Hollow graphene-polyaniline hybrid spheres using sulfonated graphene as Pickering stabilizer for high performance supercapacitors

Jing Luo[*], Yaxin Chen, Yuan Zheng, Chenbeibei Wang, Wei Wei, Xiaoya Liu

Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi, Jiangsu, 214122, China

ABSTRACT

Hollow structured graphene-polyaniline spheres (GSA/PANI HS) were prepared via a facile and efficient Pickering emulsion polymerization using sulfonated graphene (GSA) as Pickering stabilizer. In our procedure, amphiphilic sulfonated graphene (GSA) was first synthesized and used to stabilize an oil phase containing aniline. Upon aniline polymerization at the oil/water interface, graphene-polyaniline hollow sphere (GSA/PANI HS) with a rough outer surface and a smooth inner surface, was generated. The size as well as the electrochemical properties of GSA/PANI HS could be easily adjusted by varying the amphipathicity and concentration of GSA, and the oil-water volume ratios of the Pickering emulsions. The synthesized GSA/PANI HS exhibited superior performance in supercapacitors compared to the common stacked two-dimensional GSA/PANI composite owing to its unique hollow structure, which provides a larger accessible surface area and reduces the transport length for both charge and ion The specific capacitance of GSA/PANI HS can reach $546\,F\,g^{-1}$, more than two folds higher than stacked two-dimensional GSA/PANI composite. In addition, GSA/PANI HS reveals enhanced capacitance retention at higher scan rates (76% from 5 to $500\,mV\,s^{-1}$) and current densities (83.5% from 0.5 to $10\,A\,g^{-1}$), demonstrating superior electrochemical accessibility of the 3D hollow nanostructure. Furthermore, good cycling stability is also demonstrated, which render them interesting candidates for future electrochemical energy storage systems. This approach represents a simple, convenient and controllable route for the preparation of hollow graphene-polyaniline nanostructures for high performance supercapacitor applications.

1. Introduction

Graphene/polyaniline composites have received significant attention in recent years due to their unique electrochemical properties and promising applications in energy storage. Graphene, an ideal electrode material for double-layer capacitor, exhibits outstanding electrical conductivity, high specific surface area, as well as good mechanical properties. While polyaniline (PANI), one of the most promising electrode materials for pseudocapacitors, possesses superior redox properties, much high specific capacitance than carbon materials and easy synthesis. Combining the advantages of both materials with synergistic effects, the hybrid nanomaterials of graphene and PANI are considered as promising electrode materials for supercapacitor [1—5]. Various synthesis procedures have been reported to prepare graphene—PANI composites, including in situ chemical polymerization or electropolymerization of aniline monomer in the presence of graphene or graphene oxide, direct mixing of PANI and graphene solutions, and layer-by-layer assembly technique [6—18]. The obtained graphene—PANI composites are mainly in the form of two-dimensional planar structure, in which graphene and PANI stacked with each other, making an obstacle for the penetration of ions.

In recent years, three-dimensional graphene or polyaniline structures (hollow structure and hydrogel/aerogel), have attracted great interest in order to meet the requirements arising from energy storage applications [19—22]. The hollow micro/nano-structured materials with the nanoscale shell, inner cavity and pore structures, exhibited remarkable enhanced supercapacitor performance owing to the enhanced specific surface area and shortened diffusion length for both charge and mass transport. In contrast to the well-developed two-dimensional planar structure, the pursuit

of hollow graphene–PANI hybrid structure is relatively less investigated [23–28]. Liu et al. [23] reported the fabrication of three-dimensional graphene–PANI hollow spheres by wrapping graphene oxide on a polyaniline hollow sphere via electrostatic interaction and subsequently electrochemical reducing GO. Choi et al. [24] reported a clever method to fabricate graphene-PANI hybrid hollow balls through the self-assembly of graphene oxide and poly(methyl methacrylate) particle, followed by the in situ polymerization of aniline and removal of the PMMA core. Our group has just prepared a graphene-polyaniline hybrid hollow nanosphere via layer-by-layer (LBL) assembly of negatively-charged reduced graphene oxide (RGO) and positively charged polyaniline (PANI) on polystyrene (PS) microsphere, followed by the removal of the PS template [25]. Owing to the unique hollow structure, the resulted graphene–PANI composites showed enhanced electrochemical properties, including high specific capacitance and good cycling stability. However, these approaches involve complicated synthetic steps and require subsequent etching or removal of the hard template (such as PS and PMMA spheres) which was frequently associated with hazardous materials such as HF. It still remains a great challenge to develop a simple and convenient strategy to fabricate graphene-polyaniline hollow spheres.

