A Photoresponsive Azobenzene-Graphene-Gold Nanocomposite Using Cationic Azobenzene-surfactant as Stabilizers and Its Electrochemical Behavior

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ABSTRACT

A novel photoresponsive azobenzene-reduced graphene oxide-gold nano particle (Azo-RGO-GNP) nanocomposite was prepared using Gemini-type Azo-surfactants as stabilizers and the electrochemical performance was investigated. The Azo-RGO-GNP nanocomposite features a uniform distribution of GNPs and was fabricated by electrostatic interactions, GNP growth and chemical reduction in one pot. The chemical structure and the photoresponse of the nanocomposite materials were measured by TEM, XRD, XPS, and UV-Vis absorption. The electrochemical behavior of the nanocomposite was estimated using cyclic voltammetry. Results show that the Azo-RGO-GNP nanocomposite has the ability of photochemical behavior because of the presence of the Gemini Azo-surfactant stabilizers. Additionally, the electrochemical performance of this nanocomposites can be governed by light irradiation.

Keywords: Azobenzene; Surfactant; Graphene; Nanocomposite; Photoresponsive

Introduction

One important development in graphene utility has been the use of metal nanoparticles (MNPs) to decorate graphene and to fabricate Graphene-MNP nanocomposites that have MNPs on the surface of graphene ^[1]. Of these MNPs, gold nanoparticles (GNPs) attract considerable interest from both academia and industry, due to their interesting and diverse properties. Although some significant physical-deposition methods such as radio frequency sputtering has been reported to fabricate and control the nanostructure of gold on substrate ^[2-3], how to stabilize GNPs on graphene sheets is still a scientific issue.

Graphene-MNP nanocomposites are commonly fabricated using stabilizers to attach the MNPs on the surface of graphene which usually refer to graphene oxide (GO) or reduced graphene oxide (RGO) because they are easily accessible and processable

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^[4]. GO and RGO are negatively charged materials that contain carboxyl groups on basal planes and edges. Therefore, the surface of GO or RGO are often functionalized by cationic polymers such as PDDA through electrostatic interactions. This polymer also stabilize the assembly between the graphene sheet and the MNPs ^[5-6]. However, the intrinsic polydispersity of polymers may limit the reproducibility of these nanocomposites. Furthermore, using small cationic surfactants has been shown to improve the dispersion of graphene in aqueous solution ^[7], and the morphology of graphene can also be controlled by tuning the molecular structure of the surfactants ^[8]. While there have been many benefits from these small surfactants, their single cationic group has limited their use in directly growing MNPs on the surface of graphene. Therefore, further development of small cationic surfactants is necessary to use them as stabilizers for fabrication of Graphene-MNP nanocomposites.

The development of graphene materials is also being driven by reports of graphene-based materials that can change in response to their surroundings ^[9-10]. Azobenzene (Azo) has been particularly interesting due to its widely-applicable performance, photochemical stability, and fast photoresponse. Some significant and functional approaches to modifying graphene with Azo have been reported such as covalent ^[9] and π -stacking ^[10] modification. Although these Azo-Graphene materials have been reported, issues regarding the affirmation of steric conformation, microstructure, chemical bonding energy and electronic properties upon light irradiation are still scientific challenges. Therefore, future studies focusing on these scientific issues and new modification techniques are important and necessary. Currently, no photoresponsive Graphene-MNP nanocomposites have been reported using photoresponsive Azo-surfactants as stabilizers via electrostatic interactions' modification to introduce the Azo groups into the Graphene-MNP nanocomposites, although it may prove to be a vital tool for graphene functionalization.

Here, a novel photoresponsive azobenzene-reduced graphene oxide-gold nanoparticle (Azo-RGO-GNP) nanocomposite was fabricated using Gemini Azo-surfactants ($\text{AzoC}_{10}\text{N}_2\text{O}_2^{2+}$) as stabilizers through electrostatic interactions, one-pot in-situ growth and chemical reduction, where the GNPs with small size are

uniformly distributed onto RGO surface. The Azo-RGO-GNP nanocomposite has photochemical behavior due to the presence of Azo units. This photochemical behavior allows the nanocomposite to have significantly different electrochemical properties depending on the Azo configurations. This is the first example of a photoresponsive Graphene-MNP nanocomposite using cationic Gemini Azo-surfactants as stabilizers, and enables the selection of appropriate condition of light for the Graphene-based nanocomposites' switch properties.

Experimental

The detailed materials preparation and characterizations are shown in supporting information.

