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Facile coordinating decoration of salophen Al on graphene nanosheet: Salophen Al complex functionalized graphene nanocomposite with electrochemical properties

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ABSTRACT

Salophen Al complex functionalized graphene (SCFG) nanocomposite was synthesized by simple coordination of phenol functionalized graphene (PFG) and as-prepared salophen Al complex. This process is facile, convenient and high efficient. We also investigated the structure, optical properties and electrochemical properties of the obtained SCFG composites. The results showed that salophen Al conjugated and incorporated onto the graphene sheet surface and the composites maintained the micro-structure of graphene sheets without agglomeration. The photoluminescence of salophen Al was completely quenched by graphene, due to the charge transfer between the salophen Al and the graphene nanosheets. Moreover, a significant electrochemical signal emerged on the SCFG modified electrodes compared with those of the graphene sheets or salophen Al complex. Owing to preliminary results of the excellent electrochemical property, SCFG nanocomposite is a promising electrochemical redox probe material.

1. Introduction

Graphene has emerged in recent five years as a “star” material with a two-dimensional atom-thick sheet consisted of sp^2 hybridized carbon arranged in a hexagonal honeycomb lattice [1–3]. Because of its unique thermal, mechanical and electrical properties of potentially superior performance, graphene has been applied in a broad range of fields [4–7]. In comparison with the traditional methods, reduced graphene oxide (RGO) prepared by exfoliation and chemical reduction of graphite oxide (GO) is the most promising method to obtain large scale graphene with low expense [8–11]. The RGO achieved by the chemical reduction way is decorated with oxygen functional groups on both the basal plane, whereas carboxylic groups were mainly found at the edges [12]. Due to the amount of hydrophilic groups on the surface, RGO can form a stable dispersion in aqueous solution by vigorous ultrasonication. In addition, further chemical modification will also improve its water solubility [13].

Graphene is like a giant aromatic “poly-molecule” with a wide open double-sided surface which enables graphene to undergo a broad class of bonding interactions with functional groups to the both sides as a platform [14,15]. There is a wide range of covalent methods for such double-sided decorations, e.g. cycloadditions, click reactions and carbene insertion reactions. As for the non-covalent interactions, molecules with large planar aromatic structures can be attached onto the surface of graphene sheets via π–π stacking [5,7,15]. Decorations on both sides of graphene not only make graphene more dispersible in various solutions but also offer graphene composite films with a great diversity of tunable properties in various applications.

Diverse salophen (N,N′-disalicylidene-*o*-phenylenediaminate) derivatives are very widely used as ligands similar to salen (N,N′-disalicylidene-ethylenediamine) derivatives. Such aluminum complexes can be conveniently coordinated with trivalent aluminum salts in a mild atmosphere [16]. Because of the excellent luminescent and catalytic properties, these aluminum complex derivatives can be applied as luminescent labeling agents, emitting materials for organic light-emitting diodes [17–19], and catalysts for the asymmetric syntheses [20,21] and ring-opening polymerization [22]. However, the applications of aluminum complexes in electrochemistry field are neglected and underestimated. In this work, we synthesized a salophen Al complex functionalized graphene (SCFG) nanocomposite with luminescent aluminous coordination compound as a precursor (Scheme 1) and easily performed modified strategy (Scheme 2). Within salophen Al modifying to the graphene matrix surface by coordination, SCFG composite exhibited excellent electrochemical properties, similar to $K_3Fe(CN)_6$, ferrocene, prussian blue and naphthol etc., which were utilized as electrochemical reagents [23–25]. As well as the biocompatibility and planar structure, SCFG would be a potential redox probe material.

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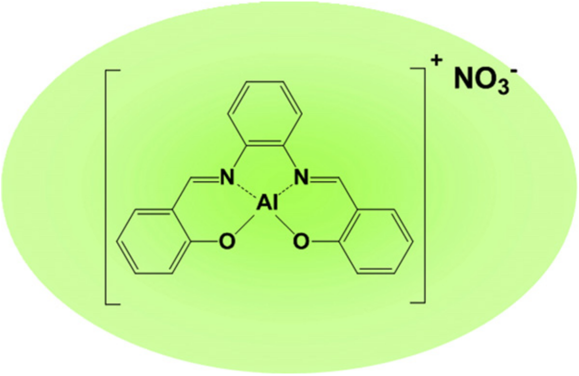


Scheme 1. The chemical structure of salophen Al.

