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A Green Approach to the Synthesis of High-Quality Graphene Oxide Flakes via Electrochemical Exfoliation of Pencil Core

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A simple, green and cost-effective approach has been reported to synthesize high-quality graphene oxide (GO) flakes via electrochemical exfoliation of pencil core in aqueous electrolytes. The exfoliated GO flakes exhibit excellent electrocatalytic activity and toxicity tolerance for oxygen reduction reaction (ORR) in alkaline solution.

Since graphene, a single layer of carbon atoms in a closely packed honeycomb two-dimensional lattice, was discovered in 2004 by Geim et al.[1], it has attracted tremendous attention for a wide variety of applications such as energy storage and conversion devices,[2] high-performance composites,[3] molecular electronics,[4] field-emission devices,[5] and sensors[6] because of its extraordinary and unique electrical, mechanical and thermal properties. Geim et al. synthesized graphene sheets by mechanical exfoliation of highly oriented pyrolytic graphite (HOPG),[1] however, this method is not suitable for the large scale production. Currently many synthesis methods such as chemical synthesis through oxidation of graphite, CVD, plasma enhanced CVD (PE-CVD), electric arc discharge, epitaxial growth on electrically insulating surfaces such as silicon carbide (SiC), and un-zipping of carbon nanotubes (CNTs) have already been developed to produce graphene.[7] Some of these methods are efficient to produce large quantities of graphene with lower cost. Particularly, reduced graphene oxide (RGO) produced by chemical reduction of graphite oxide (GO) derived based on Hummer's chemical exfoliation of graphite[8] is advantagesous in term of cost and controllable solution-processing, however this method employing some hazardous chemicals (e.g., H_2SO_4/$KMnO_4$, hydrazine) which are environmentally harmful and time-consuming. Recently, researchers have drawn much attention to produce graphene sheets by electrochemical exfoliation method which is simple, environmentally friendly and substrate free.[9] Su et al.[10] synthesized high-quality graphene thin sheets by electrochemical exfoliation of natural graphite flakes (NGF) or highly oriented pyrolytic graphite (HOPG) using various electrolytes such as HBr, HCl, HNO_3, and H_2SO_4. Singh et al.[11] prepared pure GO and graphene nanosheets (GNs) via electrochemical exfoliation of pencil in ionic liquid medium. Despite much progress has been made, the relatively high cost of HOPG or ionic liquid are still impeding its practical applications.

In this study, we report a simple, green and cost-effective electrochemical approach to synthesize high-quality graphene oxide flakes by electrochemical exfoliation of pencil cores in aqueous electrolytes (H_2SO_4 or H_3PO_4). The exfoliated GO flakes range in lateral size from 1 to several μm with the thickness mainly between 3 and 9 nm. The exfoliated GO flakes are used as metal-free catalyst for oxygen reduction reaction (ORR) and exhibit excellent electrocatalytic activity and toxicity tolerance in alkaline solution.

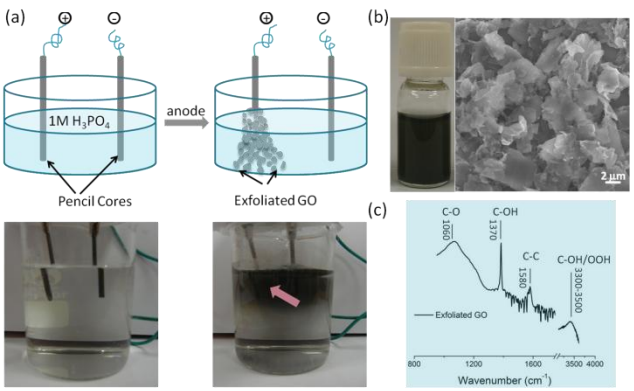

Fig. 1 Schematic illustration of electrochemical exfoliation of pencil cores. (a) Experimental setup (left) and exfoliation of the pencil anode (right). The red arrow indicates the exfoliation of the anode. (b) Photography of exfoliated graphite oxide flakes dispersed in DMF solution and the corresponding low magnification SEM images. (c) FTIR of exfoliated graphite oxide flakes.

