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Structural Analysis of Liquid-Exfoliated Graphene as Building-Blocks for Anti-Corrosion thin films

Wen Qian,[1] Roman Schmidt,[1] Joseph A. Turner[1], Kaleb Hood,[2] Jun Jiao[2]

[1.] Department of Mechanical and Materials Engineering, University of Nebraska-Lincoln, Lincoln, NE, USA
[2.] Department of Mechanical and Materials Engineering, Portland State University, Portland, OR, USA
* Corresponding author: wqian2@unl.edu

Recently, studies of graphene thin films as anti-corrosion coatings have emerged extensively with an aim to protect metals from oxidation in corrosive and extreme conditions [1]. The previous studies have been focused on using graphene oxide (GO) sheets created via multiple-step processes, which are often highly defective. In addition, surfactants are required for the graphene-oxide thin film formation to prevent graphene oxide sheets from unmanageable aggregation [2]. In this report, we demonstrate that mono- and few-layer exfoliated graphene (EG) sheets can be produced by a “Thermal Expansion--Liquid Exfoliation” process [3]. The specific experimental procedures include the use of the expanded graphite as the precursor and the N-methyl-2-pyrrolidone (NMP) as a dispersion solvent. The yield of few-layer graphene is up to 10-12 wt %. The centrifuge speed can be used to produce mono-layer and few-layer graphene sheets. The entire exfoliation process does not involve a stabilizer or chemical modifications. Thus, the approach minimizes the structural defects significantly. These EG sheets show great potential for use as anti-corrosion thin films.

Transmission electronic microscopy (TEM) and electron diffraction (ED) were used to investigate the morphology and crystal structure of the EG sheets. Fig. 1a shows the TEM image of few-layer graphene with edges tending to scroll and fold slightly. The corresponding ED pattern is displayed in Fig. 1b. The intensity profile of a line through the (1-210)-(0-110)-(-1010)-(-2110) axis for the pattern in Fig. 1b is plotted in Fig. 1c. The inner peaks {1100} are less intense than the outer ones {2100}, the ratio of $I_{\{1100\}}/I_{\{2110\}}$ is less than 1 (~ 0.5), which is ascribed to bilayer graphene [3]. Fig. 1d is the optical image of a silicon wafer coated with EG sheets. Note that EG film coverage is high with a coating density of more than 90%. The Raman spectrum (Fig. 1e) on some of the EG sheets exhibits two peaks at 1577 cm^{-1} and 2721 cm^{-1} corresponding to the G band and 2D band respectively. The G position is shifted down 3 cm^{-1} from that of thick flakes while the 2D position is shifted down 5 cm^{-1} from that of thick sheets, which is in good agreement results from three- or four-layer graphene [4]. The 2D band fit is enlarged in the inset of Fig. 1e. The yield of few-layer graphene is up to 10-12 wt %. The x-ray diffraction (XRD) pattern of GO, reduced GO and EG are depicted in Fig. 1f. The GO result reveals a diffraction peak at 10.04° that corresponds to the (002) planes of GO. A weak diffraction peak at 24.3° is distinguishable for reduced GO. The EG result shows a strong peak at 26.37° confirming a well-crystallized structure.

Atomic force microscope (AFM) was used to characterize the thickness and size of the exfoliated graphene sheets (Fig. 2). The thickness of the graphene sheets is about 3.7-4.0 nm, as shown in the height profiles in Fig. 2c and 2d. Considering the monolayer crumpled ripples owing to thermal fluctuations, the EG sheets are around three graphitic layers. It is expected that by systematic tailoring the process paramters, the thickness of the EG sheets could be optimized.

Both TEM and AFM characterizations also suggest that the EG sheets are well-crystallized with fewer defects. This surfactant-free fabrication process shows the potential to produce graphene sheets as building blocks for graphene coating films. Ongoing work intends to optimize the EG sheet production and EG coatings and test the anti-corrosion performance, coating stability, and mechanical durability [5].

