Current Opinion in Colloid & Interface Science 20 (2015) 346–353

Contents lists available at ScienceDirect

Current Opinion in Colloid & Interface Science

journal homepage: www.elsevier.com/locate/cocis

Understanding fundamental processes in carbon materials with well-defined colloidal graphene quantum dots

Qiqi Li, Benjamin W. Noffke, Yijun Liu, Liang-shi Li *

Department of Chemistry, Indiana University, Bloomington, IN 47405 USA

ARTICLE INFO

Article history:
Received 20 September 2015
Accepted 24 October 2015
Available online 5 November 2015

Keywords:
Graphene
Quantum dots
Colloidal

ABSTRACT

Carbon materials have played very important roles in our society. Due to their complexity and inhomogeneity, however, our understandings of these materials have seriously lagged behind. As a result, development of new carbon materials has been largely based on trial and error. Here, we review our recent work on using well-defined colloidal graphene quantum dots as model systems to study fundamental processes in carbon materials. The future directions and limitations of this approach are also discussed.

1. Introduction

It is impossible to overestimate the importance of carbon materials in our society. Indeed, they are ubiquitous, ranging from lead in pencils, carbon black in tires, to adsorbents in gas masks, and electrodes in batteries. In addition, carbon constitutes a large portion of the energy supply we have today (i.e., coal), yet with the unfortunate side effect of releasing a large amount of CO_2 to the atmosphere. Driven by concerns about the adverse impact due to human activities and demands for technologies to enable global sustainability, research efforts have intensified in recent years to broaden the use of carbon materials. Important directions include developing new carbon materials for renewable energy applications and to carry out functions that traditionally require rare and precious metals [1–3].

In sharp contrast to the wide applications of the graphitic carbon materials is our limited and mostly empirical understanding of fundamental processes in them; primarily because of the heterogeneity and complexity of these materials. As a result, the development of new carbon materials has been largely based on trial and error. A molecular understanding will undoubtedly facilitate the advancement, which however demands a model system to study these complex materials.

Can graphene, a single atomic layer of graphite, provide a natural model system for studying graphitic carbon materials? After all, the graphitic carbon materials, such as graphite, carbon black, activated carbon, carbon fibers, and nanotubes, are overwhelmingly made of conjugated framework of sp^2-hybridized carbon atoms. Additionally, single domains of graphene, up to millimeters in size, can be readily isolated through mechanical exfoliation and can be studied with various experimental techniques. However, graphene has a few intrinsic disadvantages. For example, it has been demonstrated that either the support underneath [4] or mechanical strain [5,6] can significantly alter the electronic properties of graphene and its chemical reactivity. In addition, graphene consists of only surface and in essence a single molecule. This means that to study the chemical processes involving graphene, sophisticated techniques with high sensitivity are required. Further, many processes occurring in the graphitic carbon materials involve heteroatoms. The functionalization (or doping) of graphene is mostly achieved with high temperature, plasma, or strong oxidants [7–9]. The harsh doping conditions and poorly controlled chemistry result in defects and are not capable of controlling the location, density, or bonding configurations of the heteroatoms, making accurate characterization of the materials difficult. The same difficulties also exist in doping of carbon nanotubes or graphite, and thus alternatives are needed as model systems for the graphitic carbon materials.

In this perspective, we discuss recent work in our research group that uses well-defined colloidal graphene quantum dots (GQDs) [10,11] as model systems to understand fundamental processes in graphitic carbon materials. We will first briefly introduce the GQDs, followed by their applications in studying carbon materials for catalysis and mechanisms of chemical reactions in carbon materials.

