Direct and sensitive detection of sulfide ions based on one-step synthesis of ionic liquid functionalized fluorescent carbon nanoribbons†

Tao Luo, Xiaobo Wang, Yuting Qian, Junjie Liu, Lequn Li, Jiyang Liu and Jie Chen

 Despite widely reported fluorescence sensors for cations, direct detection of anions is nevertheless still rare. In this work, ionic liquid-functionalized fluorescent carbon nanoribbons (IL-CNRs) are one-step synthesized and serve as the fluorescent probes for direct and sensitive detection of sulfide ions (S\(^{2-}\)). The IL-CNRs are synthesized based on electrochemical exfoliation of graphite rods in a water-IL biphasic system. The as-prepared IL-CNRs exhibit uniform structure, high crystallinity, strong blue fluorescence (absolute photoluminescence quantum yield of 11.4%), and unique selectivity towards S\(^{2-}\). Based on the fluorescence quenching of IL-CNRs by S\(^{2-}\), a fluorescence sensor is developed for direct, rapid and sensitive detection of S\(^{2-}\) in the range of 100 nM to 1 μM and 1–300 μM with a low detection limit (LOD, 85 nM). Moreover, detection of S\(^{2-}\) in a real sample (tap water) is also demonstrated.

1. Introduction

Inorganic anions play a crucial role in industrial, biological and environmental fields. For instance, the sulfide (S\(^{2-}\)) ion is highly toxic and harmful to human health and the ecological environment. Usually, the S\(^{2-}\) ion is frequently distributed in natural water and wastewater samples because it is widely used in industrial processes (e.g. sulfur and sulfuric acid production, petroleum refineries, paper and pulp manufacturing, and sewage processing industries) and is also produced in biological systems (e.g. via reduction of sulfate ions by microbes or anaerobic processes of S-containing enzymes). As the S\(^{2-}\) ion can stimulate the mucosa and has an extreme effect on the nervous system, exposure to S\(^{2-}\) ions leads to unconsciousness and respiratory paralysis and is closely related to various diseases including Alzheimer’s disease, Down’s syndrome and cirrhosis of the liver. Therefore, simple, rapid and sensitive detection of S\(^{2-}\) is of great importance.

In comparison with other technologies including gas chromatography, ion chromatography, titrimetry, colorimetry, and electrochemical method, fluorescent sensors are particularly attractive because of high sensitivity, simple operation and rapid detection. Recently, fluorescent sensors based on different fluorescent probes have been widely reported for detection of cations. However, only few researches focus on indirect detection of anions using fluorescent off-on strategy. For instance, Na et al. reported that Cu\(^{2+}\) ions caused aggregation of the GQDs and thereby quenched fluorescence. As the GQDs-Cu\(^{2+}\) aggregates can be dissociated by adding S\(^{2-}\) ions and result in fluorescence turn-on, fluorescent detection of S\(^{2-}\) ions could be realized. Based on the same off-on strategies, graphitic carbon nitride quantum dots-Hg\(^{2+}\), nitrogen and sulfur co-doped carbon dots (CDs)-Hg\(^{2+}\), CDs-gold nanoparticles, silver nanoparticles capped with CDs, CDs-MnO\(_2\) nanosheets, quinoline-Zn\(^{2+}\), calix[4]arene-Cu\(^{2+}\), and organic semiconductor polymer nanodots-Cu\(^{2+}\) systems were also applied for the detection of S\(^{2-}\) ions. However, it still remains a great challenge for improving the chemical selectivity of fluorescent probe to realize the direct detection of S\(^{2-}\).

Carbon-based fluorescent nanomaterials have attracted considerable interests as probes in fluorescent sensing due to good solubility, highly tunable photoluminescence properties and biocompatibility. Carbon nanoribbons (CNRs), which is thin elongated strips of sp\(^2\) bonded carbon atoms, have emerged as an exciting one-dimensional nanomaterial because of their large length-to-width ratio, abundant edge sides, high effective surface area, good flexibility, high conductivity, and tunable fluorescence. Due to the large interfacial area for π–π stacking in basal planes, CNRs exhibit potentials for the synthesis of advanced functional materials through simple modification or functionalization.

Ionic liquids (ILs) have been widely used in many fields because of a series of excellent physical and chemical properties. Particularly, ILs can easily combine with carbon

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‡The two authors contributed equally.
nanomaterials due to π–π or cation–π interactions and the obtained composite materials exhibit unique characteristics.21,28–31 For instance, Wang et al. prepared highly charged CDs through one-pot pyrolysis with citric acid as carbon source and ionic liquid (1-aminopropyl-3-methylimidazolium tetrafluoroborate (BMIMBF4) under ultrasonic treatment. The as-prepared IL-modified CDs exhibit capability of anion exchange and are able to act as fluorescent probe for direct detection of Fe(CN)63– anion. Our group also prepared IL-GQDs nanomaterial through post-modification of hydroxyl-functionalized GQDs (OH-GQDs) with 1-butyl-3-methyl imidazolium tetrafluoroborate (BMIMBF4) under ultrasonic treatment. The as-prepared IL-GQDs composite also displayed sensitive response towards Fe(CN)63–, owing to the anion exchange ability of IL.32 Inspired by these evidences, IL modified fluorescent nanocarbon materials possess great potentials for the direct detection of anions.