Results and Discussion

Gemini cationic surfactants usually contain two cationic groups and have good interfacial adsorption ^[11]. In the case of $\text{AzoC}_{10}\text{N}_2\text{O}_2^{2+}$, one cationic group can modify the negative GO into the cationic Azo-GO hybrid (Figures 4S, supporting information) and the other cationic group can direct the growth of the negative GNP precursor (AuCl_4^-) on the surface of Azo-GO via electrostatic interactions between negative AuCl_4^- and cationic Azo-GO to form Azo-GO-GNP precursor. In this regard, the photoresponsive Azo-RGO-GNP nanocomposite was fabricated using $\text{AzoC}_{10}\text{N}_2\text{O}_2^{2+}$ as stabilizers through one pot in situ growth and chemical reduction. The synthetic pathway of Azo-RGO-GNP nanocomposite is schematically summarized in Figure 1a. NaBH_4 serves as reductant for both the GO and GNP precursor. Figures 1b-c show the TEM images of Azo-RGO-GNP at different magnifications. The randomly dispersed dark spots indicate that the GNPs are uniformly distributed onto the Azo-RGO-GNP surface. In contrast, the GNPs severely aggregate on the surface of RGO-GNP when no $\text{AzoC}_{10}\text{N}_2\text{O}_2^{2+}$ stabilizer is used (Figure 1d). This is because the two cationic groups of $\text{AzoC}_{10}\text{N}_2\text{O}_2^{2+}$ form strong interactions with the GNPs while the nonpolar tail prevents nanoparticle aggregation by confining the nanoparticle ^[12]. Besides, the interfacial adsorption of Gemini surfactants ($\text{AzoC}_{10}\text{N}_2\text{O}_2^{2+}$) could improve the interfacial adhesion energy ^[13] between GNPs and RGO due to the electrostatic interactions leading to the stabilization and ripening of GNPs on RGO surface. Figure 1c shows

that the interplanar spacings of the adjacent lattice fringe is about 0.23 nm. This spacing is attributed to the (111) plane of the Au lattice. Furthermore, from TEM images, the GNPs surface density on Azo-RGO-GNP surface is about 1.05×10^{12} GNPs/cm², and the size distribution of GNPs on Azo-RGO-GNP surface shows that the size of GNPs is about 5.69 ± 1.19 nm (Figure 1e). These results indicate that using $\text{AzoC}_{10}\text{N}_2\text{O}_2^{2+}$ as stabilizers achieves Azo-RGO-GNP nanocomposite with uniform deposition of GNPs.

Figure (1) (a) Schematic illustration of the synthesis of Azo-RGO-GNP; (b-c) TEM images of Azo-RGO-GNP at different magnifications, (d) RGO-GNP without using $\text{AzoC}_{10}\text{N}_2\text{O}_2^{2+}$; (e) The particle size distributions of the GNPs on the surface of Azo-RGO-GNP

Figure 2a shows the XRD intensity of RGO and Azo-RGO-GNP. In the XRD pattern of Azo-RGO-GNP, the diffraction peaks centered at $2\theta = 38.16^\circ$, $2\theta = 44.44^\circ$, $2\theta = 64.64^\circ$ and $2\theta = 77.53^\circ$ correspond to the (111), (200), (220) and (311) facets of pure metallic Au, respectively. This indicates that crystalline GNPs exist on the surface

of RGO. Meanwhile, comparing to the XRD pattern of RGO, the peak of Azo-RGO-GNP centered at $2\theta=24.2^\circ$ (002) becomes un conspicuous, suggesting that the decoration of GNPs onto graphene in a 2D sandwich manner^[14] effectively prevents the typical π -stacking of the graphene sheets^[15]. This result also responds that the Azo-RGO-GNP nanocomposites are well dispersed in water. Figure 2b shows digital photos of the dispersibility in water of (i) Azo-RGO-GNP and (ii) RGO-GNP without $\text{AzoC}_{10}\text{N}_2\text{O}_2^{2+}$. The Azo-RGO-GNP is clearly more dispersible due to the presence of $\text{AzoC}_{10}\text{N}_2\text{O}_2^{2+}$ as stabilizers. To further monitor the composition and the grafting degree of Azo-RGO-GNP nanocomposite, X-ray Photoelectron Spectroscopy (XPS) experiment was conducted. The grafting degree was calculated by Eq.S1 (supporting information). Azo-RGO-GNP contains about 4.10% N-atoms and about 1.02% Au-atoms, whereas no N-atoms and Au-atoms are found in RGO (Figure 2c). In Figure 2d, the C1s can be fitted with four groups: C-C (284.6 eV), C-O (286.7 eV), C=O (288.6 eV) and C-N (285.6 eV). The N1s of Azo-RGO-GNP can also be fitted with two peaks at N=N (399.3 eV) and N-C (402.1 eV) (Figure 2e), which indicates that the Azo groups remain existence on the surface of RGO after chemical reduction. The Au4f peaks corresponding to Au4f 7/2 (84 eV) and Au4f 5/2 (87.7 eV)^[16] are also observed in Figure 2f. This result supports that the surface of the RGO is effectively decorated with GNPs when $\text{AzoC}_{10}\text{N}_2\text{O}_2^{2+}$ is used as stabilizers.

