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

Dan Luo ^{a, b}, Feng Wang ^a, Binh V. Vu ^b, Jianfa Chen ^a, Jiming Bao ^c, Dong Cai ^a, Richard C. Willson ^{b, d}, Zhifeng Ren ^{a, *}

^a Department of Physics and TcSUH, University of Houston, Houston, TX 77204, United States

^b Department of Chemical and Biomolecular Engineering, University of Houston, Houston, TX 77204, United States

^c Department of Electrical and Computer Engineering, University of Houston, Houston, TX 77204, United States

^d FEMSA Center for Biotechnology, ITESM, Monterrey, Nuevo León 64849, Mexico

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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 micro-spheres, 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.

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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

* Corresponding author. E-mail address: zren@uh.edu (Z. Ren).

https://doi.org/10.1016/j.carbon.2017.09.102 0008-6223/© 2017 Elsevier Ltd. All rights reserved. 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,





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 (AIN) [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. AIN 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 AIN 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 \times 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 \times 6 nm \times 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 (KMnO₄) 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 (H₂O₂) 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% CaCl₂ 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.

a)

observation.

2.4. Surface wettability measurements

Glass slides were cleaned by soaking in HNO₃/H₂O₂/H₂O (1:1:1 vol ratio) system for at least 1 h before being rinsed with DI water, and then air-blown dried. To measure the contact angle of GO, GO was deposited on the glass slide via drop casting, and dried at room temperature. To measure the contact angle of AJN, AJN dispersion in DI water was firstly injected into the heptane/brine biphasic system. An interfacial film was generated through vigorous shaking. A glass slide was used to lift the film from below to capture the film with hydrophobic surface facing upward. To make the film with hydrophilic surface facing upward, a glass slide was pressed onto the interfacial film from above and then lifted out. In both cases, the glass slides with interfacial film deposition were dried at room temperature. All contact angle measurements were conducted using a CCD camera with releasing a volume of 0.5 μ L DI water onto the sample surfaces.

2.5. Characterization

Scanning electron microscopy (SEM; LEO 1525) was employed to image the morphology and surface of tapioca starch particles with 5 kV acceleration voltage. A fluorometrer (Tecan Infinite 200Pro) was used to detect the fluorescence excitation and emission signals. Fourier Transform Infrared Spectroscopy (FTIR) spectra were measured using a Nicolet iS50 FTIR Spectrometer equipped with an Attenuated Total Reflectance (ATR) accessory. UV-Vis spectra were recorded on a Cary 5000 UV-Vis-NIR spectrophotometer. Raman measurements were conducted on a custom-built confocal micro-Raman setup equipped with a HORIBA iHR320 spectrometer and a Synapse CCD. A continuous-wave laser with 532 nm was chosen as the excitation source. The samples of GO and AJN were deposited on Si substrates via drop casting for the measurements. Morphology and chemical composition of GO and AJN were examined using a transmission electron microscope (TEM, JEOL 2010F) coupled with energy dispersive X-ray spectroscopy (EDS). The chemical information of GO and AJN were also characterized by XPS (Physical Electronics Model 5700).

3. Results and discussion

The attachment of GO to the surfaces of tapioca starch microspheres in aqueous solution may have been due either to direct hydrogen bonding between GO and the starch particles, or to indirect bonding with a layer of water between them. However, after washing with ethanol, water may be extracted to the bulk ethanol phase, leaving all GO directly bond to the starch microspheres. The formation of hydrogen bonding was because of the interactions between oxygen-containing functional groups presented on the surfaces of both GO and starch microspheres [34]. Molecular dynamic simulation was then performed to demonstrate their interaction. In the simulation, the molecular structure to represent tapioca starch was shown in Fig. 1a), with a chemical formula of $(C_6H_{10}O_5)_4$. GO contained oxygen functional groups of hydroxyls, epoxies and carboxyls (Fig. 1b). At the beginning, single graphene oxide molecule, 6 starch molecules, and 6810 water molecules were randomly distributed in the simulation box. After running the simulation till to the final equilibrium state, the distribution of molecules was shown in Fig. 1c). Three out of six starch molecules were bonded with GO. This is due to the electrostatic repulsive force generated by the oxygen functional groups from the bonded starch molecules when the bonding between GO and starch molecules was saturated which prevented further attachment. With



b)

