Electrochemically Exfoliated Graphene: Production and High Performance

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ABSTRACT

Graphene flakes with tunable layer number, sheet size, defects, pores and hybridization were realized by electrochemical approches. Electrochemically exfoliated graphene can exhibit high performances in thermal management, electrocatalysis, supercapacitor and battery. Here, >30 μm of large literal sheet size of 1-2 layer graphene flakes were used to fabricate robust, flexible and free-standing graphene films with high thermal diffusivity. Small graphene microsheets of <1 μm of sheet size were produced from natural microcrystalline graphite (minerals) at the scale of tons. The microsheets are highly dispersible with the concentration of ~20 wt%. They are potentially applied for conductive additive or electrode material of lithium ion battery. Our study demonstrates that electrochemical route is very promising for the production and practical application of graphene.

Keywords: graphene, electrochemistry, thermal conductivity, supercapacitor, battery.

1. Intruduction

Graphene has a well-defined two-dimensional carbon structure with intrinsic high electrical and thermal conductivity, large specific surface area as well as high chemical stability. However, for some practical application (such as battery conductive additive), it is necessary for good dispersion of graphene that can ideally be chemically tunable by functional groups. More importantly, for practical application, it is desirable to produce graphene by green process at large scale at low coat. In China, there are abundant and cheap storage of flake graphite and microcrystalline graphite minerals. The production of graphite mateirals and the storage of graphite in China are both ~70% of the world. So it is a good choice from nature resource to produce graphene at low cost in China.

So far, it is still challenging to produce low-defective graphene below 5 layers by using a cost-effective and environmental friendly approach. Graphene oxide prepared by Hummers's method is extensively investaged, however, it has drawbacks of low quality of graphene, high-cost production and chemical waste (such as strong sulfur acid) treatment. Using electric power to replace chemical reactions is a green route. Electrochemical exfoliation of graphite to prepare graphene has attracted increasing interests in recent years. A series of electrolytes, i.e. aqueous inorganic acids or salts, ionic liquids (ILs), polar oragnic solution have been used to charge graphite to prepare graphene. However, it still lacks the production line equipments to eletrochemically produce graphene from graphite.

Through ten-year work, we have successfully prepared graphene with tunable atomic layers, sheet sizes, defects, pores and hybridization of graphene using electrochemical approaches.[1-15] Here, we outline scalable synthesis of electrochemically exfoliating graphite into few-layer graphene with high performance. The electrochemically exfoliated graphene-based materials exhibit high performances in thermal management, supercapacitor, batteries, electrocatalysis, photodetector and biosensor. [1-14] Very recently, atomic iron in electrochemically exfoliated graphene-based matrix working as electrocatalyst show superior performance on oxygen[9,14] or CO_2 reduction reaction.[15]

2. Methods

The electrochemical methods were used to prepare graphene flakes or sheets from graphite. The graphite foils, powder or rods can work as electrodes or electrode arrays, aqueous solution, carbonate solution, or ionic liquid as the electrolyte. The charging was usually conducted in the potential range of 2-10V. Details were most presented in previsous work [1-4]

FESEM and TEM images were collected on a JSM-7001F and JEM-2100F electron microscopes (200 kV, JEOL Ltd., Japan). Raman spectra were recorded using Jobin-Yvon HR-800 Raman system with 532 nm line of Ar laser as excitation source. Thermal diffusivity measurement was done at LFA447 (NETSCH, Germany). Graphene films were cut into discs with a direction of 25mm. Electrochemical characterization was performed in Autolab instrument of PGSTAT204. Galvanostatic discharge-charge tests were performed on a Land battery analyzer (CT-2001A, China).

3. Results and discussion

Using flake graphite, we can now prepare >30 μm of large literal sheets of 1-2 layer graphene flakes, as shown in Figure 1. The inset ED pattern shows good crystallinity of graphene flake. The graphene ones have less defects than reduced graphene oxide. The flake ink was used to fabricate robust, flexible and free-standing graphene films without any additive. Figure 2 presents the photograph and SEM images of graphene films rolled and folded. Mechincal strength measured of a film is around 40 MPa with 3.6% strain, as shown in Figure 3.

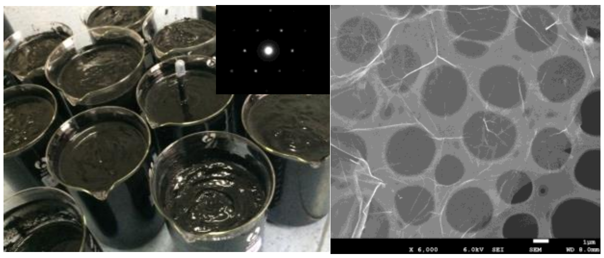

Figure 1. (left) graphene conductive ink, (b) SEM image of graphene flake.

