

A graphene-organic composite as a fluorescent chemosensor for Ag⁺

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A novel reduced graphene oxide (rGO) decorated organic binol based receptor ((S)-1) has been designed and synthesized. The resulting nanocomposite (rGO-(S)-1) material was then utilized as a selective fluorescent chemosensor for Ag⁺ ion in aqueous media at physiological pH. In addition, the nanocomposite showed no cross-reaction with any of the potential interfering metal ions. The reduced graphene oxide-organic nanocomposite was characterized using various spectroscopic, microscopic and analytical studies.

Keywords: rGO, Binol, nanocomposite, Fluorescence, Silver, off-on probe.

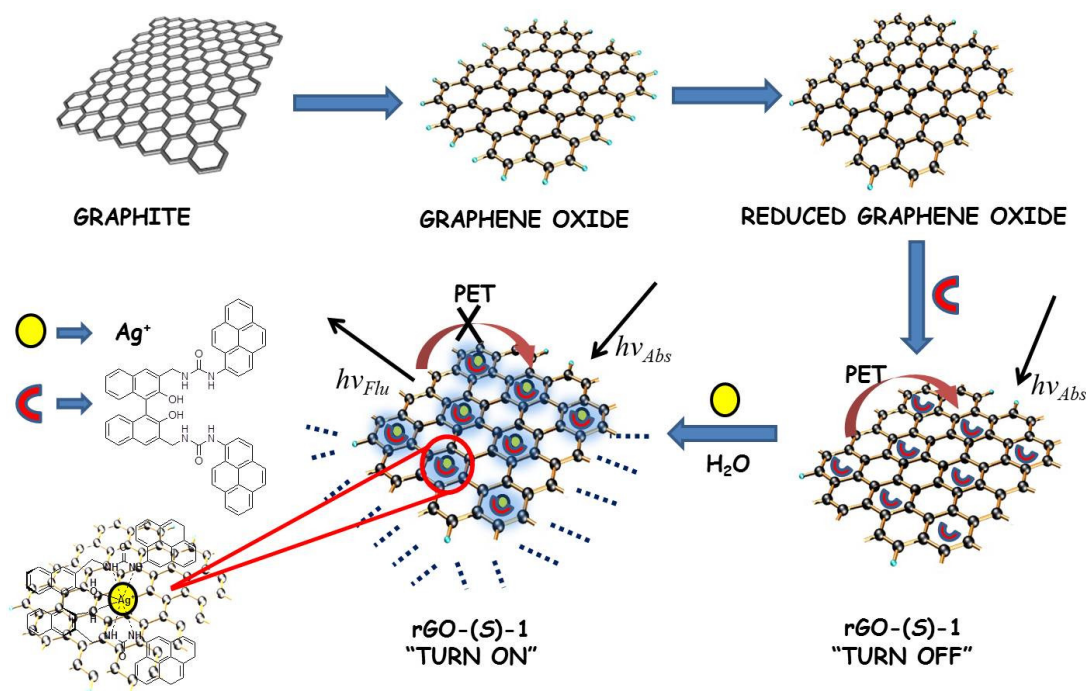
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1. Introduction

Graphene, possessing unique planar structure, remarkable mechanical properties, fascinating electron transfer and exceptional optical properties, has attracted considerable attention in recent years [1]. As a “rising star” in materials science and nanotechnology, it holds great promise for potential applications in many fields, such as nanocomposites [2], chemical sensors [3], energy storage [4], electronics [5], photonics [6], and catalysis [7]. Graphene oxide (GO), a two-dimensional nanosheet produced by the oxidation of graphene, has attracted great interest because of its unique characteristics, such as good dispersibility and facile surface functionality [8,9]. For a long time it has been well known that silver ions have the ability to kill harmful bacteria [10–12]. Silver has always been regarded as a precious metal. Silver ions, however, can cause severe damage to both the environment and to humans [13,14]. As one of the most toxic heavy metals, surpassed only by mercury, silver ion has been assigned to the highest toxicity class [15]. Silver ions may damage bacteria, and inhibit their growth, thereby affecting their reproduction [16]. Excessive intake of silver ions can also lead to long term insoluble substances formed in eye and skin cells [17]. Ag⁺ is widely used in the electrical industry, photography/imaging industry, and pharmaceutical industry [18,19], because of the high toxicity of Ag⁺ in aquatic organisms, monitoring of Ag⁺ levels has become an important issue. Indeed, almost all the reported sensors for Ag⁺ still suffer from serious drawbacks, such as poor water solubility, poor sensitivity, and poor selectivity. Traditional analytical methods used for the trace determination of Ag⁺ ion are generally based on different instrumental techniques. Especially in recent years, with the recent development of nanoscience, various silver nanoparticle products, such as nano-Ag catalyzer and antimicrobial reagents, have been widely used in research and in clinics. After being discharged into the environment, some of the silver nanoparticles are oxidized to silver ions and dissolve in environmental water and some are deposited in mud. Thus, they may cause more serious pollution to the environment and damage to human health. Therefore, it is of great significance to develop a rapid, selective, sensitive and simple detection method for silver ion in environmental samples and human fluids. We herein designed and synthesized an rGO-(S)-1 nanocomposite as shown in Fig. 1. The composite material is then utilized as a selective fluorescent chemosensor for Ag⁺ ion in aqueous media at a neutral pH. The synthesis, characterization and the selectivity studies with different metal ions are reported here.

