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Synthesis of graphene-based amphiphilic Janus nanosheets via manipulation of hydrogen bonding

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ABSTRACT

The economical synthesis of amphiphilic Janus nanosheets in large amounts for practical applications is a grand challenge. This work reports a facile and scalable method to prepare graphene-based amphiphilic Janus nanosheets with much higher efficiency than the previously-reported wax template masking method. Graphene oxide (GO) was immobilized by hydrogen bonding on the surfaces of starch microspheres, confirmed by both experiments and Molecular Dynamics simulations. After selective functionalization of the exposed surface with alkylamine, amphiphilic Janus nanosheets (AJN) were obtained by releasing the nanosheets from the starch microspheres via breaking the hydrogen bonding. The interfacial behavior of AJN shows its amphiphilicity and the asymmetrical surface wettability indicated from the difference of contact angles, further demonstrated its Janus nature. In addition, avoiding of dissolving the template materials in comparison with wax masking method was also benefit for environment and recycling.

1. Introduction

Amphiphilic Janus particles can act as special solid surfactants due to their asymmetric surface wettability, which causes them to dwell at immiscible liquid interfaces for relatively longer periods of time than do homogeneous particles [1,2]. With corresponding stimulus, the change of interfacial behavior of Janus particles induces a phase inversed emulsion [3,4]. With appropriately decorated catalysts, amphiphilic Janus particles can greatly increase the yield and selectivity of reactions between two immiscible phases by interfacial catalysis [5–7]. Moreover, when dispersed in a single phase, the interactive forces between amphiphilic Janus particles trigger self-assembly to build controllable architectures [8,9]. For preparation of amphiphilic Janus particles, methods based on microfluidics [10,11], phase separation [12–15], masking [16–18], and click reactions [19] have been reported.

In the case of amphiphilic Janus two dimensional materials, various kinds of synthesis methods have also been raised in recent years, including template masking method [17,18,20], selective modification via manipulation of π-π stacking interactions [21] or utilization of special surface functional groups [22], and evaporation induced polymer crystallization at immiscible liquid interface [23], *etc.* One of the most widely applications of these nanosheets was to emulsify immiscible liquids as nanosheets demonstrated longer stability than other shapes of particles at liquid/liquid interfaces from the view of thermodynamics [2,24,25]. In addition, a simple stable nanofluid of amphiphilic Janus nanosheets was also found to effectively enhance underground oil recovery at low concentrations [26–28].

However, in order to produce amphiphilic Janus particles starting from chemically homogeneous nanosheets in large quantities, the required fabrication of nanometer-thickness channel severely limits the viability of the microfluidic method [29]. Usually, the phase separation method was used to obtain soft Janus particles. Meanwhile, click reactions restrict the chemical properties of the synthesized Janus particles and therefore are limited to specific applications [30]. When scaling up with properly tuning of the formation of emulsion template, the masking method can produce amphiphilic Janus particles in relatively large quantities,

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although particles are needed to stabilize monolayers for selective modification [16].

Previously, we employed a wax-in-water emulsion template masking method to synthesize graphene-based amphiphilic Janus nanosheets (AJN) [26]. In brief, graphite was first exfoliated and oxidized to graphene oxide (GO) [31]. Wax was then stirred with GO in water for a few hours to generate a Pickering emulsion at a temperature above its melting point. Wax microspheres covered with GO were obtained by cooling. Single-side surface hydrophobization with alkylamine was conducted in ethanol for 12 h, after which the wax microspheres were dissolved with organic solvents, *e.g.,* chloroform or toluene. However, the yield was still low (7.5 wt% of the initial GO). Moreover, the large amount of organic solvents used to dissolve the wax raised health concerns. From the economic and environmental perspective, it is urgent to find alternative methods to economically synthesize large amounts of AJN for industrial applications, *e.g.,* applications in the oil and gas industry.

Here, we report a highly-scalable method to synthesize graphene-based amphiphilic Janus nanosheets by manipulating hydrogen bonding. As shown in Scheme 1, by simply mixing GO and tapioca starch microspheres in water for a few hours at room temperature, GO is immobilized on the surface of tapioca starch microspheres by hydrogen bonds. After successive washing with water and ethanol, the single-side surface hydrophobization of GO was conducted with alkylamine in ethanol at room temperature. After washing, AJN was released from the starch microspheres by sonication and heating in ethanol. The mixture separated into two phases, with starch microspheres at the bottom portion and AJN dispersed in ethanol at the upper portion. In contrast to the previous method, no organic solvent was used to dissolve the solid support, and the separated starch microspheres can be easily recycled. Moreover, the starch microspheres were natural products available at low cost. With a much higher yield of around 70 wt% of the GO fed, we anticipate that this method would apply to production of a wide range of amphiphilic Janus particles.

