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Porous graphite oxide pillared with tetrapod-shaped molecules

Jinhua Sun [a], Francisco Morales-Lara [b, c], Alexey Klechikov [a], Alexandr V. Talyzin [a, *], Igor A. Baburin [d], Gotthard Seifert [d], Francesca Cardano [b], Michele Baldrighi [b], Marco Frasconi [e, **], Silvia Giordani [b, c, f, ***]

[a] *Umeå University, Department of Physics, S-90187, Umeå, Sweden*
[b] *Istituto Italiano di Tecnologia (IIT), Nano Carbon Materials, Via Morego 30, Genoa, Italy*
[c] *Istituto Italiano di Tecnologia (IIT), Graphene Labs, Via Morego 30, Genoa, Italy*
[d] *Technische Universität Dresden, Theoretische Chemie, Bergstraße 66b, 01062, Dresden, Germany*
[e] *University of Padova, Department of Chemical Sciences, Via Marzolo 1, Padova, Italy*
[f] *University of Turin, Department of Chemistry, Via Giuria 7, Turin, Italy*

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ABSTRACT

Porous pillared graphene oxide (GO) materials were prepared using solvothermal reaction of Hummers GO with solution of Tetrakis(4-aminophenyl)methane (TKAm) in methanol. The intercalation of TKAm molecules between individual GO sheets, performed under swelling condition, results in expansion of inter-layer distance of GO from ~7.5 Å to 13-14 Å. Pillaring GO with bulky, rigid 3D shaped TKAm molecules could be an advantage for the preparation of stable pillared structures compared to e.g. aliphatic or aromatic diamines. Insertion of TKAm molecules into inter-layer space of GO results in formation of interconnected network of sub-nanometer slit pores. The expanded GO structure prepared with optimized GO/TKAm composition shows Specific Surface Area (SSA) up to 660 m^2/g which is among the highest reported for GO materials pillared using organic spacers. Modelling of GO structures pillared with TKAm molecules shows that maximal SSA of about 2300 m^2/g is theoretically possible for realistic concentration of pillaring molecules in GO interlayers. Hydrogen sorption by pillared GO/TKAm is found to follow standard correlation with SSA both at ambient and liquid nitrogen temperatures with highest uptakes of 1.66 wt% achieved at 77 K and 0.25 wt% at 295 K. Our theoretical simulations show that pillared GO structures do not provide improvement of hydrogen storage beyond well-established physisorption trends even for idealized materials with subnanometer pores and SSA of 2300–3700 m^2/g.

1. Introduction

The unique properties of graphene oxide (GO) multilayers are promising for variety of applications, e.g. for preparation of mechanically strong papers [1], membranes for gas and liquid mixtures separation [2–8], nano-filtration [9,10], water desalination [11,12], etc. The hydrophilic nature of GO was reported in very early studies [13,14], and by the 60-s it was already well known that GO swells in polar solvents with expansion of the interlayer distance from 6-7Å up to 40-50 Å depending on the molecular size and amount of intercalated solvent [2,15,16]. Swelling enables penetration of various molecules into inter-layer space of GO. The stronger is expansion of GO lattice due to swelling, the larger molecules can be inserted and used as "pillars" for preparation of porous structures. Perhaps the most studied GO solvates by now are those with alcohols [17]. It is known that GO prepared by Hummers method [18] (H-GO) exhibits much stronger expansion of lattice due to swelling compared to GO prepared by Brodie method (B-GO) [13] while B-GO shows better ordered structures with well-defined layer by layer intercalation of solvents [8,19–22]. Graphite and graphene oxides provide enormous possibilities for chemical modification with the aim to prepare materials with porous structures using pillaring molecules [23–26]. Pillared GO materials (PGO) with high surface area could be useful for many possible

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* Corresponding author.
** Corresponding author.
*** Corresponding author.

E-mail addresses: alexandr.talyzin@physics.umu.se (A.V. Talyzin), marco.frasconi@unipd.it (M. Frasconi), silvia.giordani@iit.it (S. Giordani).

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applications, e.g. gas storage [24], materials for supercapacitors [27] and membranes [28]. PGO's have been considered also as a promising material for hydrogen storage applications thanks to theoretical predictions of improved gravimetric sorption in sub-nanometer slit pores formed by graphene planes [29]. Graphite shows ~3.35 Å spacing between graphene sheets. According to theoretical studies the optimal separation of graphene sheets for maximal hydrogen sorption is predicted to be on the level of 7–12 Å [29,30]. However, these theoretical simulations simply postulated variations of inter-layer distance while experimental realization requires some pillaring molecules which could hold the graphene sheets separated from each other.

