

Characterization of graphene based conductive paste

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Abstract. With the discovery of graphene and the development of related research, graphene has been applied in various fields. The excellent properties in mechanical, electrical and energy storage due to the two-dimensional conjugated structure and high surface area of graphene make it ideal conductive material. Graphene can form a complete three-dimensional conductive network, by which can be used as a conductive agent for the electrode material. In this work, a commercialized graphene based conductive paste (GCP) was characterized. AFM was implemented to study morphology and thickness, XPS, ICP, Raman were used to reveal element results and basic properties of graphene. The solid content, static stability and kinematic viscosity for conductive paste were also characterized.

1. Introduction

The conductive paste is a paste formed by uniformly dispersing a conductive agent into a dispersant, which is widely used in the fields of electronic components packaging, electrodes, electronic preparation, and the like. Conductive paste can be roughly divided into the metal conductive paste, metal oxide conductive paste, carbon-based conductive paste and composite conductive agent [1-3]. Conductive paste used in lithium-ion battery is mainly carbon-based materials, which have good cycle performance but low initial charge and discharge efficiency [4].

As a newly discovered carbon-based material, graphene and its derivatives have aroused tremendous interests and are gradually applied in a wide variety of fields owing to the unique electronic and physicochemical properties arising from the layered 2D structure [5-7]. A continuous 3D conductive network formed by graphene can effectively improve the electron and ion transportation of the electrode materials [8]. Besides, graphene can improve the electrode material's cycle life performance, enhance the conductivity of metal electrode material, control the growth of metal oxide particles and also improve lithium storage capacity for most metal oxide composite materials with graphene [9].



Recently, the development of various methods of preparing graphene as well as the abundant graphite resources [10] have allowed the large-scale production and applications of graphene materials. That make graphene based conductive paste become one of the industrialized products. In order to prepare a highly dispersed and conductive graphene paste, graphene must be well dispersed and stabilized in solvents [11, 12]. In this paper, a commercialized graphene based conductive paste, prepared by uniformly dispersing graphene into NMP, were characterized. By using characterization method related to both graphene and conductive paste, our purpose is to establish a scheme for analyzing products of graphene based conductive paste, as well as other products based on graphene.

2. Method

Graphene based conductive paste was provided by Xiamen Knano Graphene Technology Co. Ltd. X-ray photoelectron spectroscopy (XPS) was performed on Thermofisher Escalab 250Xi. All binding energies were referenced to the C 1s neutral carbon peak at 284.8 eV. The Raman spectra were recorded by using a Horiba's LabRam HR high resolution spectrometer. Atomic force microscopy (AFM) characterization was performed on a Bruker Dimension FastScan under tapping mode with samples prepared by spin-coating onto freshly peeled mica substrates at 1000 rpm from diluted sample solutions. The laser diffraction particle size analysis of GCP was carried out using a Malvern Mastersizer.

3. Results and discussion

3.1. Characterization of graphene in the conductive paste

The GCP was made by the exfoliation of graphite platelets into graphene in a liquid medium of N-methyl-2-pyrrolidone (NMP). The graphene was identified and characterized using Raman spectroscopy, XPS, particle size distribution and atomic force microscopy. Raman spectroscopy is a versatile tool for studying the properties of graphene that common features are in the wavelength region of 800–3,000 cm^{-1} [13]. Three major peaks of are found in the Raman spectra, respectively (Figure 1a). The disorder-induced D band indicate the concentration of defects is at 1360.8 cm^{-1} , G band associated with the doubly degenerate phonon mode at the Brillouin zone is at 1581.4 cm^{-1} , the 2D band sensitive to the number of layers appears at 2742.7 cm^{-1} .

