



## Full Length Article

# Polyoxometalate-coupled graphene nanohybrid via gemini surfactants and its electrocatalytic property for nitrite

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## ABSTRACT

A novel graphene oxide (GO)-polyoxometalate (POM) nanohybrid is prepared using gemini surfactants (Gem) as stabilizers for the first time. The electrostatic interactions, chemical structure, and morphology of this Gem-GO-POM nanohybrid are systematically characterized, which have been manifested that the Gem-GO-POM nanohybrid provides uniform distribution of POM nanoparticles on the GO nanosheets and exhibits excellent electrochemical activity and stability due to the use of Gem as linkers and stabilizers. The prepared Gem-GO-POM catalyst used as electrode displays an enhanced electro-oxidation of nitrite compared with pure GO and DTAB-GO-POM hybrid using dodecyl trimethyl ammonium bromide (DTAB) as stabilizers. The proposed nanohybrid structure capitalizes on the enhancing in the oxidation reactions ability of the POM through the Gem linkers to provide more binding sites for POM on the surface of GO.

## 1. Introduction

Graphene with a two-dimensional sheet of carbon atoms is well known for its unique properties [1,2]. The addition of inorganic nanoparticles to graphene is an effective way to develop an electrochemically sensitive nanohybrid [3–5] where the graphene serves as a template for the growth of nanoparticles and prevents their agglomeration. Of these nanoparticles, polyoxometalates (POMs) are currently the focus of research activity in the fields of catalysis [6,7], medicine [8], and material science [9,10] due to their excellent properties. Recently, POMs also have attracted widespread attention as a key component of electrode materials [11,12]. Thus, one important development in graphene materials is the use of POMs to fabricate the graphene-POM nanohybrids that have great potential for energy conversion and storage [13,14], catalysis [15], and sensor devices [16–19]. Graphene has been proposed as a template for anchoring POMs due to its large surface area and high levels of conductivity [13–19]. Although several significant methods have been reported for fabricating and controlling POM nanostructures on graphene, controlling the density and position of POM on a graphene surface is difficult, and thus, stabilizing the POMs on graphene sheets has remained a scientific problem.

Graphene-POM nanohybrids usually are fabricated using stabilizers to anchor the POMs on the graphene sheets. POMs are composed of

anionic metal-oxygen clusters, and the redox potential or acidity of POMs can be controlled by selecting counter cations. Therefore, the anionic POMs are commonly functionalized using cationic polymers such as polyaniline hydrochloride [15], poly(dimethyl-diallylammonium chloride) [18], and polypyrrole sulfates [19] through electrostatic interactions. These polymers also can serve to stabilize the assembly between POMs and graphene. However, the molecular structure of polymers usually are not clear due to the molecular weight distribution and polydispersity, which may limit the reproducibility of the graphene-POM nanohybrids. Unlike cationic polymers, small cationic surfactants have clear molecular structures and controllable physical properties [20]. Researchers have found that small cationic surfactants can improve the dispersity of graphene [21] and control the morphology of POMs by tuning the molecular structures of small surfactants [6]. However, compared to cationic polymers, the single cationic group of these small surfactants may limit the growth of POMs on the surface of graphene. Therefore, it is necessary to design a new type of surfactant as stabilizers to fabricate the graphene-POM nanohybrid.

Gemini surfactants (Gem) contain two cationic groups, two hydrophobic chains, and a spacer, and they have attracted much attention due to their higher surface activity, lower critical micelle concentration, stronger solubility, surface wetting capability, and complicated self-assembly behavior in comparison to conventional single-tailed surfactants [22,23]. Thus, Gem have important potential applications in the

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pharmaceutical industry, gene delivery, and material science [24–28]. Specifically, Gem can enhance sensitivity in electroanalysis and promote electron transfer. For example, various Gem with different hydrophobic chains and spacers have been used to fabricate carbon nanotube composite, and the modified electrode of this composite material can improve the response to Sudan I [27]. Although Gem offer many benefits, to the best of our knowledge, using Gem as stabilizers to fabricate the graphene-POM nanohybrid has not yet been reported.