Figure (2) (a) XRD patterns of RGO and Azo-RGO-GNP; (b) Digital photos of dispersibility of Azo-RGO-GNP and RGO-GNP in H₂O; XPS spectra of (c) survey scan of the peak assignments for RGO and Azo-RGO-GNP, (d) C1s of Azo-RGO-GNP, (e) N1s of Azo-RGO-GNP and (f) Au4f of Azo-RGO-GNP.

UV-Vis absorption spectroscopy was used to investigate the photochemical behavior of Azo-RGO-GNP. In Figure 3a, the peak at 230 nm of GO red-shifts to 280 nm of Azo-RGO-GNP. This redshift indicates that electronic conjugation has occurred within the reduced graphene sheets from GO to RGO [17]. The UV-Vis spectrum of AzoC₁₀N₂O₂²⁺ shows a maximum absorption band at 350 nm due to the π - π^* transition of trans-Azo [18]. This band is also found in the spectra of Azo-RGO-GNP. Besides, the band at 515 nm is assigned to the GNP [19]. These results prove that Azo and GNPs exist at the surface of RGO. The time evolution UV-Vis spectra of Azo-RGO-GNP with the wavelength range 335-365 nm was measured to demonstrate the trans-cis isomerization of Azo-RGO-GNP upon UV light irradiation for different times (Figure 3b). Upon UV light irradiation from 0 min to 30 min, the 350 nm band decreases gradually until a photo-stationary balance is established. This result implies that the trans-Azo-RGO-GNP converts to cis-Azo-RGO-GNP. From all of these results, it is clear that the Azo-RGO-GNP have the ability of photochemical behavior due to using AzoC₁₀N₂O₂²⁺ as stabilizers. Furthermore, we further investigate the changes of CV curves of Azo-RGO-GNP upon UV light irradiation for different times. In Figure 3c, the CV wave current densities of Azo-RGO-GNP nanocomposite is higher than the bare glassy carbon electrode (GCE) and RGO-GNP without using AzoC₁₀N₂O₂²⁺. This result suggests that the electrochemical performance is dependent on the GNP distribution on RGO surface [20]. The Azo-RGO-GNP nanocomposite has uniformly distributed GNPs with small size, there is more active surface area of the GNPs which leads to the higher conductivity. In Figure 3c, there is a gradual increase in the highest CV current intensity with increasing UV irradiation time. After UV irradiation for 30 min, the highest CV current intensity of Azo-RGO-GNP increased from 18.1 A·g⁻¹ to 22.5 A·g⁻¹. These data suggest that the conductivity can be controlled by the photoresponsive behavior of Azo-RGO-GNP due to the conformational change of the Azo between trans and cis forms upon UV light irradiation. The cis-Azo are more

conductive than the trans-Azo due to the decrease in tunneling barrier length of Azo molecules connected graphene [9]. For our case of Azo-RGO-GNP, after UV light irradiation, more conductive cis-Azo exposes on the surface of Azo-RGO-GNP, leading to the higher conductivity. It is interesting and possibly practically useful that the trans-Azo-RGO-GNP and cis-Azo-RGO-GNP nanocomposites have distinct electrochemical performances.

Figure (3) (a) UV-Vis spectra of GO (0.5 mg/mL), $\text{AzoC}_{10}\text{N}_2\text{O}_2^{2+}$ (2 mM/L) and Azo-RGO-GNP (0.5 mg/mL) and (b) changes of UV-Vis absorption band at 350 nm for Azo-RGO-GNP (0.5 mg/mL) upon UV light irradiation for different times; (c) CV curve of bare GCE, RGO-GNP and Azo-RGO-GNP upon UV light irradiation for different times at a potential scan rate of 50 mV/s in the aqueous solution of 5 mM $\text{Fe}(\text{CN})_6^{4-}$ and 1M KCl.

Conclusion

A novel strategy to prepare photoresponsive Azo-RGO-GNP nanocomposite using $\text{AzoC}_{10}\text{N}_2\text{O}_2^{2+}$ as stabilizers was developed. The nanocomposite can be suspended in water and has photochemical activity because of the $\text{AzoC}_{10}\text{N}_2\text{O}_2^{2+}$ stabilizer units. Interestingly, this photo-response influences the electrochemical performance which could be a key factor for its applications, for example, for optic and photonic devices as photoswitch conducting material. Furthermore, We expect that the Azo-surfactants with different structures could be used as stabilizers to fabricate photoresponsive graphene-based nanocomposites with various MNPs such as PtNPs and PdNPs and may become a generally universal approach to developing these types of materials.

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