Fig. 1. Molecular Dynamics simulations of graphene oxide (GO) and starch molecules. **a)** The molecular structures of **a)** starch and **b)** GO; **c)** The simulation box; **d)** The magnified region of GO molecule interacting with starch molecules. Oxygen atoms are in red color, carbon atoms in grey, and hydrogen atoms in white. The green dotted lines represent hydrogen bonds. (A colour version of this figure can be viewed online.)

magnifying the interaction region between GO and starch molecules, both epoxies and hydroxyls on GO surfaces formed hydrogen bonding with starch molecules as the simulated results displayed in Fig. 1d).

As pictured in Fig. 2a and b), SEM images show smooth surfaces of tapioca starch microspheres before mixing with GO, but wrinkles appeared after GO is attached. To further demonstrate the successful immobilization of GO, fluorescence microscope was employed to detect the fluorescent signal of GO before and after stirring with starch microspheres. Since GO has broad emission band between 400 nm and 800 nm [35], an excitation scan at 620 nm emission wavelength was first used to optimize the excitation wavelength. As shown in Fig. 2c), water and pure starch in water showed negligible emission over a range of excitation wavelengths. Both GO and GO mixed with starch (*i.e.*, GO-onstarch) displayed peak emission with excitation near 370 nm. As shown in Fig. 2d), with excitation at 370 nm, GO exhibited a wide emission band as reported [35]. In contrast to pure starch in water, the spectrum of GO-on-starch showed a distinct shoulder centered



Fig. 2. SEM images. **a)** Tapioca starch microspheres; **b)** Graphene Oxide (GO) on the surfaces of tapioca starch microspheres. Fluorescent measurement. **c)** Excitation scan at 620 nm emission wavelength; **d)** Emission scan at 370 nm excitation wavelength; Supernatant here is the upper liquid of starch-on-GO dispersion after a low speed centrifuge. (A colour version of this figure can be viewed online.)

at approximately 640 nm, very close to the GO emission peak at around 635 nm. On the contrary, after low-speed centrifugation of the GO-on-starch dispersion, the supernatant gave no observable emission in the same region. Instead its emission curve was very similar with that of water, confirming that the washing process was complete. All the GO present in the system after washing was attached to starch particles rather than dispersed freely in the water phase. Above all, it experimentally demonstrated the attachment of GO on starch surface.

Single-side surface conjugation of immobilized GO with alkylamine was then carried out to synthesize AJN via nucleophilic substitution reaction [36]. The release of AJN was achieved by breaking the hydrogen bonding under sonication and elevated temperature in a non-aqueous environment. As depicted in Fig. 3a), the single-phases fluid system before ultrasound separated into two phases after ultrasound. The bottom portion was solid starch microspheres with higher density than ethanol. The AJN was dispersed in the upper portion. With further filtration and drying, purified AJN were obtained.