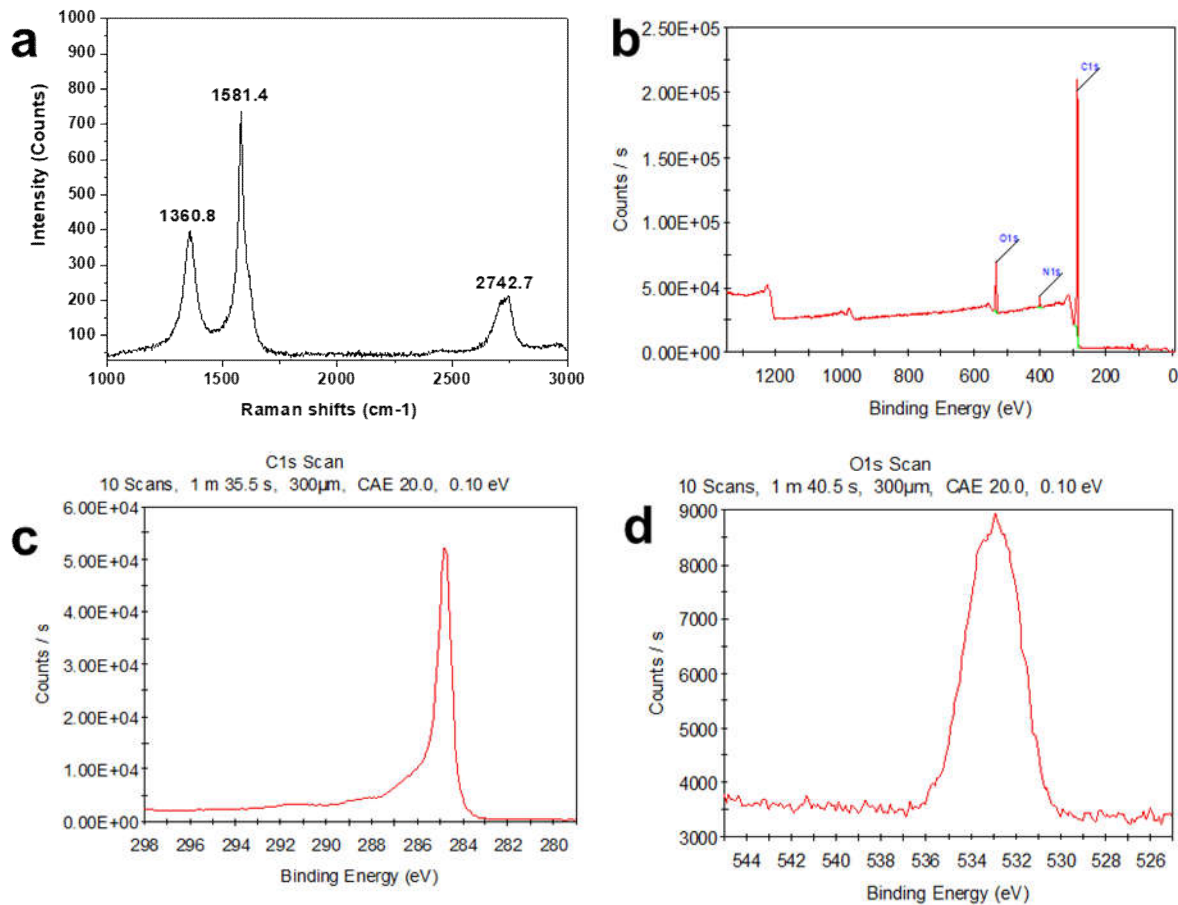


Figure 1. (a) Raman spectrum of graphene in the GCP, (b) full-range XPS spectrum of GCP, and high-resolution C1s (c) and O1s (d) spectra of the GCP.

The quantitative element compositions of GCP were measured by XPS. The full range XPS analysis (Figure 1b) of the GCP clearly shows the presence of carbon (C), oxygen (O) and nitrogen (N) with atomic percentages of 89.14%, 7.99% and 2.87%, and the corresponding C1s, O1s and N1s peaks centers at ~ 285.16 eV, ~ 400.28 eV and ~ 532.75 eV, respectively (Figure 2b). The N 1s (~ 400.28 eV) signal may come from NMP that absorbed on graphene sheets. Accordingly, the GCP had a molar ratio of carbon to oxygen atoms ($[C]/[O]$) of 11.16. The high-resolution C1s and O1s spectra of the GCP is presented in Figure 1c,d as well.

3.2. Morphological Properties of the GCP

The AFM is extensively used due to its high longitudinal resolution and surface profiling for the morphological analysis of graphene[14, 15]. In this work, we disperse 0.2~0.5 mL sample into ethanol using 40 KW ultrasonic dispersion for 30 min and spin-coated onto mica plate. The AFM characterization was carried out by randomly select the testing range on the mica film. Statistical results of thickness of graphene in GCP show that the thickness range from 0.918 nm to 2.596 nm (Figure 2b), most of graphene sheet we tested are over 1 nm thick. The average thickness of graphene sheets is 1.718 nm. Further observation of graphene revealed strip-shaped sheet structure with flat morphology, topological size of around 2 μm in width and 10 μm in length (Figure 2c-e). Besides, the measurement of particle size distribution indicates that the D10, D50 and D90 of this powder are 1.535, 3.886 and 14.647 μm (Figure 2a), respectively.