Pickering emulsion route, an attractive "soft template" method, has been demonstrated to be a facile and eco-friendly approach for preparing hollow-structured composites in which solid particles (Pickering stabilizer) are used as a surfactant to stabilize a liquid dispersion [29,30]. When the in situ interfacial synthesis occurs at the interface of a Pickering emulsion, not like the normal bulk interfacial synthesis that normally yield some blocky nanoparticle composites, hollow-structured composites could be produced. Graphene oxide (GO), with the hydrophobic basal planes of the carbon networks and hydrophilic oxygen-containing functional groups (e.g. hydroxyl, ketone, epoxide and carboxylate), is an amphoteric (hydrophilic–hydrophobic) molecule and could behave like a colloidal surfactant trapped at liquid interfaces in minimizing surface energy. Several literatures have reported the utilization of GO as a Pickering stabilizer for preparing various core-shell polymer/GO composites with advanced properties by Pickering emulsion stabilizer [31–34]. Benefiting from the remarkable physiochemical properties of nanoparticle/GO composites, they show potential applications in many fields such as lithium ion batteries, proteins separations, gas adsorption, and fluorescent probe for metal ions. Very recently, hollow hybrid polymer–graphene oxide nanoparticles with a shell of GO was successfully prepared through a cross-link polymerization at the interface of GO stabilized Pickering emulsion by Thickett et al. [35] And the influence of the factors influencing the preparation of hollow polymer-graphene oxide microcapsules, including monomer, cross-linker and initiator type, was studied in detail [36]. Raston et al. prepared a 3D structure of interconnected few-micron-sized GO hollow spheres via the formation of highly stable micron-sized Pickering emulsions in the presence of polyvinyl alcohol (PVA) and subsequent freeze-drying of the mixture for preserving the unique 3D hollow spherical structures [37]. Bian et al. obtained a hollow ZIF-8/GO composite with the interfacial growth of ZIF-8 nanoparticles at the n-octanol/water interface of a Pickering emulsion stabilized by graphene oxide (GO) [38]. Despite of the above research, this field is just in its initial stage and further development is necessary to gain sound knowledge and explore new application. In addition, GO was used as Pickering stabilizer in most of previous literatures, while graphene itself is seldom utilized as Pickering stabilizer owing to its inert surface. But due to the severe disruption of the conjugation network, GO lacks several advanced properties of graphene, such as electrical conductivity,

thermal conductivity and stability. Therefore, it would be much more advantageous to utilize graphene with proper modification as a Pickering stabilizer while retaining its outstanding properties.

In this work, we present a simple, rapid and efficient synthesis method for fabricating graphene-polyaniline hollow sphere via Pickering emulsion polymerization and investigated its use as an advanced electrode material for supercapacitor application. Fig. 1 illustrates the concepts of the GSA/PANI hollow sphere (GSA/PANI HS) fabrication via Pickering emulsion route using graphene as Pickering stabilizer developed in this study. Graphene is first covalently functionalized with sulfonic acid groups by the modification reaction with potassium 2-aminoethanesulfonate. The obtained sulfonated graphene (GSA), which is amphiphilic due to the hydrophobic graphene plane and the hydrophilic sulfonic acid, is used as a Pickering stabilizer to stabilize an oil phase containing aniline monomer. Aniline molecules are adsorbed to the oil-water interface owing to the electrostatic interaction between amino groups of aniline and sulfonic groups of GSA. Therefore, the subsequent polymerization of aniline is expected to occur at the interface of Pickering emulsion droplet. Upon the removal of the oil phase, the hollow graphene-polyaniline spheres were generated without any other manipulation. The synthesis process was considerably time and energy saving with the feasibility of scale-up, which is a facile and environmentally friendly route compared with the hard template method. The effects of preparation conditions, such as the amphiphilicity and concentration of graphene stabilizer as well as the ratio of oil to water phase, on the properties of the graphene stabilized Pickering emulsions were investigated extensively. And the electrochemical properties of the obtained GSA/PANI HS were systematically investigated. To the best of our knowledge, this is the first attempt to fabricate the hollow graphene-polyaniline composite through the in situ interfacial growth induced by Pickering emulsion, which achieve a breakthrough for the fabrication of graphene-polyaniline hybrid hollow structures.

2. Experimental section

2.1. Materials

Ammonium persulfate (APS, AR), aniline (AR), toluene (AR), hydrochloric acid (AR) and concentrated sulfuric acid (98%, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. Natural graphite powder (8000 mesh, Carbon content 99.85%, AR), sulfanilic acid (SA, 99.8%, GR) and isopentyl nitrite (95%, Contains 0.2% sodium carbonate stabilizer) were purchased from Shanghai Aladdin Chemical Reagent Company. Aniline was purified by distillation, and other reagents were used as received.

2.2. Preparation of sulfonated graphene (GSA)

Sulfonated graphene (GSA) was prepared according to the literature [39]. In the experiment, graphene oxide (GO) was prepared from natural graphite powder using a modified Hummers method [40]. GO (90 mg) was reduced by using hydrazine monohydrate, and then the fresh reduced GO (RGO) was dispersed in deionized water (15 mL) in a three-neck flask with ultrasonication for 1 h. Subsequently, a certain amount of sulfanilic acid and isopentyl nitrite was added into the above dispersion under vigorous stirring. The reaction flask was kept at 80 °C for 24 h. The resulting sulfonated graphene was subsequently centrifuged, washed with water, and finally freeze-dried. To study the effects of the sulfonation degree of graphene, detail preparation parameters were listed in Table 1.