Engineering graphene for high-performance supercapacitors: Enabling role of colloidal chemistry

Ke Zhang¹, Xiaowei Yang², Dan Li^{*1,3}

1. Department of Materials Science and Engineering, Monash University, Melbourne 3180
2. School of Materials Science and Engineering, Tongji University, Shanghai 200092
3. Department of Chemical Engineering, the University of Melbourne, Melbourne 3010

Keywords: graphene, colloidal chemistry, supercapacitors, nanoporous structure, two-dimensional materials

Abstract

The high electrical conductivity and high specific surface area of graphene are traditionally regarded as the most intriguing features for its promise as the electrode material for supercapacitors. In this Perspective, we highlight that from the engineering point of view, the unique colloidal chemistry of chemically functionalized graphene is the key property that has made graphene stand out as a promising nanoscale building block for constructing unique nanoporous electrodes for capacitive energy storage. We present several examples to demonstrate how the non-covalent colloidal forces between graphene sheets can be harnessed to engineer the nanostructure of graphene-based bulk electrodes for supercapacitors based on both the electrical double layer storage and the redox reaction or pseudo-capacitance mechanisms. The colloidal engineering strategy can be extended to enable other nanomaterials to achieve high energy storage performance.

Materials requirements for high-performance supercapacitors

Electrochemical capacitors or supercapacitors represent a unique class of electrochemical energy storage devices which offer reliable, long life-cycle and fast charge delivery for high power demanding applications including consumer electronics, smart grid energy levelling, and regenerative energy recovery in automotive.^[1-5] Supercapacitors are particularly useful in applications which require high power density at high charging rates and dynamic operating conditions with varied charging and discharging current or voltage. Therefore, it has raised great research interest in developing supercapacitors featuring high energy density and good power delivery.^[6-8]

An actual supercapacitor is a multicomponent system including electrolyte, separator, electrodes, and aluminum current collector. To achieve supercapacitors with high energy density, the ideal electrodes need to meet the following requirements: (1) large specific surface area; (2) high packing density of active materials; (3) thick electrodes; (4) high pore connectivity and ionic conductivity.^[9, 10] Unfortunately, some of the criterion is in conflicting with each other and pose great challenge to electrode optimization. For example, both ion accessibility and pore interconnectivity would tend to decrease with increased packing density, sacrificing the rate capability and specific capacitance.^[11] Thus, engineering the performance of supercapacitors needs to balance all these parameters and involves a complex systems engineering process.

The ultimate performance of supercapacitors is essentially dependent on the extent to which these parameters can be optimized. Porous carbon-based materials are traditionally used as electrode materials because of their large surface area and good electrical conductivity. In principle, the conventional porous carbon is largely comprised of one or few layered graphene and some regions containing disordered structures.^[12, 13] The porous network defined by the graphene-based basic units will significantly affect the properties of the electrode materials since good pore connectivity and pore accessibility are essentially the foundation of good power

Commented [KZ1]: These factors are not self-conflicting but conflicting with one another.

performance. Thus, the key lies in how graphene can be assembled in an appropriate way to optimize all the above parameters.

Challenges in engineering traditional activated carbon

Commercial porous carbon materials for supercapacitors are based on activated carbon which are fabricated from the high-temperature carbonization of organic precursors such as nut shell, woods and other biomass materials, followed by either high temperature physical activation with the presence of oxidizing gases or chemically etching at relatively lower temperature with agents like potassium hydroxide and phosphoric acid to transform the precursor into a porous conductive network.^[12] During the activation process, an extensive porous network with a wide pore distribution is created via this top-down activation. This high temperature top-down activation approach will result in relatively poor control over the porous structure especially for the randomly-oriented graphene layers and the blockage of a considerable amount of pores by reactants or inorganic residue during the activation process.^[12, 13] In particular, numerous macropores will inevitably be generated, resulting in low volumetric energy density because of the excessive pore volume. These intrinsic limitations of this top-down approach may explain why the energy density of supercapacitors based on activated carbon has not been substantially improved despite of decades of research.