2. Experimental section

All solvents were purchased commercially with reagent grade quality. rGO and compound (S) – 1 were prepared using a reported procedure [20,21]. Scanning Electron Microscope (SEM) studies were carried out on JEOL model JSM-6390. Absorption spectra were recorded on a Shimadzu UV-240 spectrophotometer. Fluorescence measurements were taken using a Jasco FP-8200 spectrofluorimeter equipped with quartz cuvettes of 1 cm path length. IR Studies were performed on a Shimadzu Prestige 20 IR spectrometer. All absorption and emission spectra were recorded at 24 ± 1 °C. Stock solutions for analyses were prepared (2 × 10⁻³ M) for rGO-(S)-1 (H₂O, HEPES=50 mM, pH=7.0) immediately before the experiments. The solutions of metal ions were prepared from the

FIG. 1. Synthesis and sensing of **rGO-(S)-1**

nitrate salts of Al^{3+} , Pb^{2+} , Ce^{3+} , Cd^{2+} , La^{3+} , Mg^{2+} , Zn^{2+} , Ba^{2+} , Hg^{2+} , Ag^+ , Fe^{3+} , Fe^{2+} , Ni^{2+} , Cr^{3+} , Ca^{2+} , Mn^{2+} , Na^+ , K^+ , Cu^{2+} and Co^{2+} .

2.1. Synthesis of **rGO-(S)-1** nanocomposite

The graphene-organic nanocomposite was prepared by the hydrothermal method [22]. Briefly, 2 mg of reduced graphene oxide was sonicated to make to a clear solution in distilled water (pH=7.0) and then 4 mg of **(S)-1** added to it. The resulting solution was transferred to an autoclave and kept in a hot air oven at 180 °C for 24 h. After the completion of the reaction, the autoclave was allowed to cool to room temperature. The formed precipitate was washed with a copious amount of water and ethanol and filtered. The final product **rGO-(S)-1** was obtained after drying the precipitate at 50 °C overnight.

3. Results and discussion

We have designed and synthesized a novel **rGO-(S)-1** nanocomposite through hydrothermal method as a selective and sensitive chemosensor for Ag^+ . The chemosensor **rGO-(S)-1** was confirmed by IR, SEM, UV and fluorescence studies. The UV and fluorescence spectra for **rGO**, **(S)-1** and the nanocomposite **rGO-(S)-1** are very distinct, and for the nanocomposite, the fluorescence is quenched. The IR spectrum of **(S)-1** shows a characteristic absorption bands at 1658 and 3441 cm^{-1} , which were assigned to the uryl C=O and the binol -OH groups, and the **rGO** characteristic absorption band appeared at 1573 and 1224 cm^{-1} [23]. In the case of the **rGO-(S)-1** nanocomposite, the 1658 cm^{-1} band was downshifted to 1637 cm^{-1} and the 3441 cm^{-1} band disappeared followed by the appearance of a new one at 2356 cm^{-1} . Conversely, in **rGO**, the bands at 1573 cm^{-1} were shifted to 1523 cm^{-1} after nanocomposite formation, as shown in Fig. 2. These shifts in the absorption bands are due to the $\pi - \pi$ stacking between the aromatic rings and the non-covalent interactions between **(S)-1** and the **rGO** composite.

The newly-prepared composite material and its precursor were analyzed by scanning electron microscopy. Accordingly, the SEM images of the **(S)-1** and **rGO-(S)-1** were recorded. The organic molecules **(S)-1** had rod like structure. However, in the case of nanocomposite material, the organic molecules were uniformly distributed over the surface of the 2D graphene sheet as a result of hydrothermal treatment. This composite formation between graphene and organic compound enhances the sensing properties of metal ions due to the high electron conductivity (Fig. 3).