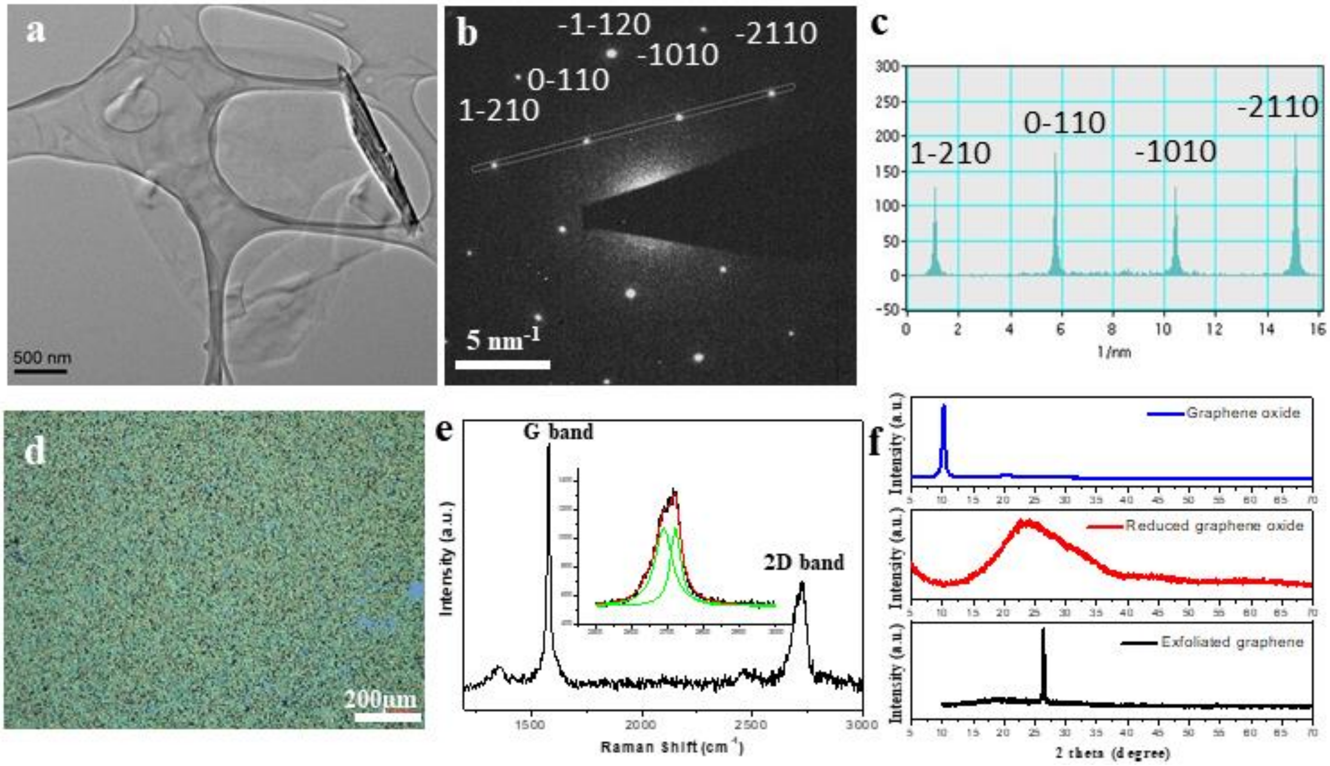

Figure 1. (a,b) TEM image of few-layer graphene and the corresponding ED; (c) Intensity profile plot along the line indicated in (b); (d) optical microcope image of the graphene-coated silicon wafer; (e) Raman spectrum of exfoliated graphene; f) XRD patterns of GO, reduced GO and EG;

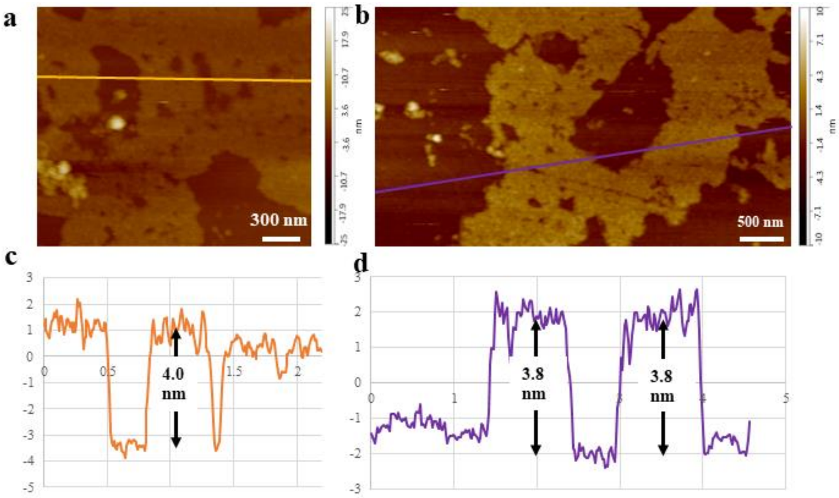

Figure 2. (a,b) AFM height images of few-layer EG sheets by tapping mode; (c,d) the average graphene thickness is around 3.7-4.0 nm;

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