As shown in Figure 1a, a two-electrode electrochemical cell was set up for electrochemical exfoliation of pencil, where pencils were employed as both anode and cathode to get GO flakes during electrochemical exfoliation process. A static potential of +1 V was applied initially across the two electrodes for 3-5 minutes, in order to wet the surface of electrode, facilitating accumulation of charges around anode or gently intercalation of anions into surface of anode.[10] The electrode potential was subsequently ramped to 7 V and maintained for 5-8 minutes. The potential of 7 V was high enough to drive the anions in electrolyte solution into the intercalation space (i.e. surface, grain boundary or structure defect sites) and make the exfoliation process to proceed. The polarity of the electrodes was then reversed. The alternating between + 7 V and - 7 V took place every 5-8 minutes repeatedly. Colour change of aqueous

electrolyte from transparent to dark was clearly observed after only a few minutes of electrolysis (shown in Figure 1a). The bias alternating between + 7 V and -7 V enabled more efficient and higher exfoliation rate of this electrochemical process and hence significantly enhanced the production rate of GO flakes as compared to that reported in literature[11,12]. After a few minutes' electrolysis, the colour change of aqueous electrolyte from transparent to dark was clearly observed (shown in Figure 1a). Moreover, both of pencil electrodes could be exfoliated by alternating the bias between + 7 V and -7 V, indicating more efficient and higher exfoliation rate of this exfoliation process and hence to a significantly higher production rate of GO flakes as compared to that reported in literature[11,12]. In additions, our synthesis method for GO flakes exhibits several advantages over the existing methods such as low-cost, easier processing and environmentally friendly. The exfoliated GO flaks were washed, collected and re-dispersed in dimethylforamide (DMF) solution (Figure 1b). Corresponding low-magnification SEM image of corresponding GO flakes was shown in Figure 1b, in which the average lateral size of the exfoliated GO flakes is 1- 5 µm. Figure 1c represents the FTIR spectrum of GO, the broad and intense peak at 3300-3500 cm^{-1} is characteristic of O–H groups. The peaks at 1580 cm^{-1}, 1370 cm^{-1}, and 1060 cm^{-1} are attributed to the C-C, C -OH and C–O stretching, respectively. The above FTIR data indicate that there are oxygen functionalities on the GO surface, which resulted from anodic oxidization, hydroxylation and carboxylation of graphite electrode triggered by positive voltage applied to electrodes[13].

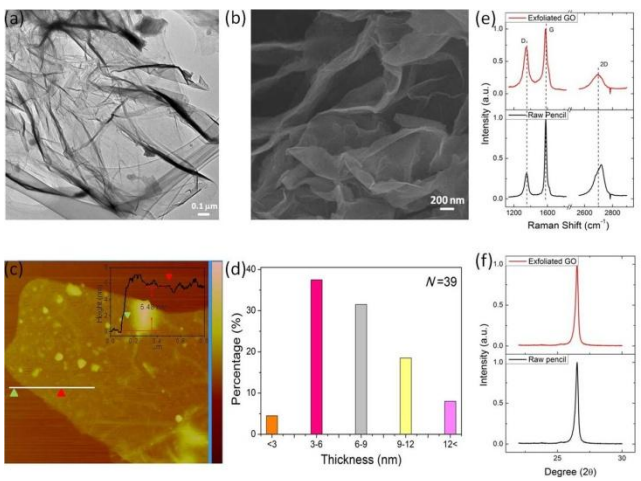

Fig. 2 (a) TEM image and (b) SEM image of exfoliated GO flakes. (c) AFM image of exfoliated GO flakes. The thickness is 5.45 nm with lateral size around 2 mm. (d) Thickness distribution histograms for exfoliated GO sheets, as estimated from corresponding AFM analysis. The graphene flakes are mainly distributed in the range of 3-9 nm thickness (69%) with lateral size about 1 to few mm. (e) Raman spectra and (f) XRD patterns for both pencil core and exfoliated GO flakes, respectively.