New nanoengineering strategies enabled by colloidal chemistry of graphene

Progress in the recent years in the synthesis of solution-processable graphene has opened entirely new ways to synthesize and engineer the nanostructure of carbon-based porous electrodes. In 2008, my group has demonstrated that chemically converted graphene, also known as reduced graphene oxide, can be well dispersed in water to form a stable colloidal dispersion without the need for any surfactants.^[14] The success of this approach lies in the utilization of the colloidal chemistry of graphene. As shown in Fig. 1, when the graphene is functionalized by oxygen-containing groups, several colloidal forces will be activated when the functionalized graphene is in contact with water, namely electrostatic, hydrophilic, hydrophobic and solvation forces.^[14-17]

Pristine graphene is intrinsically hydrophobic and attractive van der Waals forces among graphene sheets will lead to restack of graphene sheets which is challenging to be dispersed in liquid.^[18] However, chemically converted graphene has drastically different properties with numerous oxygen-containing functional groups which result in hydrophilic domains that are energetically favorable for the adsorption of water molecules. Furthermore, the electrostatic forces between graphene sheets which are primarily introduced by ionized carboxyl groups also act as a repulsive force among graphene sheets.

Figure 1 Domains and colloidal interactions of solvated graphene. Left: pristine graphene; middle: graphene oxide; right: reduced graphene oxide. Reproduced with permissions from [19]. Copyrights 2013 Wiley-VCH.

Colloidal chemistry plays an enabling role in not only the dispersion of graphene, but also how individual graphene sheets can be assembled. The successful synthesis of solution-processable graphene has made it possible to use the bottom-up approach to synthesize new porous carbon materials at ambient conditions without the need for subsequent chemical activation as required by the activated carbon production. Our group has demonstrated that chemically reduced graphene oxide, microscopically corrugated in solution, can be assembled to form a highly porous film simply by a directional-flow induced bottom-up assembly process as shown in Fig. 2.^[20, 21] Contradictory to the traditional conception that restacking would occur in direct face-to-face assembly of graphene sheets, our chemically converted graphene (CCG)

remains largely separated with highly porous structure. This is because of the repulsive intersheet solvation and electrostatic forces induced by the surface functional groups.

Figure 2 Structure and electrochemical characterization of solvated graphene films (SSG) A,B) Schematic of microscopically corrugated graphene sheets and bottom-up assembly process. Reproduced with permission from [21]. Copyrights 2011, The Royal Society of Chemistry C) SEM Image of the cross-section of the SSG films. D) Electrochemical performance of SSG. Reproduced with permission from [20]. Copyrights 2011, Wiley-VCH.

One of the most important features of this solvated graphene film electrodes is its extraordinary high rate performance with a capacitance of 156 Fg⁻¹ at an ultrafast discharge rate at 1080 Ag⁻¹. This is because the excellent pore connectivity in the gel-based electrodes ensure ions to be fast transported in a relatively short pathway through the porous network. An open and interconnected porous structure is critical for high power demanding supercapacitors which require fast ionic transport.

Figure 3 (A) Schematic of liquid mediation process in graphene hydrogel films (B-G) Electrochemical characterization and performance of liquid electrolyte-mediated graphene films (EM-CCG). Reproduced with permission from [11]. Copyrights 2013, American Association for the Advancement of Science.

Colloidal chemistry can be further utilized to fine tune the nanostructure of graphene gel materials electrode to optimize its performance. As the prepared graphene gel-electrode has a large interlayer distance, the volumetric capacitance of the gel-electrode is low due to its low packing density (0.069 g cm^{-3}). To further densify the gel-electrode for compact energy storage, our group has demonstrated a capillary pressure assisted compression method for preparing high volumetric capacitance electrodes as shown in Fig. 3.^[11] The as-prepared graphene gel-electrode has a metastable and adaptive pore structure like traditional polymer hydrogels. Therefore, it can be irreversibly compressed by capillary pressure through controlled evaporation of the solvent trapped in the gel. This capillary compression process greatly increases the packing density of the electrode up to 1.25 g cm^{-3} , much higher than that of conventional activated carbon. More importantly, the densified graphene films retained relatively good power delivery because of its excellent ion accessibility. During the controlled evaporation process, non-volatile solvent molecules between graphene sheets activate the repulsive colloidal forces, effectively counterbalance the attractive van der Waals force and prevent the collapse of pores created by graphene sheets. Thus, the densified graphene films

maintain a continuous channel network for fast ionic transport in the gel-electrode and the highly densified electrodes can still provide a high specific capacitance when the electrode thickness is increased to 80 μm . Porous yet densely packed carbon electrodes with high ion-accessible surface area and low ion transport resistance can thus be prepared with the aid of colloidal chemistry, leading to the successful fabrication of supercapacitors with a volumetric energy densities approaching 60 watt-hours per liter. It has been particularly challenging to achieve high energy and power density for densified electrodes with thickness close to commercial products ($\sim 100\ \mu\text{m}$) because of its large ionic resistance which results from the small pore size and tortuous ionic diffusion channels.^[9, 10, 22, 23]