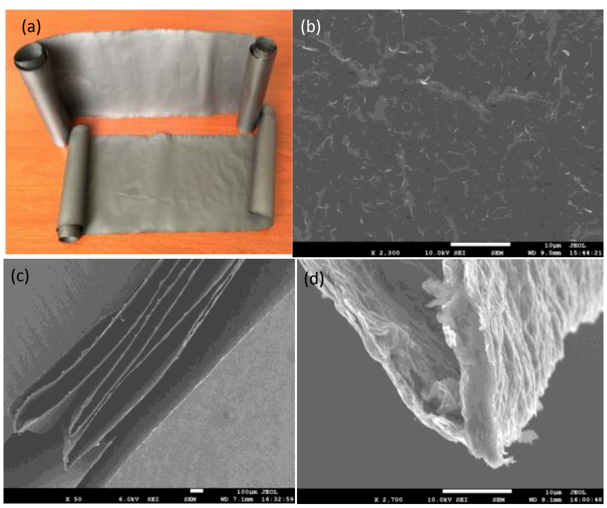

Figure 2. Graphene films. (a) optical image and (b-d) SEM image of films folded.

Very interestingly, the thermal diffusivity of graphene films seems to be very high and linearly dependent on the thickness of the films in the range from 60 μm to 1 μm, as presented in Figure 3. The data were measured by flash point method that might be roughly reliable for very thin graphene films. But we believe that the irradiative heat dissipation of graphene are very high. The thermal diffusivity of the hybrids of cellulose and graphene flakes with roughly same thickness are dependent on the mass ratio of graphene in the hybrids, as shown in Figure 4. The electrical conductivity can be enhanced by high-temperature annealing, and the real high thermal conductivity can be realized.

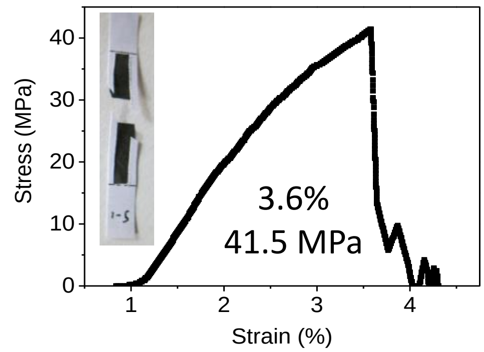

Figure 3. Mechanical measurement of graphene film.

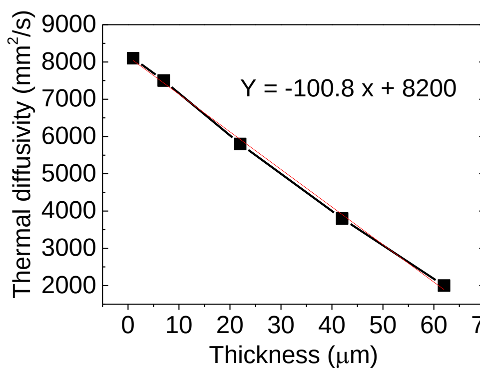

Figure 3. Thickness-dependent thermal diffusivity of graphene films.

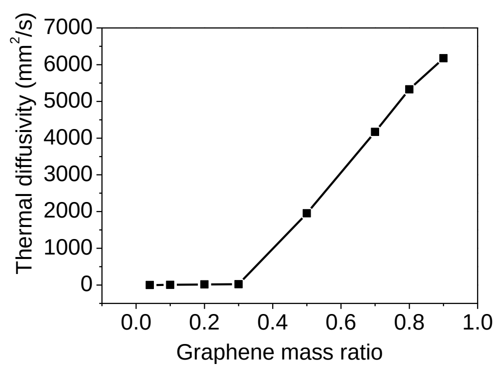

Figure 4. Mass ratio-dependent thermal diffusivity of graphene/cellulose hybrid films.