In this work, in contrast to anion detection based on fluorescence off–on mode, a new type of ionic liquid-functionalized fluorescent carbon nanoribbons (IL-CNRs) were prepared using one-step electrochemical method, which is able to achieve direct and sensitive detection of sulfide ions. The IL-CNRs were in situ synthesized based on electrochemical exfoliation of graphite rods in water-IL (1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][PF6]) biphasic system. The obtained IL-CNRs exhibit bright fluorescence, high crystallinity and uniform structure. Based on the selective quenching by S2–, IL-CNRs can be served as fluorescent probes for direct and sensitive detection of S2–. In comparison with the previous cation-based fluorescent sensor, we for the first time demonstrate the application of IL-CNRs for direct and selective detection of S2–.

2. Experimental

2.1 Materials and reagents

High-purity graphite rods were purchased from China National Medicines Co. Ltd (China). 1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF6]) (>99%), ascorbic acid (AA), and 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES), Na2S were purchased from Sigma Aldrich. Aqueous solutions of Na+, K+, Zn2+, Mg2+, Fe3+, Ca2+, Al3+, Ni2+, Cu2+, Cd2+ were prepared from their chloride salts. Solutions of Pb2+, Ag+ and Hg2+ were prepared from their nitrate salts. Aqueous solutions of CH3COO−, HCO3−, H2PO4−, HPO42−, NO2−, S2−, SO32− were prepared from their sodium salts. SCN−, Cl−, NO3−, NO2−, Br− were prepared from their potassium salts. All chemicals were of analytical grade and used without further treatment. Aqueous solutions were prepared with ultrapure water (18.2 MΩ cm, Milli-Q, Millipore).

2.2 Characterizations

Transmission electron microscopy (TEM) micrographs were obtained using a JEM-2100F transmission electron microscope (JEOL Ltd, Japan) at accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a PHI5300 at operating voltage of 14 kV (PE Ltd., USA). The Fourier transform infrared spectra (FTIR) were conducted with a Nicolet 5700 FTIR spectrometer (Thermo Electron Scientific Instruments Corp., USA). Fluorescence spectra were measured using FL 3C-11 spectrophotometer (Horiba Scientific, USA).

2.3 One-step electrochemical synthesis of IL-CNRs

The IL-CNRs were one-step synthesized by electrochemical exfoliation of graphite rods. A two electrodes system was adopted with graphite rods (d = 3 mm) as both anode and cathode. The electrolyte was water-IL ([BMIM][PF6]) biphasic system (V/V, 4 : 6). Graphite rods were vertically inserted into electrolyte solution at a distance of 3 cm.21 A static voltage of 8 V was applied on graphite rod for 4 h with stirring the electrolyte. Afterwards, the resultant solution was centrifuged at 12 000 rpm for 10 min to remove large particles. To acquire IL-CNRs, the supernatant solution was then filtered using a 0.22 μm membrane and dialyzed in a dialysis bag (with cut-off molecular weight of 1000 Da), which is followed by freeze-drying.

2.4 Fluorescent detection of S2–

The selectivity of IL-CNRs towards different anions and cations were evaluated by measuring the fluorescent intensity of IL-CNRs solution in presence of different cations (Na+, K+, Zn2+, Mg2+, Fe3+, Ca2+, Al3+, Ni2+, Cu2+, Cd2+) or anions (CH3COO−, HCO3−, H2PO4−, SCN−, HPO42−, S2−, Cl−, NO3−, NO2−, Br−, SO32−).

For S2– detection, standard stock solutions of S2– (0.1 M) were prepared and further diluted stepwise to obtain different concentrations. HEPES buffer (0.1 M, pH 7.0) containing AA (25 μM) was applied as the buffer solution. After reaction of IL-CNRs with different amount of S2– for 1 min at room temperature, the fluorescent intensity of the solution was recorded with the excitation wavelength fixed at 340 nm.

The relative fluorescence ratio (F/F0) or relative fluorescence quenching ratio (F0 – F/F0) were used to evaluate the quenching of IL-CNRs caused by ion, where F0 and F represent the fluorescent intensity of IL-CNRs solution in the absence and presence of ion, respectively.