TEM, FESEM, AFM, Raman and XRD were employed to shed more light on morphology and crystalline structure of as-prepared exfoliated GO flakes. TEM image (Figure 2a) of GO flakes reveal wrinkled or folden morphology with a few stacked layer (about 1-5 layers, SI, Figure S1) at the edge. The transparent looking GO flakes are found to be similar to those graphene synthesized by other researcher using chemical and electrochemical process.[11, 14], , indicating a very low thickness. The curled, overlapped morphology as well as the increase in interlayer spacing for GO flakes was further confirmed from FESEM image in Figure 2b. The morphologies and layers of the obtained GO flakes were also analyzed by atomic force microscopy (AFM). Figure 2c shows the typical AFM image of the exfoliated GO flakes which are deposited on SiO_2/Si substrate by spin coating. The GO flakes had a thickness of about 5.45 nm with very sharp edges and flat surface. The lateral size of the GO flakes obtained from our method was 2 µm. It was estimated on the basis of statistical sampling of exfoliated GO flakes using AFM (Figure 2c and Figure S2) that approximately 37% of the GO flakes have thicknesses in the range of 3-6 nm while nearly 32% are in the range of 6-9 nm (Figure 2d).

Raman spectroscopy is a very important and useful tool for characterizing the structure and quality of graphene, particularly to determine the defects, the ordered and disordered structures, and the layers of graphene.[14a] Figure 2e presents the Raman spectra of raw pencil core and graphene sheets obtained from our process. The Raman spectrum of the raw pencil core showed a prominent G peak at 1587 cm^{-1} related to the first-order scattering of the E2g vibration mode of sp^2 carbon which can be used to explain the degree of graphitization and a D band at 1365 cm^{-1} associated with structural defects and partially disordered structures of the sp^2 carbon.[14a] It was clearly shown that the intensity of the D-band in graphene sheets was higher than that of raw pencil (I_D/I_G = 0.32) and the I_D/I_G value of graphene sheets increased to 0.71 due to the generation of defects on the surface, which were attributed to the unavoidable oxidation of graphene by phosphoric acid during electrochemical process. However, the intensity of G band was significantly higher than that of D band for the graphene sheets, which suggested that the graphene sheets prepared by this method had low defect compared to other reports.[11, 15] It was also clearly seen that the graphene sheets exhibited a broader and up-shifted 2D band at around 2700 cm^{-1} compared to single layer graphene, this result revealed that the present electrochemical process resulted in few-layer NGs. This result consist with the AFM, SEM and TEM characterizations well. The XRD of pencil exhibits a sharp peak at 26.52 ° (Figure 2f) corresponding to the (002) interplanar spacing of 3.36 Å. The graphene sheets confirmed the strong diffraction peak locates nearly at the same position with similar background signal intensity as that of raw pencil, suggesting less defects were introduced with our electrochemical exfoliation approach when compared to the chemical methods.[15,16]

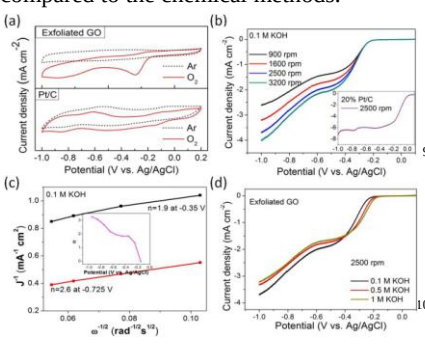

Figure 3. (a) Cycle Voltammerty curves for exfoliated GO flakes and 20% Pt/C electrodes in Ar-saturated (dashed line) and O_2-satureated (solid line) 0.1 M KOH at the scan rate of 100 mV/s. (b) The polarization curves of

exfoliated GO flakes in O_2-saturated 0.1 M KOH at various rotating rates. (c) Corresponding Koutecky-Levich plots at different potentials for RDE curves in (b). The inset in (c) electron transfer number n derived from Koutecky-Levich plots at different potentials. (d) Comparison of polarization curves obtained in O_2-satureated (solid line) KOH solution with concentration at 0.1 M, 0.5 M and 1M, respectively. The rotation rate is 2500 rpm.