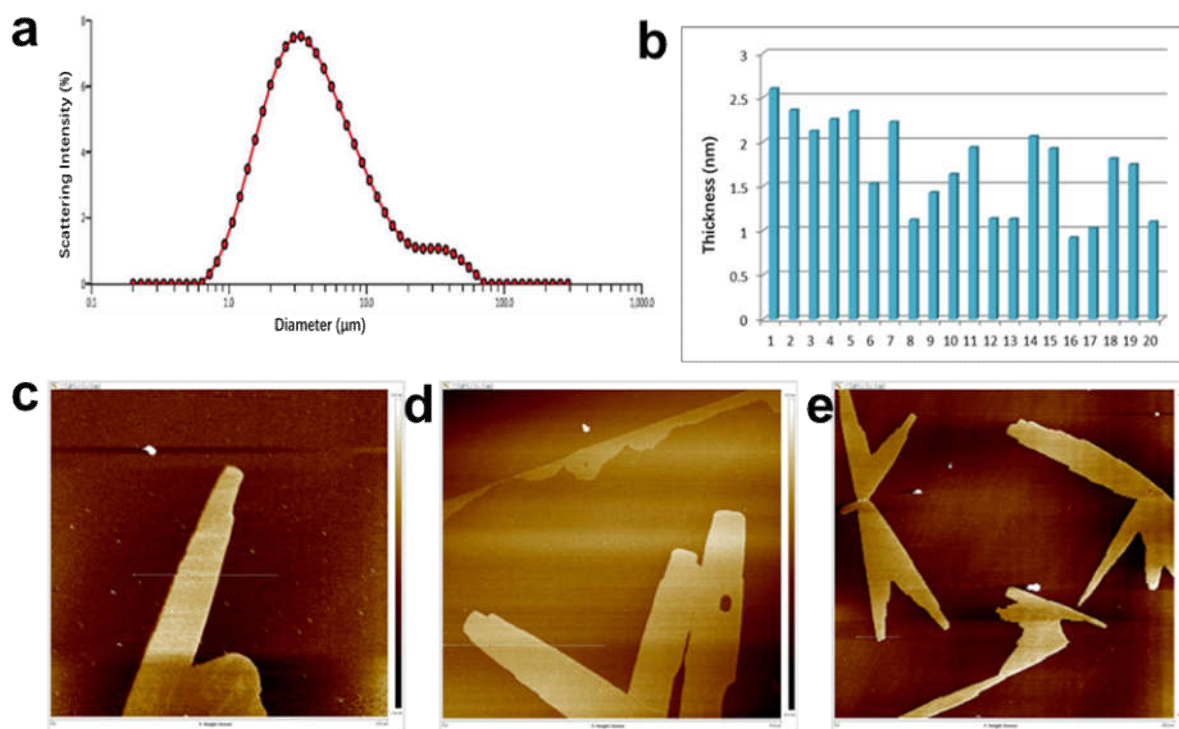


Figure 2. (a) Size distribution of graphene in GCP, (b) Chart of graphene thickness and its distribution, (c-d) AFM images of graphene in GCP with flat morphology.

3.3. Macro-characteristics of the GCP

Except for the test used to characterize graphene in GCP, macro-characteristics of the dispersion system consist of graphene and solvent may greatly affect the operating process and application of the GCP. The GCP is a product that solid graphene sheets which are in different phase formed a dispersion system. The solid content reflects the content of graphene that dispersed into the solvent, the static stability decides the uniformity of the products, water content have relationship with the performance of electrodes, kinematic viscosity is a basic parameter that must be tested before using. The solid content, static stability, water content and kinematic viscosity that affect the performance of GCP during production have been tested in this work.

The solid content and stability were tested using an oven drying method. Evenly blended GCP was place into a pre-dried and weighed glass watch, transfer to a drying oven of 130 °C for 1 h, then placed into a dryer and weighed after cooling. The total solid content is calculated according to $X_1 = (m_3 - m_1) / m_2 \times 100$, whereas m_1 means weight of the glass watch (g), m_2 means weight of the sample before drying (g), m_3 means total weight of the glass watch with sample after drying (g). For the test of static stability, the sample was kept in 60 °C oven for 24 h, taking the upper layer 30% solution and carry out the drying test to obtain the solid content X_2 by the formula $X_2 = (m_6 - m_4) / m_5 \times 100$ whereas m_4 means weight of the glass watch (g), m_5 means weight of sample before drying (g), m_6 means total weight of the glass watch with sample after drying (g). The changed value compared with solid content X_1 is used to characterize the stability using formula $\zeta = |X_1 - X_2| / X_1 \times 100\%$. The average solid content was 5.92% and statistic stability (value of solid content change) was 4.11 %.

