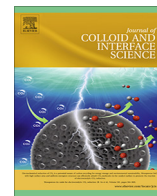




Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

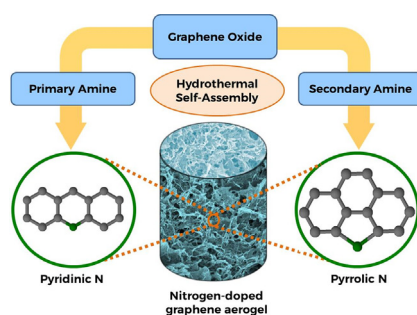
journal homepage: www.elsevier.com/locate/jcis

Regular Article

New insights into the role of nitrogen-bonding configurations in enhancing the photocatalytic activity of nitrogen-doped graphene aerogels

Yiqun Jiang^{a,1}, Shamik Chowdhury^{b,1}, Rajasekhar Balasubramanian^{a,b,*}^aDepartment of Civil & Environmental Engineering, National University of Singapore, 1 Engineering Drive 2, Singapore 117576, Republic of Singapore^bCentre for Advanced 2D Materials, National University of Singapore, 6 Science Drive 2, Singapore 117546, Republic of Singapore

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 16 June 2018

Revised 17 September 2018

Accepted 18 September 2018

Available online 19 September 2018

Keywords:

Graphene aerogels

Nitrogen doping

Bonding configuration

Photocatalysis

Visible light

Acridine orange

ABSTRACT

Nitrogen (N)-doped graphene aerogels (GAs) have recently emerged as a promising class of photocatalytic materials for a multitude of environmental applications. Their photocatalytic activity depends strongly on the type of N bonding configurations created in the host lattice, which in turn relies on the choice of nitrogen sources employed as molecular precursors. However, there is still no systematic assessment of the photocatalytic activity of N-doped GAs (NGAs) synthesized using different nitrogen containing precursors. Herein, we developed a series of NGAs using different kinds of amine, such as primary and secondary amines, as nitrogen precursors and rigorously evaluated their photocatalytic activity toward degradation of acridine orange under visible light irradiation. The bonding state of N atoms in the NGAs could indeed be effectively modulated by a judicious selection of an appropriate nitrogen precursor. Primary amines resulted mainly in pyridinic N structures whereas pyrrolic N was predominantly obtained from secondary amines. Irrespective of the source of nitrogen, the photocatalytic efficiency of the NGAs was directly correlated to the concentration of pyrrolic N defects in their constituent graphene building blocks. Further, the photodegradation byproducts did not present any significant antibacterial activity, reflecting the ecofriendly nature of the as-prepared novel photocatalysts.

© 2018 Elsevier Inc. All rights reserved.

* Corresponding author at: Department of Civil & Environmental Engineering, National University of Singapore, 1 Engineering Drive 2, Singapore 117576, Republic of Singapore.

E-mail address: ceerbala@nus.edu.sg (R. Balasubramanian).

¹ These authors contributed equally to this work.

1. Introduction

Graphene aerogels (GAs) have recently emerged as a highly promising class of photocatalytic materials for a variety of environmentally related applications [1–4]. Their seamlessly

interconnected networks and superior graphene building blocks provide exceptional light-harvesting capabilities, facilitate rapid spatial separation of photogenerated electron–hole pairs, and promote fast interfacial electron transfer in three-dimensional (3D) space [5]. However, their overall performance is not satisfactory from a practical viewpoint due to the absence of an intrinsic band gap in graphene itself [6]. Among the various techniques explored to create a tunable and sizable band gap in graphene, chemical modification through doping with heteroatoms such as nitrogen (N) has been extensively reported to be the most promising option [6,7]. The introduction of N atoms with different electronegativity from carbon (C) atoms into the graphitic lattice rearranges the electrons in the sp^2 hybridized network [8,9], which in turn enriches the free charge-carrier density and hence the photocatalytic activity of the bulk material. In light of these merits, N doping of GAs is widely studied for developing efficient and advanced photocatalytic materials for a wide range of environmental applications [10–13].

Generally, N atoms are present in three common bonding configurations when incorporated into the honeycomb lattice of graphene (Fig. 1): pyridinic N (two C–N bonds in a hexagon), pyrrolic N (two C–N bonds in a pentagon) and graphitic-like N (three sp^2 C–N bonds in the form of substitution) [8,15]. Among them, the pyridinic N and pyrrolic N are widely regarded as the active sites of catalysis because of their highly delocalized valence electrons [16]. It is, therefore, highly desirable to develop N-doped GAs (NGAs) with a high concentration of pyridinic and pyrrolic N moieties for realizing highly efficient photocatalysts for environmental remediation applications. However, the relative proportions of these two N-structural motifs in the host lattice depend strongly on the type of nitrogen source employed as precursor [17]. This is conceivable because the molecular structure of the nitrogen precursor applied may dictate how the conjugated π -electron system of graphene is attacked, and thus the type of N doping configurations generated in the sp^2 carbon framework. Nevertheless, systematic studies on the effect of the nitrogen precursor type on the relative amount of the different forms of N dopants as well as the photocatalytic potential of NGAs are sparsely reported in the literature.