2. Why graphene quantum dots?

The graphene quantum dots (GQDs) discussed in this perspective have well-defined structures and are soluble (dispersible) in solvents (examples in Fig. 1) [12]. They are synthesized from small aromatic compounds through stepwise solution chemistry (e.g., Fig. 2) and have excellent size uniformity. To make them soluble in common solvents such as chloroform, toluene, and so forth, we recently developed

* Corresponding author.
E-mail address: li23@indiana.edu (L. Li).

http://dx.doi.org/10.1016/j.cocis.2015.10.008
1359-0294/

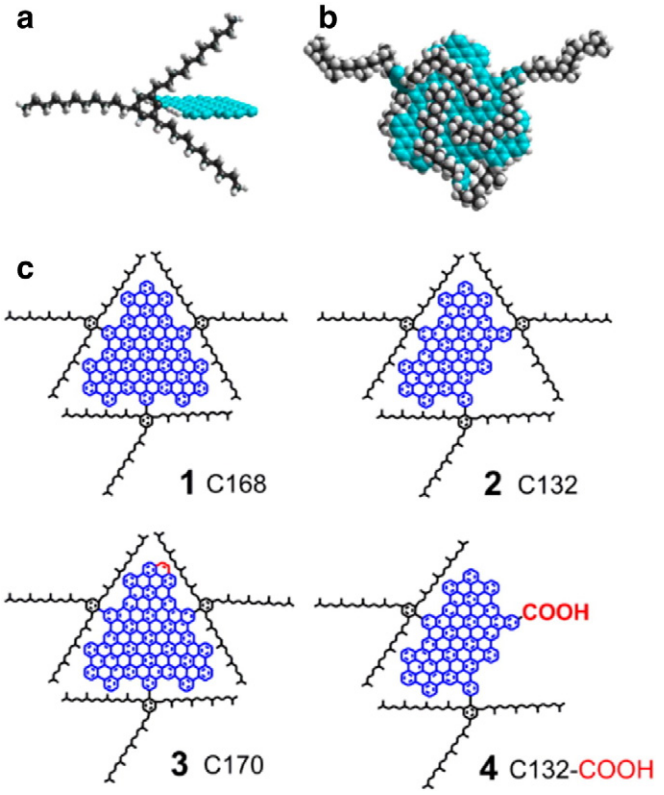

Fig. 1. Colloidal graphene quantum dots (GQDs) with well-defined structures. (a) A 2′,4′,6′-trialkylphenyl moiety (black) is covalently attached to the edge of the graphene (blue) so that the crowdedness on the edge forces the peripheral phenyl groups to twist from the plane of the graphene. (b) An energy-minimized geometry of GQD **1** (in c), showing the three-dimensional cage made of the flexible alkyl chains (black) around the graphene core (blue). (c) Structures of examples of colloidal GQDs, with the graphene core containing 168, 132, 170, and 132 conjugated carbon atoms. The structures of the GQDs are controlled with stepwise solution chemistry (Fig. 2) so that they have excellent size uniformity. (Adapted with permission from ref. [10]. Copyright 2013 American Chemical Society.)

a new solubilization strategy for large polycyclic aromatic hydrocarbons [13,14]. This was achieved by covalently attaching multiple 2′,4′,6′-trialkyl-substituted phenyl moieties (at the 1′-position) to the edges of graphene (Fig. 1a). The crowding on the edges forces the peripheral phenyl groups to twist from the plane of the graphene, resulting in the alkyl chains forming a three-dimensional "cage" around it (Fig. 1b). This leads to increased distance between the conjugated systems in all three dimensions and thus greatly reduces the intermolecular π–π attraction. The new solubilization approach enabled us to synthesize colloidal graphene quantum dots (GQDs) with well-defined molecular structures, e.g., **1**–**4** in Fig. 1c that contain 168, 132, 170, and 132 conjugated carbon atoms in the graphene core (marked blue), respectively.

