



Nitrogen-doped graphene hydrogels as potential adsorbents and photocatalysts for environmental remediation



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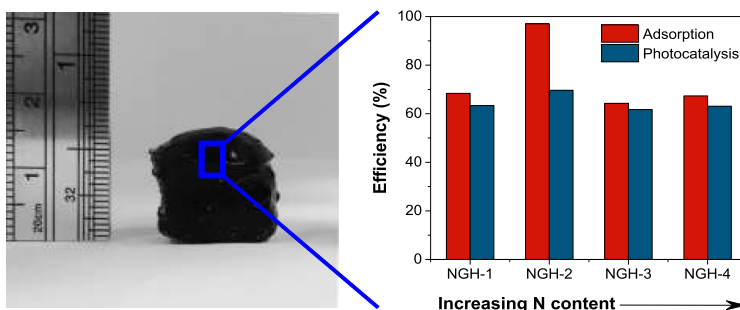
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HIGHLIGHTS

- N-doped graphene hydrogels developed by facile one-step hydrothermal reaction.
- N content inversely proportional to doping amount.
- Brunauer-Emmett-Teller specific surface area increases at all doping levels.
- Maximum dye adsorption and highest photodecolorization at N loading of 6.78 at.-%
- Better photooxidation due to synergistic effect of N-doping and 3D network structure.

GRAPHICAL ABSTRACT



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ABSTRACT

The chemical modification of self-assembled graphene hydrogels is a topic of emerging interest to harness the excellent physicochemical properties of two-dimensional (2D) graphene for macroscopic applications. We synthesized a series of mechanically strong and lightweight nitrogen (N)-doped graphene hydrogels (NGHs), with different doping concentrations, through a simple one-pot hydrothermal reaction and systematically evaluated their performance as both adsorbents and photocatalysts for environmental remediation. Acridine orange (AO) was chosen as a model pollutant. The successful incorporation of N atoms into the carbon lattice of the macroscale 3D graphene-based materials was verified by Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). Although the N content of the graphene macroassemblies varied inversely with doping density, a conspicuous increase in specific surface area was observed at all doping levels, resulting in a higher adsorption capacity and surface reactivity than the undoped hydrogel. The adsorption equilibrium was best represented by the Langmuir isotherm (with maximum monolayer coverage of 124 mg g^{-1} at 25°C) while the adsorption kinetics followed both the pseudo-first and pseudo-second order rate expressions. Further, the NGHs could effectively photodegrade 20 mg L^{-1} AO aqueous solution by almost 70% within 5 h of visible light irradiation. The fairly good photooxidative ability of the NGHs originates from the synergistic effect of N functionalization and 3D interconnected mesoporous network structure, leading to greater uptake of AO, better absorption of visible light and rapid spatial separation of photogenerated electron-hole pairs.

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1. Introduction

Two-dimensional (2D) graphene, by virtue of its many interesting properties, has proved itself as an exciting material with a wide range of opportunities for new scientific knowledge generation and technological innovations [1–3]. However, 2D graphene tends to form irreversible agglomerates or even restack to form graphite, causing a significant decrease in the ultrahigh surface area of individual graphene sheets [4]. In order to overcome this restacking issue and explore the macroscopic applications of graphene, the integration of 2D graphene macromolecule sheets into 3D macroscopic assemblies and ultimately into a functional system has recently emerged as an increasingly important approach [5–7]. Consequently, many exotic 3D graphene-based macrostructures (GBMs), such as aerogels, hydrogels, sponges, foams, frameworks with periodic structures, honeycomb-like structures, porous films, vertical sheets, etc., have been intensively developed during the past few years [8,9]. These rationally designed macroscopic architectures exhibit low mass density, large accessible surface area, abundant pore space, continuously interconnected networks and channels, excellent electrical conductivity, high electrochemical stability and superior mechanical flexibility [8–10]. As a result, 3D GBMs can (1) support rapid electron transport in 3D space, (2) ensure faster ion diffusion, (3) provide adequate space for molecular adsorption and (4) promote efficient mass transfer [9].

In addition, 3D GBMs have large internal pores and can therefore serve as ideal scaffolds for functionalization with heteroatoms, functional polymers, inorganic nanostructures, as well as many other carbon nanomaterials, leading to new material systems with unique properties and novel functionalities [8,11–13]. In particular, doping with heteroatoms such as nitrogen (N) offers many novel possibilities for tailoring the structural and electronic properties of graphene [14]. The incorporation of N with higher electronegativity than carbon (C) creates polarization in the sp^2 hybridized network, which in turn opens a band gap close to the Dirac point by suppressing the nearby density of states and bestows graphene with semiconducting properties [15]. Moreover, the manipulated local electronic structures greatly enhance the binding affinity of the carbon matrix [15]. In view of these considerations, N-doping of 3D GBMs represents an exciting and promising new research direction for development of next-generation of robust adsorbents and photocatalysts for environmental remediation.