Several approaches have been proposed over the past decade to make pillared graphene-related materials, including functionalization of dispersed reduced GO (r-GO), pyrolysis of intercalated GO [31–33] or pillaring with various relatively large nanoparticles. For example, pillaring with carbon black particles resulted in preparation of materials with relatively high SSA of up to ~1000 m^2/g [34]. The variability of diameter and shape of those nanoparticles has not allowed, however, to prepare ordered structure with precise size of pores. In contrast, our study is focused (i) on using molecular pillars, which have a definite shape and size, and (ii) preparation procedure, which do not include dispersion of graphite oxide on single layered graphene oxide sheets. Graphene oxide seems to be the best available precursor for the preparation of pillared materials since it can be chemically functionalized with variety of molecules. These molecules can be inserted using swelling the GO in polar solvents resulting in the expansion of inter-layer distance of GO. It is important to emphasize that the expansion of GO inter-layer distance is dependent on the solvent used as well as on temperature and pressure conditions and it is significantly different for graphite oxides prepared using e.g. Brodie or Hummers methods [17,18,29–31]. This concept was tested in several studies which include e.g. solvothermal reaction of graphite oxide powder with 1,4-benzene diboronic acid (DBA). An idealized structural model with DBA molecules linking neighboring graphene sheets was proposed for these materials [23]. Later studies demonstrated that these molecular linkers are likely to attach only on one side of GO inter-layer [24,35]. Several other linker molecules or nanoparticles have also been tested for preparation of PGO [25,28,36]. The experimental SSA reported for some of these PGO materials (~400–800 m^2/g) is significantly higher compared to pristine graphite oxide. Our earlier experiments also confirmed the formation of porous GO/DBA structures with SSA values up to 1000 m^2/g and sub-nanometer pore width [24]. However, PGO materials with SSA on that level are not competitive for hydrogen storage applications. The best values of SSA for activated graphene materials are over 3000 m^2/g [37] and several structures with SSA above 6000 m^2/g are reported for Metal Organic Framework (MOF) materials [38]. New pillared GO and pillared graphene materials with higher SSA values must be prepared for hydrogen storage applications. Therefore, there is strong interest to test new pillaring molecules for preparation of porous GO materials with high SSA.

Aliphatic and aromatic amines are promising types of molecules that have been previously tested for the preparation of PGO [15,16,39,40]. The interlayer distance of GO intercalated with linear aliphatic amines has been reported to increase linearly from ~22 Å to ~60 Å according to the size of the molecules (4–20 carbon atoms) [15]. For example, the reaction of pentylamine with GO at 40–50 °C studied by A.Lerf et al. resulted in GO interlayer distance of 19.6 Å in as-prepared sample and 13.6 Å for the washed and dried sample [41]. The insertion of pentylamine molecules into GO structure has been reported in this study mostly by intercalation and only partly by nucleophilic attack on epoxy groups of GO. On the other hand, reaction of long chain alkylamines at near ambient temperature was reported to result in three different types of intercalated species: hydrogen-bonded neutral amines, hydrogen-bonded protonated amines and protonated amines with ionic interaction to GO [42]. The intercalated amines can be removed by washing with ethanol.

The first attempt to prepare PGO or pillared graphene using prolonged ambient temperature reaction with several amines followed by reduction resulted in expanded (relative to precursor GO) interlayer distance of 11.3 Å. However, there was no increase of surface area measured by nitrogen sorption (<2 m^2/g) [39]. It was suggested that the main reaction pathway was nucleophilic addition on the epoxy groups with covalent attachment of the pillaring molecules to GO.

In recent years several attempts to prepare PGO using diamines have been performed, e.g. by reactions of GO with ethylenediamine, butylenediamine, and *p*-phenylenediamine which resulted in expansion of the GO lattice (9.1 Å, 9.7 Å and 10.1 Å respectively) but surface area of these materials was not evaluated [28]. Several other studies reported reactions of amines or diamines with GO but not SSA or gas sorption properties of prepared materials [36,43,44]. The lattice expansion, however, does not imply that diamine molecules inter-link GO planes or that a pillared porous structure is formed. Moreover, it can be expected that a pillared GO structures based on diamine linkers with linear shape would be unstable even against the slight shear stress. The highest SSA so far achieved for diamine-functionalized GO is 276 m^2/g which is a relatively small increase relative to the precursor GO used in these experiments (200 m^2/g) [35]. One of the possible reasons for the relatively small SSA values achieved so far using linear shaped amines as pillaring molecules could be the low stability of the material against shear stress which results in the collapse of pores.

Therefore, we propose here that rigid 3D shaped molecules are more likely to provide higher mechanical stability for porous pillared GO structures. To our knowledge the only amine molecule with 3D shape so far attempted for preparation of pillaring of GO is adamantylamine but the reported SSA value of this material is only 37 m^2/g, comparable to that of dispersed and freeze dried GO [45].

In this study we report novel pillared GO material prepared using solvothermal reaction with Tetrakis(4-aminophenyl) methane (TKAm). The molecule has four amine groups which makes inter-linking of GO planes more likely and a 3D shape which could be of advantage for stability of pillared structures. Optimization of synthesis conditions resulted in preparation of materials with SSA values over 600 m^2/g and interlayer distance of ~14 Å which are compatible with structural model of GO sheets functionalized with TKAm pillars. Hydrogen sorption evaluated for GO/TKAm at 77 K and ambient temperature showed correlation with observed SSA according to standard trends known for physisorption on high surface area materials.

2. Experimental

2.1. Materials

The precursor “pillaring” compound TKAm was prepared according to previously reported literature procedures with minor modifications [46], see supplementary data for details.

Commercial graphite by Alfa Aesar (natural powder, 200 mesh, 99.9999%) was used as starting material for the preparation of graphite oxide samples following the Hummers method [18]. Characterization by XRD, FTIR, TGA and XPS confirmed high quality of samples and absence of unreacted graphite impurities. A C/O = 2.5 composition was determined by XPS. H-GO samples always