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Perspective

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

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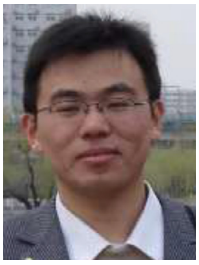
ABSTRACT

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.

Ke Zhang received his B.S. degree from the Department of Materials Science and Engineering at Monash University and Central South University in 2015. He is currently a Ph.D. candidate at Monash University under the supervision of Professor Dan Li. His research interests focus on graphene-based nanoporous electrodes and their charging kinetics for energy storage.



Xiaowei Yang is a professor at the School of Materials Science and Engineering, Tongji University. He received his Ph.D. degree from Shanghai Jiao Tong University in 2011 with Professor Zi-Feng Ma, and then carried out research on graphene-based gel in Professor Dan Li's group at Monash University from 2009 to 2014. His current research interests are centered on the synthesis and properties of two dimensional soft materials and their applications in energy storage and conversion and biomedicine.

Dan Li is a professor in materials science and engineering at the University of Melbourne, Australia. He received his Ph.D. degree in Materials Physics and Chemistry from the University of Electronic Science and Technology of China in 1999. After several years as a Research Fellow at Nanjing University of Science and Technology, University of Washington, University of California Los Angles, and University of Wollongong, he joined Monash University as an associate professor in 2008 and was promoted to full professor in 2012. He was a foundation co-director of Monash Centre for Atomically Thin Materials (2015–2017). He joined the Department of Chemical Engineering, University of Melbourne in 2017. He received the ARC Queen Elizabeth II Fellowship in 2006, the Scopus Young Researcher of the Year Award (Engineering and Technology) in 2010, ARC Future Fellowship in 2011, Dean's Award for Excellence in Research in 2012 and a Visiting Changjiang Chaired Professorship from the Ministry of Education, China in 2016. He has been named in the list of Thomson Reuters' Highly Cited Researchers in the category of Materials Science since 2014. His current research interest involves colloidal processing of advanced materials into energy storage devices, flexible electronics, and the use of graphene-based materials and related atomically thin materials into nanoionics, new ion separation technologies and materials systems engineering.

1. 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

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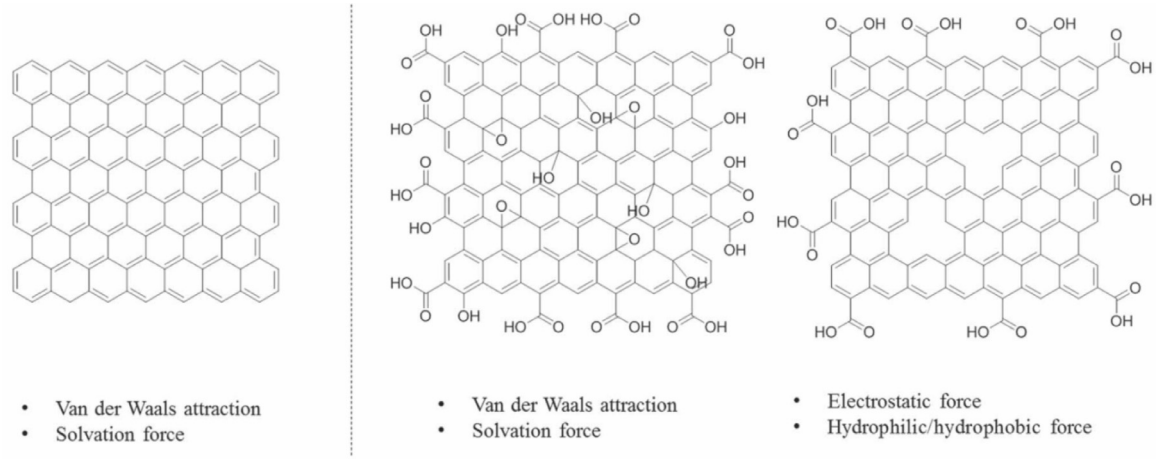

Fig. 1. Domains and colloidal interactions of solvated graphene. Left: pristine graphene; middle: graphene oxide; right: reduced graphene oxide. Reproduced with permissions from Ref. [19]. Copyrights 2013 Wiley-VCH.

energy leveling, 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 current collector. To achieve supercapacitors with high energy density, the following features are required for the electrode material: (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 criteria are conflicting with each other, posing a great challenge for 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 contain 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 performance. Thus, the key lies in how graphene can be assembled in an appropriate way to optimize all the above parameters.

2. Challenges in engineering traditional activated carbon

Commercial porous carbon materials for supercapacitors are based on activated carbon and are generally fabricated from the high-temperature carbonization of organic precursors such as nut shell, woods and other biomass materials, followed by either high temperature 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 associated with this top-down approach may explain why the energy density of supercapacitors based on activated carbon has not been substantially improved in the past decades.

3. 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 make it challenging to disperse graphene 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.

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 corru-