However, the macroscopic performance of N-doped graphene materials (NGMs) depends mainly on their N content and the type of N bonding configuration within the carbon lattice, including pyridinic-N, pyrrolic-N and quaternary-N (or graphitic-N) [16]. Among these N species, pyridinic-N and quaternary-N are sp^2 hybridized whereas pyrrolic-N is sp^3 hybridized [16]. As a result, the relative proportion of these three N bonding moieties play a key role in achieving the maximum functionality of NGMs, but were seldom investigated in previous studies. Modifying the structure and surface properties of graphene satisfactorily and synchronously through the specific type of N dopant may provide new insights to fabricate 3D GBMs with pre-programmed conformations and custom-made properties. However, to the best of our knowledge, no systematic experimental study has been conducted yet on the modulation of the physicochemical properties of 3D GBMs for environmental remediation applications by controlling the N-doping concentration and configuration.

Herein, we therefore prepared mechanically strong and lightweight N-doped graphene hydrogels (NGHs) with different doping density through a facile one-pot hydrothermal process using ammonium hydroxide as N precursor and rigorously evaluated their potential application as both an adsorbent and a photocatalyst for removal of organic pollutants from aqueous media.

Acridine orange (AO) was selected as the model contaminant since it is frequently reported to be present as one of the major recalcitrant organic pollutants in urban wastewaters and is also a highly potent mutagen [17,18]. For instance, the dye can easily intercalate between the nitrogenous base pairs of deoxyribonucleic acid (DNA) because of its planar polycyclic molecular structure (Fig. 1), resulting in elongation and unwinding of the double helix [19–21]. These structural modifications can induce functional changes, often leading to inhibition of DNA transcription, replication and repair [20]. Benefitting from the synergistic effect of N-doping and highly conductive 3D interconnected porous graphene skeleton, the as-fabricated NGH materials could afford high surface areas, short ion diffusion lengths and rapid electron/ion transport channels, thereby demonstrating excellent adsorption capacity and superior photocatalytic activity under visible light irradiation toward AO. In particular, the maximum adsorption uptake as well as the highest photodecolorization rate was observed for the hydrogel with a N loading of 6.78 at.%. Overall, our results represent one of the first studies to demonstrate that tuning the various physicochemical characteristics of heteroatom-doped graphene macroassemblies, such as the doping amount and the type of dopant bonding in the carbon matrix, is a prerequisite to realize their full potential as adsorbents/photocatalysts for environment-related applications.

2. Experimental

2.1. Materials

Graphene oxide (GO, 2 mg mL⁻¹ dispersion in water; Sigma-Aldrich), ammonium hydroxide (NH₄OH, 28–30% ammonia basis; Sigma-Aldrich), acridine orange (AO, C.I. 46005; Sigma-Aldrich), ethanol (C₂H₅OH, absolute, ≥99.8%; Sigma-Aldrich), hydrochloric acid (HCl, fuming, ≥37%; Fluka) nitric acid (HNO₃, 69%; Honeywell) and sodium hydroxide (NaOH, pellets, ≥98%; Sigma-Aldrich) were used as obtained from the supplier without any further purification. Deionized water was used throughout the experiments.

2.2. Synthesis of NGHs

NGHs were synthesized through a facile one-pot hydrothermal method. In a typical procedure, a desired amount of NH₄OH was added into 40 mL GO aqueous dispersion and stirred for 10 min at room temperature. 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-obtained NGH was washed repeatedly with water to remove any residual chemical and finally freeze-dried for 24 h. By altering the volume of NH₄OH in the reaction mixture ($V_{GO}/V_{NH_4OH} = 2.5, 5, 7.5, 10$), four

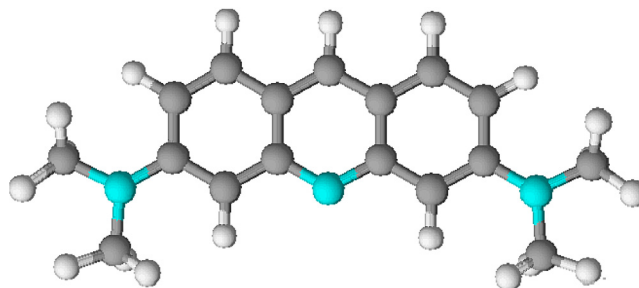


Fig. 1. Chemical structure of acridine orange (AO). Color legend: C (silver), H (white), N (cyan). (A color version of this figure can be viewed online.)

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