Here, the cationic Gem in the form of bis(dimethylhexylammonium) ethane dibromide were used as linkers and stabilizers. The interfacial adsorption of Gem can stabilize POMs on the graphene oxide (GO) sheets due to electrostatic interactions and anion exchange, leading to the adsorption of POMs on the surface of GO. As a result, we were able to fabricate the novel Gem-GO-POM nanohybrid using Gem as stabilizers. It is shown that employment of the cationic Gem results into a uniform distribution of POM nanoparticles on the GO sheets. Due to this uniform distribution, the Gem-GO-POM nanohybrid catalyst shows an enhanced electro-oxidation of nitrite compared with pure GO and DTAB-GO-POM hybrid using dodecyl trimethyl ammonium bromide (DTAB) as stabilizers. Thus, both stability and catalyst activity can be achieved due to the well distribution of POMs on GO sheets.

## 2. Materials and characterizations

### 2.1. Materials

#### 2.1.1. Synthesis of Gem

Gem ( $C_{18}N_2^{2+}Br^{2-}$ ) was synthesized according to the literature [29]. 1,2-di(dimethylamino)ethane (1 g) and 1-bromohexane (5.8 g) were added to 100 mL of acetonitrile, and the mixture was stirred at reflux temperature for 48 h. After cooling to room temperature, the acetonitrile was removed via distillation. The crude product was dissolved in 3 mL ethanol and precipitated in 100 mL diethyl ether. Gem were obtained after drying under vacuum at 40 °C. The  $^1H$  nuclear magnetic resonance (NMR) of Gem is shown in Fig. S1 (supporting information) as  $^1H$  NMR (Gem) ( $D_2O$ ):  $\delta$  0.60–0.80 (6H,  $CCH_3$ ),  $\delta$  1.00–1.35 (12H,  $CCH_2CH_2CH_2C$ ),  $\delta$  1.55–1.75 (4H,  $NCCH_2$ ),  $\delta$  2.95.00–3.15 (12H,  $NCH_3$ ),  $\delta$  3.2.00–3.4 (4H,  $NCH_2C$ ), and  $\delta$  3.70–3.85 (4H,  $NCH_2CN$ ).

#### 2.1.2. Synthesis of POM

Keggin-type POM ( $H_4PMo_{11}VO_{40}$ ) was prepared according to the literature [6].  $MoO_3$  (15.8 g) and  $V_2O_5$  (0.91 g) were added to 250 mL of deionized water, and the mixture was heated to 100 °C under stirring. Then,  $H_3PO_4$  (1.15 g, 85 wt%) was added to the above mixture. After the suspension became clear and transparent, it was cooled to room temperature. The water solution was evaporated using an evaporator and the POM was purified by recrystallization in deionized water.

#### 2.1.3. Synthesis of Gem-GO-POM nanohybrid

GO was prepared using Hummers method [30]. Gem-GO hybrid was prepared via electrostatic interactions between Gem and GO in  $H_2O$ . 100 mL GO (1 mg/mL) was allowed to drip slowly into the aqueous solution of the Gem (400 mg) and was dispersed using sonication for 2 h. After washing and filtering the mixture, the Gem-GO hybrid was obtained. The Gem-GO-POM nanohybrid was prepared by adding excess POMs to the aqueous dispersion of Gem-GO under vigorous stirring overnight. After washing the unbound POMs and filtering the mixture, the Gem-GO-POM nanohybrid was obtained.

#### 2.1.4. Synthesis of control samples (DTAB-GO-POM)

DTAB-GO-POM hybrid was prepared using DTAB as stabilizers under the same experimental conditions as for the Gem-GO-POM nanohybrid in order to provide a control to compare Gem versus DTAB. The molecular structures of Gem and DTAB are shown in Fig. S2 (supporting information).