Herein, we investigated the influence of different kinds of amines, such as primary (ethylenediamine, EDA) and secondary (diethylenetriamine, DETA; tetraethylenepentamine, TEPA) amines, as nitrogen containing organic precursors on the concentra-

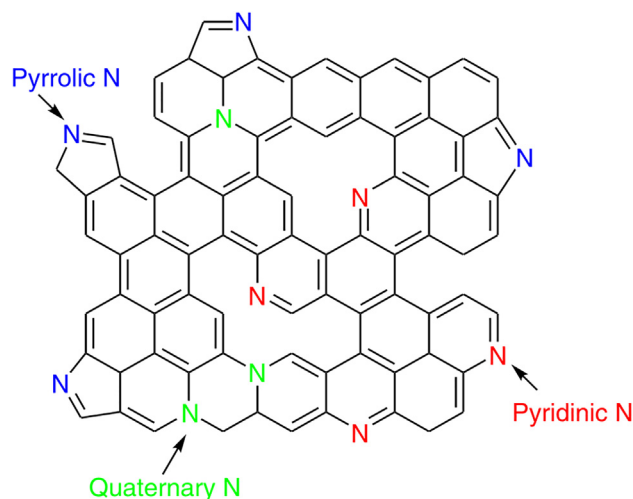


Fig. 1. Common bonding configurations of N atoms in N-doped graphene materials. Reproduced from Zhou et al. [14], Copyright 2014, with permission of Springer Nature.

tion of the various bonding state of N atoms in NGAs. The use of primary amines created mainly pyridinic N structures whereas pyrrolic N was predominantly obtained from secondary amines. Irrespective of their doping level, a direct relationship between pyrrolic N loading and increase in photocatalytic activity was observed for the NGAs based on the model recalcitrant organic pollutant, acridine orange (AO), under visible light irradiation. In order to gain additional insights into the photocatalytic degradation mechanism, the effect of pH and the role of different kinds of reactive oxygen species were explored in detail. Finally, the toxicity of AO and of the treated AO solutions was evaluated toward *Escherichia coli* (*E. coli*) cells, which shows that the photocatalysis byproducts and derivatives do not pose public health threats, exhibiting the outstanding performance of the as-developed NGAs.

2. Experimental

2.1. Materials

Graphene oxide (GO, 4 mg mL⁻¹ dispersion in water; Sigma-Aldrich), ethylenediamine (EDA, ≥99%; Sigma-Aldrich), diethylenetriamine (DETA, 99%; Sigma-Aldrich), tetraethylenepentamine (TEPA, technical grade; Sigma-Aldrich), acridine orange (AO, C.I. 46005; Sigma-Aldrich) and ethanol (C₂H₅OH, absolute, ≥99.8%; Sigma-Aldrich) were used as obtained from the supplier without any further purification. Deionized water was used throughout the experiments.

2.2. Synthesis of NGAs

NGAs were prepared through a facile one-pot hydrothermal method. In a typical procedure, 1.5 mL of the desired nitrogen precursor (i.e., EDA, DETA or TEPA) was added into 20 mL GO aqueous dispersion and stirred for 10 min at room temperature, followed by sonication for 30 min at a temperature below 30 °C in an Elmasonic S 60 H ultrasonic bath (550 W, 37 kHz) (Elma Schmidbauer GmbH, Germany). The resulting homogenous mixture was sealed in a 100 mL Teflon-lined stainless steel autoclave and hydrothermally treated at 180 °C for 12 h. The autoclave was then naturally cooled to ambient temperature. The as-synthesized N-doped graphene hydrogel was washed repeatedly with ultrapure water to remove any residual chemical and finally freeze-dried for 24 h to obtain the aerogel. The resultant NGAs were labeled NGA-X, where X is the applied nitrogen precursor. For comparison, pristine graphene aerogel (denoted as “GA”) was also produced using the same method, but without adding any nitrogen sources in the reaction mixture.

2.3. Instrumental characterization

Field emission scanning electron microscopy (FESEM) imaging was conducted on a FEI Verios 460 field emission microscope (FEI Ltd., USA). Wide angle X-ray diffraction (XRD) patterns were collected on a Bruker D8 ADVANCE X-ray diffractometer (Bruker Co., Germany) equipped with Ni-filtered Cu K α radiation source ($\lambda = 0.15$ nm). Raman spectra were acquired at room temperature using an Alpha300 R confocal Raman imaging microscope (WITec GmbH, Germany) with laser excitation wavelength of 532 nm. Fourier transform infrared spectroscopy (FTIR) was performed on a Varian Excalibur 3100 FTIR spectrometer (Varian Inc., USA) employing the potassium bromide pellet method. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a VG ESCA 220i-XL imaging system (Thermo VG Scientific Ltd., UK). Monochromatic Al K α X-ray ($h\nu = 1486$ eV) was employed for analysis with a photoelectron take-off angle of 90° to the sample plane.

Download English Version:

<https://daneshyari.com/en/article/11030017>

Download Persian Version:

<https://daneshyari.com/article/11030017>

[Daneshyari.com](https://daneshyari.com)