Graphene could significantly reduce the activation temperature of carbon resources (such as cellulose, pitch) with energy saving and safety enhancement. The hierarchical porous graphene-carbon-based supercapacitors reach ~200 F/g (3.5V) in ionic liquid and high energy density of >60 Wh/kg at high rate.[3] In addition, we also realized "carbon-concrete" of graphene integrating carbon fiber and hierarchical porous carbon to form robust flexible supercapacitor film.[4]

Small graphene microsheets were directly prepared from natural microcrystalline graphite minerals. The graphene microsheets present the feature of small sheet sizes of 0.2 - 0.6 μm^2 and ≤5 atomic layers, low defects and high purity. The unique size of graphene microsheets allow them disperse in various solvent, which is superior to reduced graphene oxide, carbon black and carbon nanotube. They exhibit high reversible specific capacity as a lithium-ion battery anode material and also its cathode material after modification.[6-8] Graphene anode material reachs high coulombic efficiency of 99.0% and high reversible specific capacity of 380 mAh/g.[6] Graphene-based Li-S batteries reach >99.5% coulombic efficiency and 2000-cycle stability.[8]

The production of >10 tons per year of high-quality graphene microsheets has been realized in Shangrao city in Jiangxi province in China using natural microcrystalline graphite (mineral) as a starting material.[7] Figure 5 shows the photographs of the factory and graphene dispersions. The aqueous disersion of graphene microsheets can be more easily casted on on alluminum foil. As shown in Figure 6, high resolution TEM image demonstrate 1-5 layer of graphene microsheets overlaid. Raman spectrum indicate that low defects of a graphene microsheet. Interestingly, the microsheets can be dispersed in water with a concentration of 15% with the assistance of polymer additive. And in cetain oil without any additive, the concentration of the dispersion can be 20 wt% (Figure 6 (left below)).

Figure 5. Mass production of small graphene microsheets. Graphene dispersion (right above), roll-to-roll coating machine and coated Al foil with graphene (medium) and SEM image (right below).

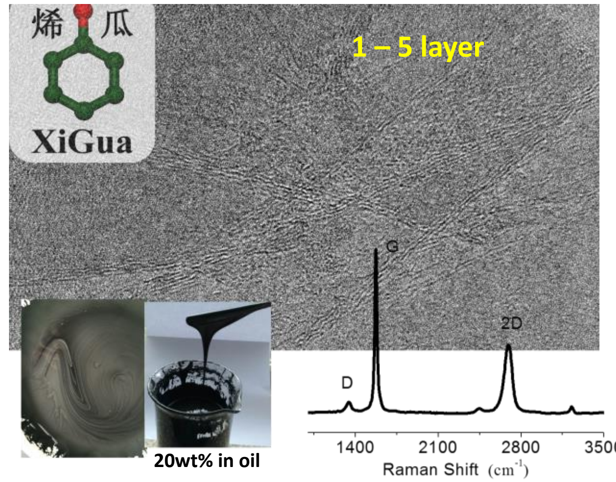

Figure 6. Graphene micrsheets produced. TEM images showing 1-5 layers. The left above is the Xigua brand of the graphene. The left below is the photographs of graphene disperisons in water and oil. The right below is Raman spectrum of graphene microsheet.

In addition, graphene materials with good performances in electrocatalysis and biology were studied. The nanostructures of porous graphene doped exhibit high performance on bi-functional electrocatalyst and Zinc-air battery.[10] Graphene dots show low cytotoxicity and can be used for fluorescent bioimaging.[11] The graphene films with the thickness of <50 µm exhibit good electromagnetic sheilding performance of 20-70 dB in the range of 1-18 GHz.[5] Amazingly, atomic iron/graphene was synthesized via electrochemical exfoliation of graphite in iron-based ionic liquid. The atomic sheets/dots was annealed with melamine to enhance the electrocatalytic performance on oxygen reduction reaction, which is even superior to Pt/C.[14] Atomic Fe embedded in bamboo-CNTs grown on graphene was synthesized as a superior CO_2 electrocatalyst with high faraday efficiency of 95%.[15]

4. Conclusion

Through long-term work, we have proved that electrochemical approaches are good routes for the synthesis and application of graphene materials. Examples shown here outline the scalable synthesis of large literal sheet size of graphene flakes with high thermal diffusivity and small microsheets with high dispersion and good battery performance. Our investigation demonstrates that electrochemical route holds great potentials for the production and wide application of graphene materials.

5. Acknowledgements

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6. References

[1] Junzhong Wang, Kiran Kumar Manga, Qiaoliang Bao, Kian Ping Loh*, "High-Yield Synthesis of Few-Layer Graphene Flakes through Electrochemical Expansion of Graphite in Propylene Carbonate Electrolyte," *J. Am. Chem. Soc.* 133, 8888–8891, 2011.