The well-defined GQDs have some unique characteristics that make them excellent model systems for studying fundamental processes in complex carbon materials. Clearly, the structural uniformity of the GQDs is matched by few other carbon nanostructures we know so far (i.e., fullerenes and nanotubes); yet the GQDs enjoy much greater structural tunability because they can be made with various sizes, shape, and symmetry. As we will see below, the solution chemistry synthesis further allows us to incorporate heteroatoms necessary for some applications into the conjugated framework with atomic precision, which has been very challenging for other carbon nanostructures. The high solubility of the GQDs in common solvents is also very important for experimental studies. It enables us to apply readily available, versatile ensemble characterization techniques, which, together with the structural uniformity, can greatly simplify the interpretation of experimental results.

What we believe will be particularly important and fruitful in carbon research is that the GQDs enable direct comparison between experiments and computational studies. Using nanoflakes as computational models for carbon materials have gained popularity in recent years due to the advances in theoretical methods and the availability of more powerful computers. However, to model carbon materials, various assumptions have to be made regarding the size of the nanoflakes, positions or bonding of dopants, etc., whereas the well-defined GQDs make such assumptions unnecessary. As will be seen in the work discussed below, the direct comparison between experimental and computational studies has been crucial in our studies to reveal active intermediates and to propose possible reaction pathways.

3. Study carbon materials for catalysis

3.1. Carbon–metal interactions

The unique features of the well-defined GQDs, together with their large sizes, make them excellent model systems to study the interaction between the conjugated carbon framework and metal nanoparticles. Graphitic carbon materials, including cokes, active carbon, carbon black, carbon fibers, and nanotubes, are often used as supports for metal nanoparticles in catalysis [15,16]. However, because of the inhomogeneity and complexity of these carbon materials, our knowledge on metal–carbon interactions comes mainly from theoretical

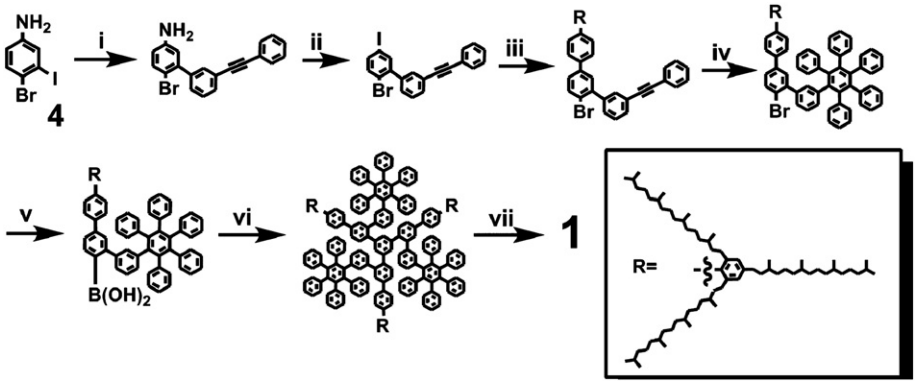

Fig. 2. Synthetic route for colloidal GQD **1**. The GQD is synthesized with stepwise organic reactions and has excellent size uniformity. Conditions: (i) 3-(phenylethynyl)phenylboronic acid, $Pd(PPh_3)_4$, K_2CO_3, toluene, EtOH, H_2O, 80 °C (94%); (ii) I2, *t*-butyl nitrite, benzene, 5 °C (54%); (iii) 4-(2′,4′,6′-trialkylphenyl)phenylborate, $Pd(PPh_3)_4$, K_2CO_3, toluene, EtOH, H_2O, 80 °C (92%); (iv) tetraphenylcyclopentadienone, diphenyl ether, reflux (61%); (v) (a) *n*-BuLi, THF, −78 °C, (b) B(*i*-PrO)$_3$, (c) HCl, H_2O (60%); (vi) 1,3,5-triiodobenzene, $Pd(PPh_3)_4$, K_2CO_3, H_2O, toluene, 80 °C (52%); (vii) $FeCl_3$, CH_2Cl_2, CH_3NO_2 (100%). (Adapted with permission from ref [10]. Copyright 2013 American Chemical Society.)