recyclability. The unique 2D morphology further also allows them to be readily recovered from the solution by filtration, which greatly reduced the processing cost. With Pd/CCG catalyst, high conversion of 97.2 % is achieved for yielding biphenyl from coupling bromobenzene and phenylboronic acid. Even after the 5th run, the conversion of bromobenzene can still be as high as 94.2 %, indicating excellent recyclability of the catalyst.

2. Experimental

2.1 Material synthesis

Synthesis of graphene oxide (GO): GO was prepared by a modified Hummers' method reported elsewhere [24, 25]. Typically, 5 g of graphite powder, 25 mL of 98 % H₂SO₄, 5 g of P₂O₅ and 5 g of $K_2S_2O_8$ was mixed at 80 °C for 4.5 h under constant stirring, yielding pre-oxidized graphite powder after washing with water and dried at 80 °C for 12 h. The pre-oxidized graphite powder was dispersed in 360 mL of 98 % H₂SO₄, followed by adding 25 g of KMnO₄ under vigorous stirring. After stirring in ice-water bath for 2 h, 350 mL of deionized water was carefully added into the mixture under continually stirring at 35 °C for 2 h. Then 500 mL of water and 20 mL of H₂O₂ solution (30 wt. %) was subsequently added in to the mixture solution, resulting in a golden suspension that was centrifuged to remove the residual ions to get aqueous suspension of GO before freeze drying.

Synthesis of the CCGs: 100 mg of GO was dispersed in 200 mL of deionized water under ultrasonic, followed by adding 2 mmol of organic base (TEA, DBU or DABCO). The mixture was then kept at 95 °C for 24 h under constant stirring. During this process, the suspension turns to black from brown. The as-prepared products, denoted as TEA-CCG, DBU-CCG and DABCO-CCG, were washed to reach neutral before use.

Synthesis of Pd/DBU-CCG: As-prepared DBU-CCG was firstly dispersed in 200 mL water with 0.05 mmol Na₂PdCl₄, followed by adjusting the pH value to 10 with 2 M NaOH. After stirred overnight, 125 mL of ethylene glycol was added into the solution and the mixture was stored at 100 °C for 6 h in N₂. The as-prepared products were harvested by several filtration-rinsing cycles with water and ethanol.

2.2 Catalysis reaction

Aryl bromide (0.5 mmol, 1 equiv), phenyl boronic acid (0.75 mmol, 1.5 equiv), K_2CO_3 (1.5 mmol, 3 equiv) and Pd/DBU-CCG catalyst (0.5 mol %) were dissolved in a mixture of 8 mL of H_2O : EtOH (1:1 in volume) in a 20 mL glass reactor, which was sealed with a Teflon screw cap and stirred at 80 °C for the time indicated. The conversion of bromobenzene was analyzed by gas chromatography (GC) with octane as interior label. For 4-bromoanisole or 4-bromobenzonitrile as substrate, upon the completion of the reaction period, the reaction mixture was added to brine (15 mL) and extracted with ethyl acetate (3×15 mL). The organic solvent was removed under vacuum, and the product was isolated by short-column chromatographyusing petroleum ether:ethyl acetate as the eluent to calculate the isolated yield.

2.3 Characterization and measurements

The samples were characterized by FEI TF30 transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250), Fourier transform infrared spectrometer

(FT-IR, Bruker Equinox 55) and X-ray diffraction (X'Pert Philips Materials Research Diffractometer, Cu Kα). An oxford X-MAX 20 energy dispersive spectrometer (EDS) was used to get elemental mapping data. Raman spectra were recorded from 1000-3000 cm⁻¹ on a DRX Raman Microprobe (Thermo Fisher Scientific, America) using a 532 nm He-Ar ion laser. UV-vis spectroscopy was carried out with a JASCO V-550 UV-vis spectrometer from 200~600 nm. The electrical conductivity of different samples was tested using a SX1934 four probe testing system. The Pd contents in the catalysts were determined using Inductive Coupled Plasma Spectrometry (ICP, Optima 2000 DV, Perkin Elmer, America). Resonance (¹H NMR) spectra were recorded on a Varian Inova 400 spectrometer using CDCl₃ as solvent. The products of catalytic reactions were analyzed by HP 6890 gas chromatography (GC) using a HP-5 capillary column.