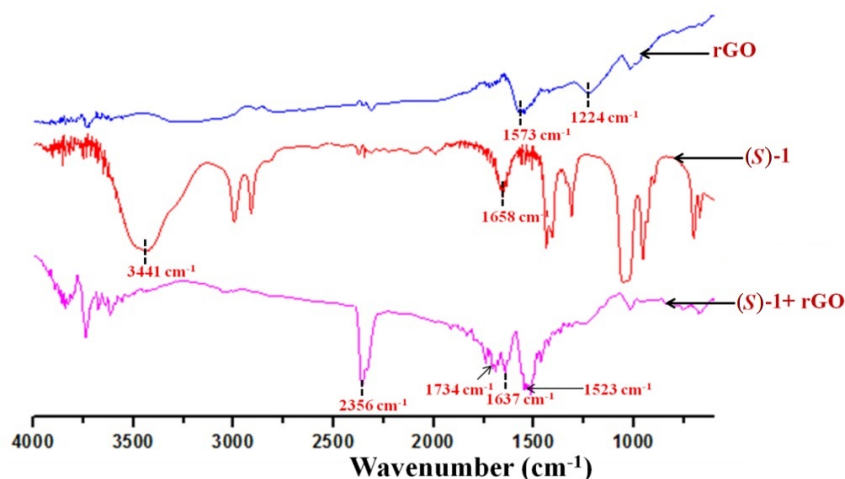


FIG. 2. IR Spectrum of rGO, (S)-1 and rGO-(S)-1

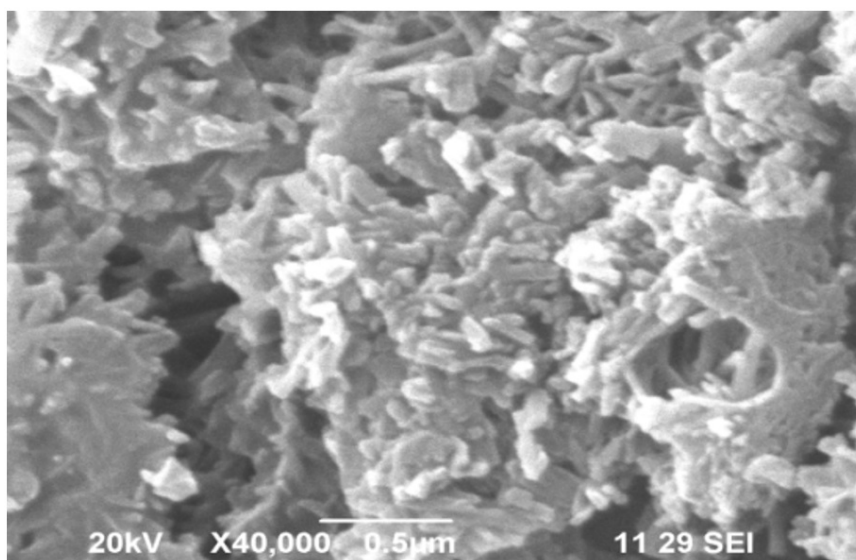


FIG. 3. SEM image of rGO-(S)-1

4. Metal selectivity studies of rGO-(S)-1 nanocomposite

The preliminary screening of the metal ion binding ability of rGO-(S)-1 nanocomposite in aqueous media at a neutral pH was performed by using the fluorescence technique. Receptor rGO-(S)-1 nanocomposite, exhibits very weak fluorescence. However, upon the addition of 100 equiv. of Ag^+ to the solution, significant enhancement of fluorescence with an emission maximum at 354 nm was observed. Interestingly, at the same concentration, other metal ions (Na^+ , K^+ , Pb^{2+} , Cu^{2+} , Cd^{2+} , Hg^{2+} , La^{3+} , Zn^{2+} , Co^{2+} , Ni^{2+} , Ca^{2+} , Mn^{2+} , Cr^{3+} , Ba^{2+} , Ce^{3+} , Mg^{2+} , Fe^{2+} , Fe^{3+} and Al^{3+}) when added to the rGO-(S)-1 nanocomposite did not produce any significant fluorescence changes. Therefore, these observations indicated that the sensor rGO-(S)-1 has an excellent selectivity towards Ag^+ in aqueous media at a neutral pH as a fluorescence “off-on” probe (Fig. 4).

For practical applicability, and to check the anti-jamming ability (i.e. the possible interferences by other metal ions), competitive complexation experiments were conducted. The fluorescence spectral changes of rGO-(S)-1 was measured by the treatment of Ag^+ ions (100 equiv.) in the presence of other metal ions at the same concentration, including Na^+ , K^+ , Pb^{2+} , Cu^{2+} , Cd^{2+} , Hg^{2+} , La^{3+} , Zn^{2+} , Co^{2+} , Ni^{2+} , Ca^{2+} , Mn^{2+} , Cr^{3+} , Ba^{2+} , Ce^{3+} , Mg^{2+} , Fe^{2+} , Fe^{3+} and Al^{3+} . All of the tested interfering metal ions showed no observable interference with the detection of Ag^+ ion. These results suggested that the receptor could be used for the selective detection of Ag^+ -ion in environmental and biological samples (Fig. 5).