In addition to electric double layer based supercapacitors (EDLCs), we have also demonstrated that pseudocapacitors can be prepared by incorporating polyaniline into the graphene gel-electrode.^[24] A layer of polyaniline film of a few nanometers is in-situ polymerized into the porous network of gel-electrode to provide faradic reactions sites. We found that the resultant pseudocapacitors could give rise to high rate performance since the graphene/polyaniline gel electrodes remain wetted. Again, the continuous ion transport network enabled by the solvation plays a key role in the high rate performance. Furthermore, the capillary compression method used for the densification of graphene gel electrodes can be extended to condense the composite gel films. Even when the pore is very small with high packing density of $1.28\ \text{g cm}^{-3}$, it still offers a combination of high volumetric capacitance and high rate capability ($548\ \text{F cm}^{-3}$ at $100\ \text{A g}^{-1}$).^[25]

Outlook

Many other electroactive nanoscale building blocks such as transition-metal dichalcogenides including 1T metallic phase MoS_2 and metal carbides such as MXenes have recently been made solution processable.^[26, 27] We expect that the colloidal strategy we have developed for graphene-based materials can be extended to optimize porous electrodes based on these emerging nanomaterials. Indeed, Gogotsi and coworkers have recently demonstrated that solution-processed high-density 2D Ti_3C_2

films can offer exciting cations intercalation capacitance of 900 F cm^{-3} (measured in a three-electrode configuration).^[28] Benefiting from the hydrophilic surface of $\text{Ti}_3\text{C}_2\text{Tx}$, its hydrogel films can also be prepared, offering facilitated ionic transport. The as-prepared hydrogel films yield better electrochemical performances in two-electrode cell with ionic liquid as electrolyte than the dried Ti_3C_2 films.^[26, 29] This work has again demonstrated that the colloid interactions can be effective for other 2D materials. It should be also possible to engineer 2D materials-based heterostructures by controlling their intersheet interactions in colloid system for better energy storage devices.

Engineering the nanoporous structure through the colloid forces represents a highly effective strategy to optimize the ion transport in nanomaterials. This strategy can be combined with techniques to enable new technological innovations. New types of assembled structures such as vertically aligned nanosheets might be possible if the colloidal forces can be made more directional, for example, with an external magnetic field. These new nanostructures also provide new experimental platforms to understand many unknown nanoconfinement effects, which will further fuel the development of new strategies for more powerful supercapacitors. Given that the pore structure also has a significant effect on the performance of many other energy storage and conversion devices such as batteries and fuel cells as well as capacitive desalination systems, we expect that the colloidal strategy we demonstrate here would be useful for the research in these areas.

References

1. Simon, P. and Y. Gogotsi, *Materials for electrochemical capacitors*. Nature Materials, 2008. **7**(11): p. 845-854.
2. Simon, P., Y. Gogotsi, and B. Dunn, *Where do batteries end and supercapacitors begin?* Science, 2014. **343**: p. pp. 1210-1211.
3. Zhang, L.L. and X.S. Zhao, *Carbon-based materials as supercapacitor electrodes*. Chemical Society Reviews, 2009. **38**(9): p. 2520-31.
4. Béguin, F., et al., *Carbons and electrolytes for advanced supercapacitors*. Advanced Materials, 2014. **26**(14): p. 2219-2251.
5. Frackowiak, E. and F. Beguin, *Carbon materials for the electrochemical storage of energy in capacitors*. Carbon, 2001. **39**(6): p. 937-950.