3. Results and discussion

The CCG made from different organic bases such as DBU, TEA and DABCO is denoted as DBU-CCG, TEA-CCG and DABCO-CCG, respectively. During the reaction with organic bases, all GO solution exhibit significant color change from brown to dark, indicating the successful deoxygenation of GO. X-ray powder diffraction (XRD) analysis shows that for DBU-CCG and TEA-CCG, no diffraction peaks from GO appear due to effective deoxygenation of GO, whereas a weak peak at 13.3° can still be identified for DABCO-CCG (see the inset in Fig. 1a). The removal of oxygen-containing groups in all CCGs is confirmed by Fourier transform-infrared spectroscopy (FT-IR), as shown in Fig. 1b. For GO, the absorption peaks at 1720 cm⁻¹, 1390 cm⁻¹, 1224 cm⁻¹ and 1059 cm⁻¹ can be ascribed to stretching vibrations of C=O, -OH, carbonyl C-O and epoxy C-O bonds, respectively. The absorption peaks at 3000-3600 cm⁻¹ correspond to O-H stretching vibrations of hydroxyl groups on GO surface and adsorbed water molecules. After deoxygenation with organic

bases, the intensity of these peaks is suppressed, indicating the partial removal of oxygen-containing groups from GO. Specifically, the intensity of the peaks from epoxy C-O bonds at 1059 cm⁻¹ has been greatly suppressed for all CCGs by effective removal of epoxy groups from GO surface. For DBU-CCGs, the intensity of the peak from stretching vibrations of C=O bond at 1720 cm⁻¹ is also reduced, indicating the strongest capability of DBU towards deoxygenation of GO. The C-H stretching vibration peak at 2930 cm⁻¹ in DBU-CCG can be assigned to stretching vibrations of C-H bonds of N-(3-aminopropyl)-caprolactam (NAPC), the hydrolysis product of DBU. To gain an insight into the effect of organic bases on chemical properties of CCG, DBU-CCG, TEA-CCG and DABCO-CCG is examined by UV-vis absorption spectroscopy, as shown in Fig. 1c. For GO, two absorption peaks appear at about 228 nm and 305 nm, corresponding to π - π * and n- π * transition of aromatic C=C and C=O bonds, respectively.[26] After deoxygenation, the peaks at 228 nm shift to nearly 260 nm for all the CCGs while the peaks at the wavelength of 305 nm disappear due to partially restored electronic conjugation of graphene sheets. Raman spectra also reveals the variation of GO in structure after deoxygenation, as shown in Fig. 1d. The spectra of GO exhibits two distinctive bands at 1357 cm⁻¹ and 1587 cm⁻¹, corresponding to the vibrations of sp³ carbon atoms of defects, namely the disorder band (D band), and the first-order scattering of the E_{2g} mode for sp^2 carbon lattice (G band), respectively.[27] The intensity ratio of the D and G bands (I_D/I_G) of GO is 0.91, while that of DBU-CCG, TEA-CCG and DABCO-CCG is increased to 1.18, 1.09 and 1.04, respectively. The increased I_D/I_G value reveals the generation of large quantities of disordered structure in CCGs after deoxygenation. However, the significant improvement in electrical conductivity, from insulation for GO to 0.01-0.14 S m⁻¹ for CCGs, suggests the significant recovery of conjugated graphitic structure in graphene (Table 1). This phenomenon can be ascribed to the

formation of numerous graphitic domains with short-range ordering in graphene lattice,[11] which is not uncommon for most of the CCGs produced by chemical approaches.[14-17, 28]

XPS is further employed to distinguish surface characteristics of all the CCG and GO in detail, as shown in Fig. 2. A full scan reveals the presence of C and O in all samples. However, the intensity of O 1s peaks for CCG is significantly reduced in comparison to that of GO. N 1s signals are also detected with N/C atomic ratio of 0.05, 0.01 and 0.015 for DBU-CCG, TEA-CCG and DABCO-CCG, respectively. For DBU-CCG, the high N content can be ascribed to the adsorption of hydrolysis product (NAPC, N-(3-aminopropyl)-caprolactam) of DBU on graphene surface [23, 29]. In C1s spectra, the intensity of the peak corresponding to sp^2 -hydridized carbon (at 284.6 eV) increases continually from GO to DABCO-CCG, TEA-CCG and DBU-CCG while the change of oxygen signals (286.7 eV for C-O, 287.4 eV for C=O and 288.5 eV for O-C=O group) is in opposite trend (Fig. 2) [11]. This observation is consistent with XRD and FT-IR results, revealing partial restoration of the conjugated graphene sheets via partially removal of oxygen-containing groups from GO in the presence of organic bases. Remarkably, the C/O atomic ratio in CCG increases from 2.41 (GO) to 3.73 (DABCO-CCG), 3.93 (TEA-CCG) and 5.00 (DBU-CCG), corresponding to an increase in pKa value of organic bases from 8.8 (DABCO) to 10.7 (TEA) and 12.0 (DBU). It implies that the organic base with higher pKa value could generate more feasible alkaline environment in solution, which may facilitate the deoxygenation of GO by repulsing and separating the oxidative debris from underlying graphene sheets [19, 30]. For DBU-CCG, high-resolution XPS N 1s spectrum of DBU-CCG shows the presence of secondary and tertiary amines of NAPC, as characterized by the peaks at 400.1 and 399.5 eV, respectively [31].