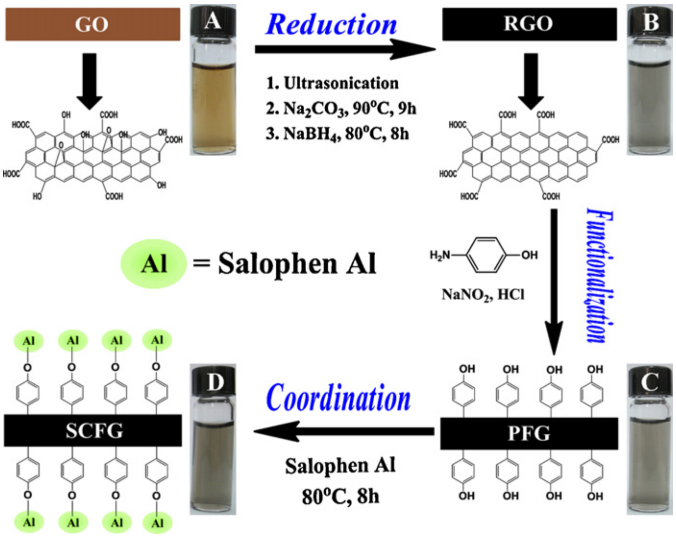
2. Experimental

2.1. Chemicals

All chemicals were of analytical grade and used as purchased without further purification. Specpure graphite was purchased from Tianjin Guangfu Fine Chemical Research Institute (China), salicylaldehyde and *o*-phenylenediamine were purchased from Chinese Medical (Group) Shanghai Chemical Reagent Co. (China), and *p*-aminophenol was purchased from Aladdin Chemistry Co., Ltd. (China). Ultrapure water was prepared with a Milli-Q-Plus system (18.2 MΩ) and used throughout the experiments.

2.2. Preparation of GO and RGO

GO was synthesized from graphite by a modified Hummers method [26]. In detail, graphite powder (1.0 g), $NaNO_3$ (0.5 g) and $KMnO_4$ (3.0 g) were slowly added to the concentrated H_2SO_4 solution (23 mL) within an ice bath. After removing the ice bath, the above mixture was intensely stirred at 35 °C for 30 min. After the reaction was completed, deionized water (46 mL) was added to above mixture while keeping the temperature at 98 °C for 15 min, followed by reducing the temperature to 60 °C with the addition of warm deionized water (140 mL) and H_2O_2 (10 mL, 30 wt%) while stirring continuously for a further 2 h. The obtained mixture was centrifuged at 3000 rpm to collect the solid product and washed with HCl solution and then with deionized water until the pH of the supernatant was neutral. Finally the GO was dried in a vacuum to obtain a loose brown powder.



Scheme 2. Graphical representation of the synthesis of SCFG.

In the reduction step, GO (100 mg) in water (100 mL) was sonicated for 1 h in order to disperse the GO sheets completely in water. Following, sodium carbonate solution (10 mL, 5 wt%) was added to adjust the pH to 10 and the solution was then stirred in a round-bottom flask at temperature 90 ± 5 °C for 9 h. This was followed by the addition of sodium borohydride (800 mg) in water (20 mL) to the GO dispersion, with pH adjusted to 10. The mixture was then kept at 80 °C in an oil bath for 3 h under constant stirring. During the reduction, the dispersion turned from dark brown to black accompanied by out-gassing. The resulting product was centrifuged at 3000 rpm and washed with water several times.

2.3. Preparation of salophen Al

A methanol solution (60 mL) of *o*-phenylenediamine (200 mg, 2 mmol) was added dropwise into the methanol solution (40 mL) of salicylaldehyde (500 mg, 4 mmol). The resulting solution became orange and was stirred at room temperature for 2 h. The orange salophen was filtered, recrystallized in dichlormethane and dried under vacuum (290 mg, 90.6%). Ethanol solution (40 mL) of $Al(NO_3)_3{\cdot}9H_2O$ (380 mg, 1 mmol) was slowly added to the ethanol solution (80 mL) of salophen (320 mg, 1 mmol). The resulting orange suspension (salophen was insoluble in ethanol) became clear and the color changed to blue, and was stirred at room temperature for 2 h. The bright blue-green solution was evaporated to dryness. The product was filtered, washed several times with dichlormethane, acetoacetate, and recrystallized in ethanol to obtain salophen Al (270 mg, 79.2%). ^1H NMR (C_2H_5OD) δ 9.27 (2H, s, HC=N), 8.06 (2H, t, Ar—H), 7.65 (2H, d, Ar—H), 7.53 (2H, m, Ar—H), 7.02 (2H, d, Ar—H), 6.88 (4H, t, Ar—H).

2.4. Preparation of SCFG

It was carried out by sonicating RGO aqueous solution (100 mL, 1 mg mL^{-1}) under ambient condition for 60 min, which was then added by as-prepared 4-hydroxyl benzenediazonium aqueous solution and stirred for 4 h at 0–5 °C. Then the reacting mixture was raised to room temperature and continued for 4 h. The resulting black product was obtained by centrifugation (3000 rpm), washed with ethanol until the supernatant was colorless and then with deionized water 5 times. Then PFG was obtained. The diazonium salt was prepared as the following procedure. $NaNO_2$ (526 mg, 7.6 mmol) was added to *p*-aminophenol (764 mg, 7 mmol) aqueous solution (80 mL) slowly in an ice bath at 0–5 °C, then HCl solution (6 mL, 10 wt%) was immediately poured into the above solution and the mixture was continuously stirred for 45 min at this temperature.

The salophen Al wrapped dispersion of graphene sheet was attained in simply one-pot coordination. Salophen Al (50 mg, 0.147 mmol) in ethanol (100 mL) was added into PFG aqueous dispersing solution (100 mL, 1 mg mL^{-1}) and refluxed at 80 °C for 8 h. The product was centrifuged (3000 rpm) and washed with ethanol until the supernatant was colorless and then with deionized water 5 times.

2.5. Electrochemical application

Cyclic voltammetric (CV) measurements were carried out with a CHI 852C electrochemistry workstation (Shanghai Chenhua Instruments, China). The glass carbon (GC) electrode (Ø = 4 mm) was first polished with 0.3 and 0.05 μm alumina slurry respectively,