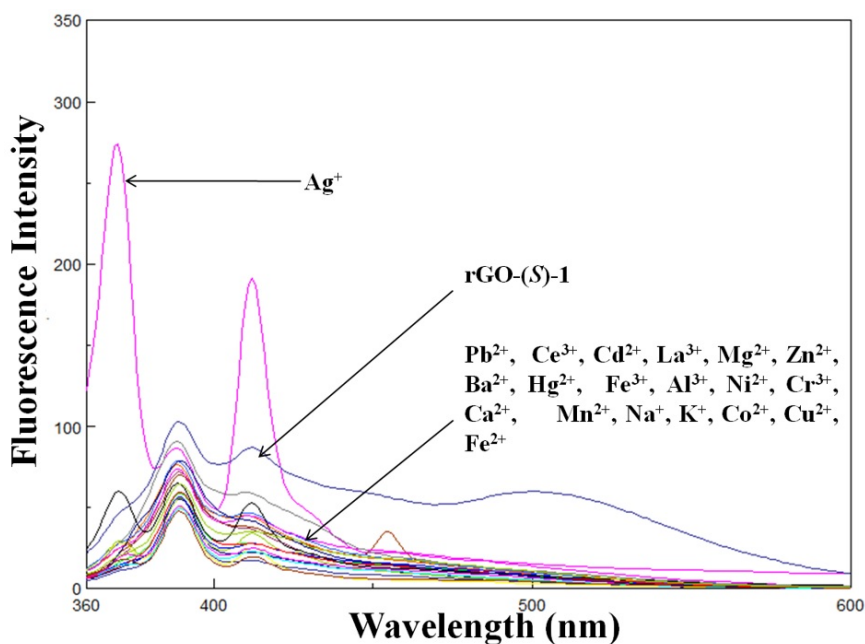


FIG. 4. Fluorescence changes of rGO-(S)-1 (4×10^{-6} M) solution (H₂O, pH=7.0) in the presence of various metal ions (100 equiv. of each, excited at 344 nm)

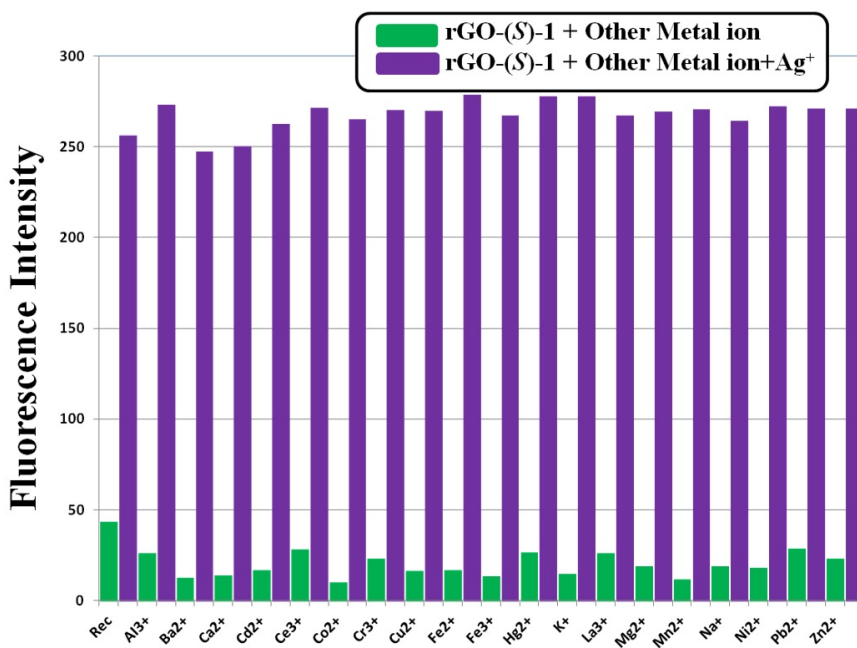


FIG. 5. Fluorescence changes of rGO-(S)-1 (4×10^{-6} M) solution (H₂O, pH=7.0) in the presence of various metal ions (100 equiv. of each, excited at 344 nm)

5. Conclusion

In conclusion, we have designed and synthesized a novel **rGO-(S)-1** nanocomposite through hydrothermal method and confirmed by usual spectroscopic, microscopy and analytical studies. The **rGO-(S)-1** nanocomposite exhibited high selectivity toward Ag^+ in comparison to other commonly-interfering metal ions in aqueous media at room temperature. This paves a pathway for further studies, such as chiral molecule sensing, anion sensing etc., which are currently underway in our laboratory. Moreover, we expect that this sensor will have tremendous potential application in biological fields, environmental monitoring works, and other relevant areas.

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