The morphology and microstructure of GO and all the CCG is characterized by transmission electron microscopy (TEM), as shown in Fig. 3. They feature with wrinkled nanosheets in shape

without significant difference in shape. However, for DBU-CCG, the presence of NAPC on its surface makes it especially feasible to anchor foreign materials via chemical bonding to N-containing sites. For example, DBU-CCG can be employed as the support for anchoring Pd nanoparticles with uniform size distribution of around 2.0 nm and homogenous dispersion, as shown in Fig. 4a and Fig. 4b. Elemental mapping (Fig. 4d-f) and XPS analysis (Fig. 2f) also reveals the presence and uniform distribution of Pd nanoparticles on CCG sheets. In XPS spectra, the presence of metallic Pd(0) is indicated by the peaks at 335.7 and 340.7 eV [32]. The Pd 3d_{5/2} and 3d_{3/2} peaks are also observed at 337.7 and 343.1 eV due to the oxidation of Pd nanoparticles in air [33]. ICP measurement shows that the loading amount of Pd is ca. 4.4 wt.%. For the catalysis of Suzuki cross-coupling reaction, 0.5 mol % Pd/DBU-CCG catalyst is used. The conversion of bromobenzene is 97.2 % within 30 min for coupling it with phenylboronic acid to yield biphenyl at 80 °C, as shown in Fig. 4h. Remarkably, Pd/DBU-CCG catalyst can be readily recovered by several filtration-rinsing cycles with ethanol and water for reuse with a slight degradation in performance. After the 5th run, the conversion of bromobenzene can be as high as 94.2 %. Without using the catalyst, however, no reaction occurs in the blank test due to the absence of Pd nanoparticles. Apparently, Pd/DBU-CCG catalyst has shown excellent catalytic properties and good recyclability towards Suzuki cross-coupling reaction.

The range of catalytic utility in Suzuki cross-coupling reactions for the preparation of other biphenyl products containing a broader range of functionality was investigated. As illustrated in Table 2, the Suzuki coupling of variously substituted aryl bromide and phenyl boronic acid reagents was carried out in 1 h at 80 °C. The yield for 4-phenylbenzonitrile could be as high as 99.5 %, while for 4-phenylanisole, the yield could reach to 83.3 % under identical conditions. Apparently, that aryl bromide containing electron-withdrawing groups could be more effectively incorporated in the coupling products than those with electron-donating groups.

4. Conclusions

In summary, a facile approach has been developed for the synthesis of CCG by the reduction of GO with various organic bases, including DBU, TEA and DABCO. The structures and properties of the CCG are highly dependent on the chemical characteristics, especially the pKa value, of organic bases employed. Remarkably, the reaction between GO and DBU can simultaneously modify the surface properties of CCG for anchoring Pd nanoparticles. The resultant Pd/CCG catalyst exhibits high conversion and good recyclability towards Suzuki cross-coupling reaction. This work may shed some light on the synthesis and property tuning of chemically converted graphene, as well as the application in catalysis.

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Figures Captions

Fig. 1 a) XRD patterns, b) FT-IR spectra, c) UV-vis absorption spectra and d) Raman spectra of GO,

DBU-CCG, TEA-CCG and DABCO-CCG.

Fig. 2. C 1s XPS spectra of a) GO, b) DBU-CCG, c) TEA-CCG and d) DABCO-CCG; e) N 1s XPS

spectrum of DBU-CCG; f) Pd 3d XPS spectrum of Pd/DBU-CCG.

Fig. 3. a) Digital pictures of GO, DBU-CCG, TEA-CCG and DABCO-CCG suspension; b-e) is TEM

images of GO, DBU-CCG, TEA-CCG and DABCO-CCG, respectively.

Fig. 4. a) TEM images of Pd/DBU-CCG catalyst; b) HRTEM image of Pd nanoparticles on CCG; c) SEM image of Pd/DBU-CCG catalyst; d-f) elemental mapping showing the homogenous distribution of C, N and Pd element in the catalyst; g) size distribution of Pd nanoparticles on CCG; h) catalytic performance and recyclability of Pd/DBU-CCG catalyst towards Suzuki cross-coupling reaction.







Fig. 2



Fig. 3



Fig. 4

Tables

Table 1. Electrical Conductivity of GO and CCGs

Sample	GO	DABCO-CCG	TEA-CCG	DBU-CCG
Electrical Conductivity $(S \cdot m^{-1})$		0.013	0.140	0.010

Table 2. Catalytic performance for different substrates under identical conditions

Substrate	Time (h)	Yield (%)
4-bromoanisole	1	83.3
4-bromobenzonitrile	1	99.5

Reaction conditions: Aryl bromide (0.5 mmol), phenylboronic acid (0.75 mmol), K_2CO_3 (1.5 mmol), H_2O (4 mL): EtOH(4 mL), and Pd/ DBU-CCG (0.5 mol%), 80 °C