## 3. Characterization

$^1H$  NMR spectra was recorded using a Varian Inova 400 MHz spectrometer (Varian Instruments, Ltd., US). Zeta potential measurements were taken using a Zetasizer Nano ZS90 instrument (Malvern Instruments, Ltd., UK). Transmission electron microscopy (TEM) images were obtained using a field-emission transmission electron microscope working at 200 kV (JEM-2100F, JEOL), and energy dispersive spectroscopy (EDS) data were acquired via TEM. Fourier transform infrared (FTIR) spectra data were recorded using a Varian 3100 FT-IR spectrometer (Varian Instruments, Ltd., US). The crystallinity of the material was measured by X-ray diffraction (XRD) (Rigaku, Ltd., JP) using  $Cu K\alpha$  radiation. Ultraviolet visible spectroscopy (UV-Vis) was performed using a Hitachi U3900 (Hitachi, Ltd., JP). Thermogravimetric analysis (TGA) (PerkinElmer) was performed to analyze the decomposition behavior of the materials. X-ray photoelectron spectroscopy (XPS) was recorded on a PHI 5000c ESCA photoelectron spectrometer.

Electrochemical experiments, including cyclic voltammetry (CV) and differential pulse voltammetry (DPV), were taken using a CHI440A (Shanghai Hua Chen) workstation using a three-electrode system. The working electrode was a glassy carbon electrode (GCE), the counter electrode was made of platinum wire, and the reference electrode was a saturated calomel electrode. The GCE was carefully polished using aluminum powder, rinsed with deionized water, and ultrasonicated in ethanol for 10 min. The electrode was then dried under nitrogen. The sample (10 mg) and 20  $\mu$ L Nafion solution (5 wt%) were added to 500  $\mu$ L of deionized water and 500  $\mu$ L of isopropyl alcohol, and the mixture was sonicated for 30 min. Then, a 5  $\mu$ L sample was dropped onto the GCE surface and allowed to dry at room temperature. 1 M  $H_2SO_4$  was used as the electrolyte. In addition, the oxidation reaction of nitrite was carried out at the scan rate of 50 mV/s in 1 M  $H_2SO_4$  that contained different concentrations of nitrite.

## 4. Results and discussion

Fig. 1a schematically illustrates the fabrication of the Gem-GO-POM nanohybrid. The Gem-GO-POM nanohybrid was obtained by electrostatic interactions between GO and Gem and then via anion exchange using POMs. The Gem was used as functional stabilizers for the nanohybrid. In our work, the Gem stabilizers (i) improved the surface reaction between the POMs and GO and (ii) provided uniform deposition sites of POMs on the surface of GO. GO is a negative flake-like material with many carboxyl groups on its basal surface and edges [30]. Some cationic compounds have been used to functionalize GO via electrostatic interactions. As for the cationic Gem used in our work, one cationic group modifies the negative GO to the positive Gem-GO hybrid, while the other cationic group anchors the anionic POMs on the surface of Gem-GO through an anion exchange to form the Gem-GO-POM nanohybrid. For comparison, the DTAB-GO-POM hybrid was fabricated using DTAB with a single cationic group as stabilizers under the same experimental conditions that were used to fabricate the Gem-GO-POM. Fig. S3 (supporting information) shows digital photos of the dispersibility in water of (i) Gem-GO, (ii) Gem-GO-POM, (iii) DTAB-GO, and (iv) DTAB-GO-POM. The Gem-GO and Gem-GO-POM are clearly more dispersible than the DTAB-GO and DTAB-GO-POM due to the presence of Gem as stabilizers. Besides, the Gem-GO has a thin, layered flake-like structure compared to DTAB-GO (Fig. S4a–b in supporting information) due to the amphiphilic property and interface behavior of Gem, which result in a more homogenous functionalization on the surface of GO. After removing the unbound Gem, an aqueous solution of POM was added to the Gem-GO suspension. The POM anions were easily exchanged with the bromine (Br) anions in the Gem-GO hybrid, and then the Gem-GO-POM nanohybrid with a uniform distribution of POMs was produced. According to current research, the halide anions ( $Br^-$ ) of surfactants are likely to be exchanged with POM anions,

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