The electrocatalytic activity of exfoliated GO flakes toward the oxygen reduction reaction (ORR), which is of great importance in the fuel cells and other electrochemical devices, was investigate via cyclic voltammetry (CV), rotating disk electrode (RDE) and chronoamperometry response. CV measurements were carried out in 0.1 M KOH at 25°C with potential ranges of -1.0 V to 0.2 V (vs. Ag/AgCl) (Figure 3a). The CV curves of both exfoliated GO flakes and Pt/C in Ar-saturated 0.1 M KOH process featureless redox reactions. In contrast, well-defined peaks are observed at -0.29 V for exfoliated GO flakes and -0.11V for Pt/C, respectively. Comparison of CV curves in Ar-versus O_2-saturated electrolyte clearly revealed the ORR catalytic activity of exfoliated GO flakes.[17]

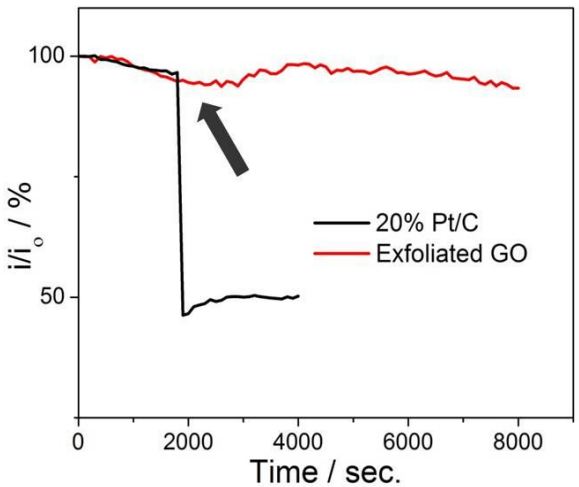

Figure 4. Chronoamperometric responses for exfoliated GO flakes (red line) and commercial 20% Pt/C (black line) obtained at - 0.5 V in 0.1 M O2-saturated KOH solution. The arrow indicates the addition of 2% wt methanol into the electrochemical cell.

To gain further insight on the ORR electrochemical kinetic process, measurements with RDE were carried out. The polarization curves for exfoliated GO flakes recorded in aqueous O_2-satureated 0.1 M KOH exhibited classical two-step process with onset potentials at around -0.21 V and -0.6 V, respectively, which were comparable with reports on pure CNT[18] and graphene[19] (Figure 3b). The limiting current density increased with the increase in rotation rate and a current density of 3.69 mA cm^{-2} are achieved at -1.0 V versus s. Ag/AgCl with rotating rate at 2500 rpm. Although the electrocatalytic activity of GO flakes toward ORR in terms of the onset potential and current density is still not as good as that of commercial Pt/C electrocatalyst (inset in Figure 3b), the as-prepared GO flakes can be used for the preparation of various metal-free catalysts with low cost for ORR, and even new catalytic materials for applications beyond fuel cells. The electron transfer number *n* was calculated from the slopes of Koutecky-Levich plots at various potentials (Figure 3c). At a low potential of -0.35 V, *n* was calculated to be 1.9, suggesting a typical two-electron reduction of O_2. When the potential was polarized in a more negative direction, *n* increase to 2.6 (at -0.725 V) and 3.2 (at -0.95), indicating a combination of two-electron and four-electron process take places in this potential region.[17, 20] Furthermore, the good linearity of corresponding KL plots suggests the first order reaction kinetics toward the concentration of dissolved O_2 on exfoliated GO flakes from -0.35 V to -0.725 V (Figure 3c & Figure S3)[21]. Moreover, with the increase in concentration of electrolyte, a decrease in limiting current density was observed (Figure 3d and Figure S4), accompanied by a positive shift in the ORR onset potential (Table S1)，consisting with previous report well[22].

The exfoliated GO flake was further subjected to test the methanol crossover via chronoamperometric responses (Figure 4). In contrast to the sharp decrease in the current upon the addition of 2% wt methanol for commercial Pt/C catalyst, relative stable amperometric response from exfoliated GO flakes remained nearly unchanged, indicating its excellent toxicity tolerance towards methanol.

In conclusion, a simple, green and cost-effective approach has been employed in this work to prepare high-quality graphene oxide flakes via electrochemical exfoliation of pencils. The exfoliated GO flakes exhibit excellent electrocatalytic activity and toxicity tolerance for oxygen reduction reaction in alkaline solution. Our present results are promising for scaled-up preparation and further commercialization of graphene oxide in a low-cost and environmental friendly way.

Notes and references

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