[2] Junzhong Wang et al, China Patent Applications, No 201310659172, No 201410476466, No 201410729808.

[3] Jianlin Huang, Junying Wang, Congwei Wang, Huinian Zhang, Chunxiang Lu and Junzhong Wang*, "Hierarchical Porous Graphene Carbon-Based Supercapacitor," *Chem. Mater.*, 27, 2107–2113, 2015.

[4]Huinian Zhang, Anni Li, Jie Wang, Yan Zhang, Zheng Zhao, Huifang Zhao, Miao Cheng, Congwei Wang, Junying Wang*, Shouchun Zhang, Junzhong Wang,* "Graphene integrating carbon fiber and hierarchical porous carbon formed robust flexible "carbon-concrete" supercapacitor film," *Carbon*, 126, 500-506, 2018.

[5] Rui Yan, Kai Wang, Congwei Wang, Huinian Zhang, Yan Song, Quangui Guo, Junzhong Wang*. "Synthesis and In-Situ Functionalization of Graphene Films Through Graphite Charging in Aqueous $Fe_2(SO_4)_3$," *Carbon*. 107, 379-387, 2016.

[6] Junying Wang, Jianlin Huang, Rui Yan, Faxing Wang, Wengang Cheng, Quangui Guo, Junzhong Wang*, "Graphene Microsheets from Natural Microcrystalline Graphite Minerals: Scalable Synthesis and Unusual Energy Storage," *J. Mater. Chem. A*, 3 3144-3150, 2015.

[7] http://www.jxgraphene.com/index.html (Jiangxi Xiniu Graphene Technology Co., Ltd., Shangrao, Jiangxi, China.)

[8] Yan Zhang, Xiaoyong Duan, Jie Wang, Congwei Wang, Junying Wang*, Jianlong Wang, Junzhong Wang,* "Natural Graphene Microsheets/Sulfur as Li-S Battery Cathode Towards >99% Coulombic Efficiency of Long Cycles," *J. Power Sources, 376,* pp 131–137, 2018.

[9] Congwei Wang, Huinian Zhang, Junying Wang, Zheng Zhao, Jie Wang, Yan Zhang, Miao Cheng, Huifang Zhao, and Junzhong Wang*. "Atomic Fe embedded in carbon nanoshells-graphene nanomeshes with enhanced oxygen reduction reaction performance," *Chem. Mater., 29 (23), pp 9915–9922*, 2017.

[10] Congwei Wang, Zheng Zhao, Xiaofeng Li, Rui Yan, Jie Wang, Anni Li, Xiaoyong Duan, Junying Wang, Yong Liu,* and Junzhong Wang*. "3D Framework of Graphene Nanomeshes-Shell/Co_3O_4 Synthesized as Superior Bifunctional Electrocatalyst for Zinc-air Batteries," *ACS App. Mater. Inter.*, 9 (47), pp 41273–41283, 2017.

[11] Rui Yan, Hao Wu, Qing Zheng, Junying Wang, Jianlin Huan, Kejian Ding*, Quangui Guo, Junzhong Wang*, *RSC Adv.*, 4, pp23097-23106, 2014.

[12] Lena Ai Ling Tang, Junzhong Wang, Kian Ping Loh*, Graphene-based SELDI Probe with Ultrahigh Extraction and Sensitivity for DNA Oligomer, *J. Am. Chem. Soc*. 132, 10976–10977, 2010.

[13] Kiran Kumar Manga, Junzhong Wang (equal first author), Ming Lin, Jie Zhang, Milos Nesladek, Venkatram Nalla, Wei Ji, Kian Ping Loh*, High-Performance Broadband Photodetector Using Solution-Processible PbSe-TiO_2-Graphene Hybrids, *Adv. Mater***.** 24, 1697–1702, 2012.

[14] Junying Wang, Huinian Zhang, Congwei Wang, Yan Zhang, Jie Wang, Huifang Zhao, Miao Cheng, Anni Li, Junzhong Wang*, "Co-synthesis of atomic Fe and few-layer graphene towards superior ORR electrocatalyst," *Energy Storage Materials*, 12, pp 1–7, 2018.

[15] Huinian Zhang, Jie Wang, Zheng Zhao, Huifang Zhao, Miao Cheng, Anni Li, Congwei Wang, Junying Wang,* and Junzhong Wang *. "The synthesis of atomic Fe embedded in bamboo-CNTs grown on graphene as a superior CO_2 electrocatalyst, " *ACS App. Mater. Inter.*, submtted, 2018.