6. Gu, W. and G. Yushin, *Review of nanostructured carbon materials for electrochemical capacitor applications: advantages and limitations of activated carbon, carbide-derived carbon, zeolite-templated carbon, carbon aerogels, carbon nanotubes, onion-like carbon, and graphene*. Wiley Interdisciplinary Reviews: Energy and Environment, 2014. **3**(5): p. 424-473.
7. Sun, Y., Q. Wu, and G. Shi, *Graphene based new energy materials*. Energy & Environmental Science, 2011. **4**(4): p. 1113-1132.
8. Zhu, Y., et al., *Graphene and graphene oxide: synthesis, properties, and applications*. Advanced Materials, 2010. **22**(35): p. 3906-3924.
9. Gogotsi, Y. and P. Simon, *True performance metrics in electrochemical energy storage*. Science, 2011. **334**: p. 917-918.
10. Zhang, S. and N. Pan, *Supercapacitors performance evaluation*. Advanced Energy Materials, 2015. **5**(6).
11. Yang, X., et al., *Liquid-mediated dense integration of graphene materials for compact capacitive energy storage*. Science, 2013. **341**(6145): p. 534-537.
12. Pandolfo, A.G. and A.F. Hollenkamp, *Carbon properties and their role in supercapacitors*. Journal of Power Sources, 2006. **157**(1): p. 11-27.
13. Pierson, H.O., *3 - Graphite Structure and Properties*, in *Handbook of Carbon, Graphite, Diamonds and Fullerenes*. 1993, William Andrew Publishing: Oxford. p. 43-69.
14. Li, D., et al., *Processable aqueous dispersions of graphene nanosheets*. Nature Nanotechnology, 2008. **3**(2): p. 101-105.
15. Sudiarta, I.W. and D.J.W. Geldart, *Interaction Energy of a Water Molecule with a Single-Layer Graphitic Surface Modeled by Hydrogen- and Fluorine-Terminated Clusters*. The Journal of Physical Chemistry A, 2006. **110**(35): p. 10501-10506.
16. Israelachvili, J. and H. Wennerström, *Role of hydration and water structure in biological and colloidal interactions*. Nature, 1996. **379**: p. 219.
17. Chandler, D., *Interfaces and the driving force of hydrophobic assembly*. Nature, 2005. **437**(7059): p. 640-647.
18. Behabtu, N., et al., *Spontaneous high-concentration dispersions and liquid crystals of graphene*. Nature Nanotechnology, 2010. **5**(6): p. 406-11.
19. Cheng, C. and D. Li, *Solvated graphenes: an emerging class of functional soft materials*. Advanced Materials, 2013. **25**(1): p. 13-30.
20. Yang, X., et al., *Bioinspired Effective Prevention of Restacking in Multilayered Graphene Films: Towards the Next Generation of High-Performance Supercapacitors*. Advanced Materials, 2011. **23**(25): p. 2833-2838.
21. Qiu, L., et al., *Controllable corrugation of chemically converted graphene sheets in water and potential application for nanofiltration*. Chemical Communications, 2011. **47**(20): p. 5810-5812.
22. Forse, A.C., et al., *New Perspectives on the Charging Mechanisms of Supercapacitors*. Journal of the American Chemical Society, 2016.
23. Wang, Q., J. Yan, and Z. Fan, *Carbon materials for high volumetric performance supercapacitors: design, progress, challenges and opportunities*. Energy & Environmental Science, 2016.
24. Wang, Y., et al., *Revisiting the capacitance of polyaniline by using graphene hydrogel films*

as a substrate: the importance of nano-architecturing. Energy & Environmental Science, 2013. **6**(2): p. 477-481.

25. Wang, Y., et al., *High-Rate and High-Volumetric Capacitance of Compact Graphene-Polyaniline Hydrogel Electrodes*. Advanced Functional Materials, 2016. **6**(11):1600185.
26. Lukatskaya, M.R., et al., *Ultra-high-rate pseudocapacitive energy storage in two-dimensional transition metal carbides*. Nature Energy, 2017. **2**: p. 17105.
27. Geng, X., et al., *Two-Dimensional Water-Coupled Metallic MoS₂ with Nanochannels for Ultrafast Supercapacitors*. Nano Letters, 2017. **17**(3): p. 1825-1832.
28. Ghidui, M., et al., *Conductive two-dimensional titanium carbide 'clay' with high volumetric capacitance*. Nature, 2014. **516**: p. 78.
29. Lin, Z., et al., *Electrochemical and in-situ X-ray diffraction studies of Ti₃C₂T_x MXene in ionic liquid electrolyte*. Electrochemistry Communications, 2016. **72**(Supplement C): p. 50-53.