The water content in the GCP was analyzed with a standard Karl-Fischer titrant, average value of water content for three entry was 590.3 ppm. The average value of kinematic viscosity is 5216.89 mPa.s which was determined by an automated SVM3000 Anton Paar rotational Stabinger viscometer-densimeter (Anton Paar GmbH, Austria) with cylinder geometry at room temperature.

4. Conclusion

Mass production of graphene from graphite have made more and more graphene-based products become reality. In this work, both the properties related to graphene in GCP and the macro-characteristics have been characterized to establish a method for analyzing products of graphene based conductive paste. The graphene sheets in GCP showed Raman D, G and 2D band at 1360.8 cm^{-1} , 1581.4 cm^{-1} , and 2742.7 cm^{-1} , carbon content of 89.14 at.%, average thickness of 1.718 nm with flat surface morphology. The GCP demonstrate macro-characteristics that solid content of 5.92wt%, static stability of 4.11%, kinematic viscosity of 5216.89 mPa.s and Water content of 590.3 ppm. The characterizing scheme combine both raw graphene materials and exact products can also be used to other products based on graphene.

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References

- [1] Y. Li, C.P. Wong, Recent advances of conductive adhesives as a lead-free alternative in electronic packaging: Materials, processing, reliability and applications, *Materials Science and Engineering: R: Reports*, 51 (2006) 1-35.
- [2] A.O. OGUNJIMI, O. BOYLE, D.C. WHALLEY, D.J. WILLIAMS, A review of the impact of conductive adhesive technology on interconnection, *Journal of Electronics Manufacturing*, 02 (1992) 109-118.
- [3] J. Jiang, Y. Li, J. Liu, X. Huang, Building one-dimensional oxide nanostructure arrays on conductive metal substrates for lithium-ion battery anodes, *Nanoscale*, 3 (2011) 45-58.
- [4] P. Simon, Y. Gogotsi, Materials for electrochemical capacitors, *Nature Materials*, 7 (2008) 845-854.
- [5] Z. Li, Z. Liu, H. Sun, C. Gao, Superstructured Assembly of Nanocarbons: Fullerenes, Nanotubes, and Graphene, *Chem. Rev.*, 115 (2015) 7046-7117.
- [6] Y. Liu, Z. Xu, W. Gao, Z. Cheng, C. Gao, Graphene and Other 2D Colloids: Liquid Crystals and Macroscopic Fibers, *Adv. Mater.*, 29 (2017).
- [7] Z. Liu, Z. Li, Z. Xu, Z. Xia, X. Hu, L. Kou, L. Peng, Y. Wei, C. Gao, Wet-Spun Continuous Graphene Films, *Chemistry of Materials*, 26 (2014) 6786-6795.
- [8] N. Li, Z. Chen, W. Ren, F. Li, H. Cheng, Flexible graphene-based lithium ion batteries with ultrafast charge and discharge rates, *Proceedings of the National Academy of Sciences of the United States of America*, 109 (2012) 17360-17365.
- [9] J. Zhu, R. Duan, S. Zhang, N. Jiang, Y. Zhang, J. Zhu, The application of graphene in lithium ion battery electrode materials, *SpringerPlus*, 3 (2014) 585-585.
- [10] Z. Liu, Z. Xu, X. Hu, C. Gao, Lyotropic liquid crystal of polyacrylonitrile-grafted graphene oxide and its assembled continuous strong nacre-mimetic fibers, *Macromolecules*, 46 (2013) 6931-6941.
- [11] Y. Hu, T. Zhao, P. Zhu, X. Liang, Y. Zhu, H. Su, R. Sun, C. Wong, Water-dispersible graphene paste for flexible conductive patterns and films, *international conference on electronic packaging technology*, 2016, pp. 200-205.
- [12] F. Su, C. You, Y. He, W. Lv, W. Cui, F. Jin, B. Li, Q. Yang, F. Kang, Flexible and planar graphene conductive additives for lithium-ion batteries, *Journal of Materials Chemistry*, 20 (2010) 9644-9650.
- [13] B. Tang, H. Guoxin, H. Gao, Raman Spectroscopic Characterization of Graphene, *Appl.*

- Spectrosc. Rev. , 45 (2010) 369-407.
- [14] Z. Xu, H. Sun, X. Zhao, C. Gao, Ultrastrong fibers assembled from giant graphene oxide sheets, *Adv. Mater.*, 25 (2013) 188-193.
- [15] X. Hu, Z. Xu, Z. Liu, C. Gao, Liquid crystal self-templating approach to ultrastrong and tough biomimic composites, *Sci. Rep.*, 3 (2013) 2374.