As measured in Fig. 3b), FTIR demonstrated the successful surface conjugation of GO. Except the peaks of epoxy at 1230 cm^{-1} , aromatic at 1620 cm⁻¹, and carboxyl at 1730 cm⁻¹ for both GO and AIN [37], AIN additionally exhibited strong asymmetric peaks of methylene groups, which are at 2850 cm^{-1} and 2920 cm^{-1} , as well as the medium peak at 1463 cm^{-1} . Meanwhile, the weak signals at 1380 cm⁻¹ and 2960 cm⁻¹ also indicated methyl groups, showing the introduction of alkyl chains to the GO surface. The UV-Vis spectrum of AIN, shown in Fig. 3c), is distinguishable from that of GO. The shoulder of GO at about 300 nm, which caused by the n- π^* transitions of C=0 bonds in oxygen-containing groups [38], became unobvious and the main peak of AIN was also slightly redshifted from GO's which should be at 230 nm due to π - π * transitions of graphitic C=C bonds [39]. The difference arose from alkylamine functionalization leading to partial restoration of the graphitic sp2 network of GO. In comparison with the Raman spectrum of natural graphite [40], GO displayed an additional D peak at 1349 cm⁻¹ and also a red-shift behavior of G peak from 1581 cm⁻¹ for graphite to 1603 cm⁻¹. This was due to the increased defects via oxidation and the existence of isolated carbon double bonds which vibrated at higher frequencies than graphite [41,42].



Fig. 3. a) Visual comparison before and after releasing graphene-based amphiphilic Janus nanosheets (AJN); **b)** FTIR spectra of graphene oxide (GO) and AJN; **c)** UV–Vis spectra of GO and AJN; d) Raman spectra of GO and AJN. (A colour version of this figure can be viewed online.)

However, after single-side modification of GO, AJN presented a blue-shift behavior of G peak from 1603 cm⁻¹ for GO to 1597 cm⁻¹ because of partial recovery of graphitic sp2 network. Meanwhile, as shown in previous reports on functionalization of GO with alkylamine on both surfaces, the G peak was shifted to 1588 cm⁻¹ [40,43]. The smaller shift for AJN here, indicates the less restoration of graphitic domains, which is consistent with the fact that only one side of GO surface was conjugated.

The sheet-like morphologies of GO and AJN were imaged by TEM. EDS mappings were further performed on the chosen regions of the samples under TEM. As the result of GO in Fig. 4a), it exhibited only two main elements, C and O. However, an additional element, N, indicative of the presence of alkylamine, was found in the AJN sample (Fig. 4b). The chemical compositions of GO and AJN were also measured by XPS, as shown in Fig. 5. Compared with GO (Fig. 5a), AJN presented an additional peak around 400 eV (Fig. 5c), which can be assigned as N1s due to the conjugation with alkylamine. After Gaussian convolution of C1s spectrum using a Shirley background, GO displayed four peaks, which were at 284.8 eV (-C-C-), 286.6 eV (-C-OH), 287.1 eV (-C-O-C-), and 288.8 eV (-O-C=O) as described in Fig. 5b). However, AJN yielded an extra peak at 285.4 eV (-C-N-) as shown in Fig. 5d), which again demonstrated the successful functionalization with alkylamine.

Nanofluid of AJN was then prepared in DI water to check its amphiphilicity. The test was performed by injecting the nanofluid into heptane and brine (containing 4 wt% NaCl and 1 wt% CaCl₂) system. As shown in Fig. 6a), the nanosheets spontaneously went to the heptane-brine interface, as observed before [26]. This was due to the salt screening of the hydrophilic side of AIN, thus the attractive force between heptane phase and hydrophobic side of AJN became the dominant interaction, which drove AJN to the interface. After full monolayer coverage of the interface by AJN, the successive injected AJN induced the concentration gradient between the two phase (heptane and brine phases) area and the three phase (heptane, brine and solid glass phases) contact region, thus generated the Marangoni stress which transferred AJN to form a climbing film like the behavior of molecular surfactant and other nanoparticles [44,45]. With vigorous shaking of the glass vial, an interfacial film appeared. When subjected to intrusion of a glass rod, the film was bent but did not break, indicating a certain elasticity. These observations are similar to those we made with the previously reported graphene-based amphiphilic Janus nanosheets, fabricated by wax masking method [26], demonstrating the amphiphilic nature of AIN prepared by this method.

