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RAPID COMMUNICATION

Nanocellulose as green dispersant for two-dimensional energy materials

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Abstract
The exfoliation/dispersion of two-dimensional (2D) materials is of great importance due to their unique properties and applications in electronics as well as energy storage devices. In this paper, we address the challenge of dispersing 2D materials in a scalable and environmentally friendly way. A methodology to efficiently disperse 2D materials [boron nitride (BN) and molybdenum disulfide (MoS_2)] in an aqueous solution using a green dispersant, nanofibrillated cellulose (NFC), was introduced. The stable high concentration BN/MoS_2 aqueous solutions allow the formation of multifunctional composites and may facilitate roll-to-roll manufacturing. Films and fibers with excellent mechanical strength were fabricated with the BN solution. Additionally, strong and flexible MoS_2 films were prepared and used as anodes for sodium ion batteries, indicating flexible battery applications.

Introduction

Two-dimensional (2D) materials with strong in-plane bonds but weak out-of-plane bonds have been extremely popular in research endeavors since the discovery of monolayer graphene in 2004 [1]. Besides graphene, there are numerous 2D materials such as boron nitride (BN), transition metal dichalcogenides (MoS_2, WS_2), and transition metal oxides (MoO_3, MnO_2) that exhibit interesting properties and offer a wide range of applications from electronics to the life sciences [2–4]. For instance, BN is an electronically insulating material with excellent thermal conductivity and stability. These unique properties make BN an outstanding candidate for many applications that are not possible for graphene [5,6]. Molybdenum disulfide (MoS_2) has also garnered much attention in electronics and as a photovoltaic

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material due to its strong absorption in the solar spectral range [7].

The exfoliation/dispersion of 2D materials yields materials with a very high surface area which is attractive in surface active and catalytic materials. The electronic band structure can also be modified through exfoliation/dispersion since the electrons are constrained to adopt a 2D wave function after exfoliation/dispersion [8,9]. For example, the band gap of bulk MoS_2 (indirect) and dispersed monolayer flakes (direct) differ dramatically. The changes in the electronic structure cause the monolayer flakes to exhibit strong photoluminescence [10,11]. The proper exfoliation method is essential to obtain a large quantity of high quality flakes. Numerous methods have been developed to disperse 2D materials; however, liquid exfoliation/dispersion remains superior since the process is potentially scalable, can lead to roll-to-roll manufacturing, and the obtained ink allows for the formation of multifunctional composites [12]. A dispersion method that utilizes greener solvents and dispersants can enable cost-effective large-scale production processes that minimize or eliminate the need for properly disposing potentially harmful chemicals [13-15].

Nanocellulose, mainly derived from wood with diameters in the nanoscale and lengths in the microscale, is considered to be a low-cost, green and inexhaustible material [16]. Owing to its impressive optical, mechanical, and thermal properties, nanocellulose has been extensively studied as a building block for films and fibers, a separator for batteries, and a substrate for electronic devices [17-21]. The presence of polar –OH groups enables hydrophilicity while the exposure of hydrophobic –CH moieties causes hydrophobic faces to form in the elementary fibrils. The existence of both hydrophilic and hydrophobic faces allows cellulose to be used as a dispersant [22]. Previously, nanocellulose has been reported as an emulsifier for perking emulsions [23], a stabilizer for magnetic nanoparticles [18] as well as a dispersant for carbon nanotubes (CNTs) [24]. The use of nanocellulose to disperse 2D energy materials is a novel concept that should be explored.

In this paper, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-oxidized nanofibrillated cellulose (NFC) was used as a dispersant to disperse 2D materials (BN and MoS_2) in water. Fig. 1 illustrates the mechanism for the dispersion of 2D materials by NFC: NFC attaches to the flakes through the interaction between its hydrophobic sites and the flake's hydrophobic plane as well as hydrogen bonding between the NFC hydroxyl groups and the defective edges of the 2D materials. The flakes are stabilized due to steric hindrance and the electrostatic repulsive forces generated by the charged NFC carboxyl groups. This method is more suitable for green, large-scale dispersion of 2D materials since proper disposal of the solvent is a non-issue. Composite films were fabricated using the NFC-assisted dispersed BN and MoS_2 aqueous solutions with great mechanical strength: 182 ± 16 MPa and 159 ± 18 MPa respectively. These values are among the highest achieved for composites with identical 2D material content [12,25-29]. Sodium ion batteries were also assembled with the MoS_2 films acting as an anode, indicating flexible battery applications.

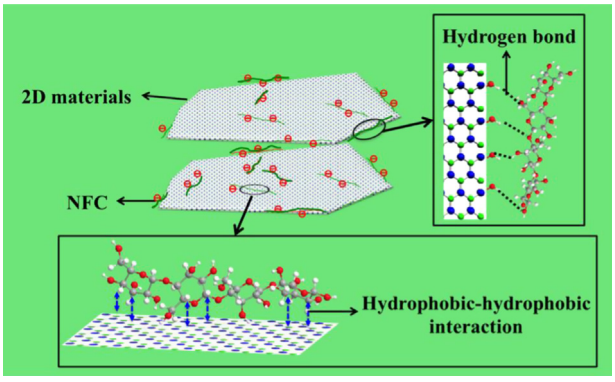

Fig. 1 Schematic to show how NFC disperses 2D materials. C, O, and H atoms are represented as gray, red, and white spheres, respectively. ⊖ represents the negative surface charge introduced by NFC carboxyl groups. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Experimental

NFC preparation

NFC was prepared according to a previously reported method [30]. Briefly, TEMPO (78 mg), sodium bromide (NaBr, 514 mg) and Kraft bleached softwood pulp (5 g) were mixed together. Then 10 mmol sodium hypochlorite (NaClO) was added under gentle agitation at room temperature to trigger the TEMPO oxidation of the cellulose fibers. During the oxidation process, the pH was maintained at 10.5 by adding sodium hydroxide (NaOH). The reaction ended when all the NaClO was consumed. After TEMPO treatment, the fibers were thoroughly washed with distilled water and disintegrated by one pass through a Microfluidizer M-110EH (Microfluidics Ind., USA) to obtain an NFC suspension. To evaluate the dispersion's stability, the Zeta potential was determined using a Zetasizer Nano ZS90 equipment. The concentration of the NFC solution for the Zeta potential tests was 0.3 wt% at a pH of 7.7 (Malvern Instruments, Worcestershire, UK). Atomic force microscopy (AFM) (Dimension FastScan, Bruker Corporation) was applied to characterize the morphology of NFC in tapping mode.

BN and MoS_2 dispersion

Commercial BN powder (Graphene Supermarket Inc., average particle size of 5 μm) and 10 wt% NFC (relative to BN powder) were mixed together in water with an initial BN concentration of 5 mg/mL. The exfoliation/dispersion process was performed through bath sonication for 30 h (FS 110D, Fisher Scientific). After sonication, the dispersion was then centrifuged at 3000 rpm for 15 min and the supernatant was kept. The absorbance spectrum of the BN dispersion was obtained with a UV-vis Spectrometer Lambda 35 (PerkinElmer, USA). The Zeta potential was determined using the Zetasizer Nano ZS90 equipment with a BN dispersion concentration of 0.7 mg/mL and a pH value of 7.8. (Malvern Instruments, Worcestershire, UK). The morphology of dispersed BN flakes was characterized by transmission electron microscopy (TEM) using a JEOL JEM 2100 (Japan) at an accelerating voltage of 200 kV.