2. Experimental section

2.1. Molecular dynamics simulations

A 24.9 Å × 25.9 Å monolayer graphene with 238 carbon atoms was used as substrate. A 30% oxidized graphene oxide (GO) was constructed by attached 4 carboxyls, 24 epoxies, and 28 hydroxyls to the substrate graphene. The structure of starch molecule was downloaded from Protein Data Bank (ID: 4BFN). The topology structures were created with TPPmktop [32]. The molecular dynamics (MD) simulation was performed using GROMACS 5.0.4 [33]. OPLS-AA force field was used for the simulation. A graphene oxide molecule was placed in the center of 6 nm × 6 nm × 6 nm box. 6 starch molecules and 6810 water molecules were then randomly added in the simulation box. After an energy minimization, the system underwent a 10 ns production simulation at 300 K and 1 bar. The time step was set to 2 fs. The information of system was recorded every 100 ps. All bond lengths were constrained using the LINCS algorithm. Cut-off of 1.2 nm was used for Lennard-Jones interactions and the real part of the long-range electrostatic interactions, which were calculated using the Particle-Mesh Ewald (PME) method. 0.16 nm grid spacing was used for PME.

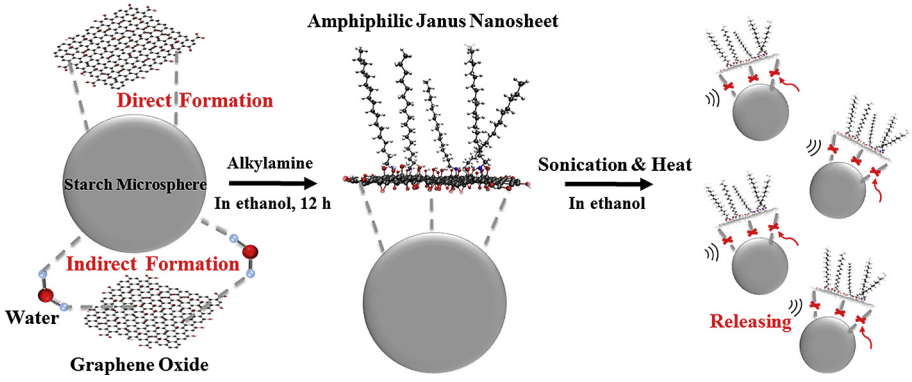
2.2. Synthesis of GO and AJN

3 g graphite powder was stirred with 360 mL sulfuric acid and 40 mL phosphoric acid for a few minutes. 18 g potassium permanganate ($KMnO_4$) was slowly added to the mixture, and followed by putting the fluid system into a water bath, keeping with mild stirring at 45 °C for at least 14 h. After that, the system was transferred to an ice bath with pouring 300 mL DI water into the fluid system. 3 mL 30 wt% Hydrogen peroxide (H_2O_2) solution was then injected and the fluid immediately turned yellow. With successive filtration and washing with 5 wt% HCl and DI water until the pH reached 5.0, the dispersion was subjected to strong sonication for 1 h in order to exfoliation. Solid GO was obtained after drying.

40 g white tapioca starch powder was mixed with 250 mL DI water with continuous stirring. 100 mg GO well dispersed in 100 mL DI water was prepared by sonication for a while. The dispersion was then slowly added to the starch-in-water mixture and stirred for 8 h at room temperature. After washing with DI water and ethanol, the starch microspheres were mixed with 200 mL absolute ethanol solution, followed by adding 300 mg alkylamine dissolved in 50 mL absolute ethanol. The reaction was allowed to proceed with mild stirring for 12 h at room temperature. After washing with ethanol, the starch microspheres were again dispersed in absolute ethanol and alternatively subjected to sonication and heating. The fluid system separated into two phases, with AJN dispersed in the upper phase. After filtration and drying, a yield of about 70 mg AJN was obtained.

2.3. Interfacial behavior testing

AJN was firstly dispersed in DI water to form the nanofluid after sonication for a few hours with the assistance of a small amount of ethanol. Then, the fluid was injected into biphasic system, containing 2 mL heptane at the upper part and 2 mL brine (4 wt% NaCl and 1 wt% $CaCl_2$ salt content) at the bottom. After injection, the fluid system was then vortexed and settled to equilibrium for



Scheme 1. Illustration of synthesis of graphene-based amphiphilic Janus nanosheets by manipulating the hydrogen bonding.