The pre-treated glass substrate as shown in Fig. 7a), had a very small water contact angle, which indicated a strong hydrophilic surface. For GO as imaged in Fig. 7b), due to the presence of oxygen functional groups on surfaces, it also exhibited hydrophilic property with contact angle much less than 90°. For AJN with hydrophilic surface facing upward by pressing the glass slide onto the interfacial film from above, it displayed a very similar contact angle with that of GO (Fig. 7c). Because it was basically unmodified GO surface. However, for the modified surface with alkylamine, which prepared by lifting the interfacial film from below with a glass slide, it possessed a contact angle larger than 90°, *i.e.*, hydrophobic surface, as measured in Fig. 7d). Therefore, the Janus amphiphilic nature of AJN was further clearly demonstrated.

Nanofluid containing 0.3 mg graphene-based amphiphilic Janus nanosheets (*i.e.*, 0.00375 wt%) in DI water (8 mL) was firstly prepared with assistance of sonication. Toluene (0.5 mL) was then added into the nanofluid. The fluid system was subjected to water bath sonicator (Model M2800, BRANSONIC, 120VAC ~ 50-60HZ input) for 15 min, followed by settling for observation. In comparison with the control experiment of toluene and DI water system as shown in the following Fig. 8a), the glass tube with the nanosheets



Fig. 4. TEM-EDS mapping of a) graphene oxide (GO) and b) graphene-based amphiphilic Janus nanosheets (AJN). (A colour version of this figure can be viewed online.)



Fig. 5. XPS spectra of Graphene Oxide (GO) and Graphene-based amphiphilic Janus nanosheets (AJN). **a)** Full spectrum of GO; **b)** Fitted peaks of C1s spectrum for GO; **c)** Full spectrum of AJN with insert showing the feature at the range of N1s; **d)** Fitted peaks of C1s spectrum for AJN. (A colour version of this figure can be viewed online.)



Fig. 6. Amphiphilicity testing of the nanofluid containing graphene-based amphiphilic Janus nanosheets (AJN). **a)** Injection of AJN in heptane and brine (containing 4 wt% NaCl and 1 wt% CaCl2) system; **b)** Elasticity testing by intrusion with a glass rod. (A colour version of this figure can be viewed online.)

displayed a white milky-like color and the interfacial area between oil and water disappeared after settling for 6 h. The optical image of the milky-like fluid shows toluene droplets were a few microns in size in the emulsion (Fig. 8b). The small size of oil droplets was due to the nanosize of amphiphilic Janus nanosheets in lateral dimension as confirmed by TEM. Even after one week settling, there was still emulsion preserved as indicated by milky-like color shown in Fig. 8c. The amphiphilic Janus nanosheets has proved to be able to effectively emulsify immiscible fluids.



Fig. 7. Surface contact angle measurements of **a**) pre-treated glass substrate, **b**) graphene oxide (GO), **c**) hydrophilic surface of graphene-based amphiphilic Janus nanosheets (AJN), and **d**) hydrophobic surface of AJN. (A colour version of this figure can be viewed online.)



Fig. 8. Emulsion stabilized by graphene-based amphiphilic Janus nanosheets. **a)** Photograph taken after 6 h; **b)** Optical microscopy images of the emulsion taken after one week. **()** Photograph taken after one week. (A colour version of this figure can be viewed online.)

4. Conclusions

In summary, a more efficient method to synthesize graphenebased amphiphilic Janus nanosheets has been found. The formation of hydrogen bonds immobilized GO on the surface of tapioca starch microspheres for subsequent hydrophobization using alkylamine. The successful conjugation of alkylamine was demonstrated by FTIR, UV–Vis, Raman, TEM-EDS mapping and XPS. By breaking the hydrogen bonding, amphiphilic Janus nanosheets were released from the surfaces. The amphiphilic Janus nature was reflected from its interfacial behavior in oil/water system and also the contact angle measurements. This method is highly facile and scalable. In comparison with the previous wax-in-water emulsion template masking method, there is no need to dissolve wax templates with large amounts of organic solvents, supporting economical production at large scale.

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