3. Results and discussion

3.1 Preparation and structure characterizations of IL-CNRs

Electrochemical synthesis has particularly attracted attention owning to the inexpensive apparatus and easy operation under...
As illustrated in Fig. 1, ionic liquid-functionalized fluorescent carbon nanoribbons (IL-CNRs) were easily synthesized through one-step electrochemical exfoliation of graphite rods in water-IL (1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][PF6]) biphasic system. Owing to high ionic conductivity and wide electrochemical potential window, ILs shows potential as electrolyte in electrochemical synthesis. In the process of electrochemical exfoliation, the colour of electrolyte turned from colourless to pale yellow and afterward turned dark brown due to rapid flaking-off of abundant IL-CNRs. In comparison with the same procedure in pure water, this phenomenon cannot be observed, indicating the importance of ILs for improved conductivity and facilitated exfoliation. The formation of IL-CNRs can be observed by transmission electron microscopy (TEM) (Fig. 2). The length and width of IL-CNRs were about 40 nm and 5 nm (Fig. 2a–c), respectively. Clear lattice lines can be seen from the high-resolution TEM (HRTEM) image (Fig. 2d), indicating good crystallinity. The lattice spaces are 0.26 nm and 0.38 nm, that are consistent with the (100) and (002) lattice of graphite, respectively.

The chemical composition of the as-prepared IL-CNRs were characterized by X-ray photoelectron spectroscopy (XPS). As shown in Fig. 3a, the XPS survey spectrum of IL-CNRs contains five distinct peaks of C 1s, N 1s, O 1s, P 2p, F 1s. The appearance of N, P, F reveals the formation of IL-CNRs nanocomposites. The C–C=C=C (sp2 C) peak is prominent in high resolution spectrum of C 1s, suggesting the graphitic structure in CNRs (Fig. 3b). This result is consistent with the good crystallinity demonstrated in HRTEM image (Fig. 2d). The appearance of C–N in high resolution spectrum of C 1s (Fig. 3b), N–C=C and quaternary N in high resolution spectrum of N 1s (Fig. 3c) confirm the existence of BMIM+ in IL-CNRs. The appearance of O 1s reveals the abundant oxygen-containing groups (Fig. 3d), suggesting good solubility of the as-prepared IL-CNRs. The F 1s peak (Fig. 3e) and P 2p peak (Fig. 3f) also prove the presence of PF6– anion in IL-CNRs, indicating the hybridization between CNRs and IL. These results evidence the successful formation of [BMIM][PF6] modified CNRs in the one-step electrochemical exfoliation of graphite. Consistently, Fourier transform infrared spectrum (FTIR) of IL-CNRs (Fig. S1 in ESI†) also shows characteristic vibrations of C–H (2962, 2922, and 2857 cm–1), C–C and C–N (1552 cm–1), OH (3457 cm–1), C–O (1640 cm–1), and PF6– (1578 and 1027 cm–1), that agree well with [BMIM][PF6]. In comparison with IL, UV-Vis spectrum of IL-CNRs exhibits the same large peak of π–π* transition (~240 nm) and new peak at about 326 nm that corresponds to n–π* transition (Fig. S2 in ESI†). Taken together, [BMIM][PF6] are proven to be composited with CNRs.

According to the above results, we propose that the mechanism for the preparation of IL-CNRs includes oxidative cleavage, ionic liquid intercalation and hybridization (Fig. 1). Firstly, the oxidation of water is expected to produce radicals (e.g. hydroxyl and oxygen radicals) when a high oxidation voltage is applied. Secondly, the oxidation of the edge planes opens up the edge sheets and leads to the expansion of the graphite anode, facilitating intercalation by PF6– between the graphene layers. Thirdly, the oxidative cleavage of the expanded graphene sheets generates CNRs. Finally, interaction between CNRs and BMIM+ via π–π or cation–π interactions leads to stable IL-CNRs nanocomposites. In comparison with the preparation of CNRs using electron or ion beam etching, chemical ultrasound, lithographic patterning, oxidative cleavage, and chemical vapor deposition (CVD), this
3.2 Fluorescence properties of IL-CNRs

The fluorescence properties of IL-CNRs were investigated and results were demonstrated in Fig. 4. The IL-CNRs show good solubility in water and appear light-yellow under daylight, while exhibit strong blue luminescence under UV light (365 nm) (inset in Fig. 4b). The maximum emission is located at 430 nm and the maximum excitation wavelength is 340 nm (Fig. 4a).

Like most luminescent carbon nanomaterials, the IL-CNRs also exhibit excitation-dependent fluorescence behavior (Fig. 4b). IL-CNRs prepared under the same conditions independently exhibit the same maximum emission wavelength and a relative standard deviation (RSD) of 2.9% in fluorescence intensity (at 430 nm), indicating high stability and repeatability of the preparation. As the excitation wavelength increases, the fluorescence emission slightly red-shifts, which could be ascribed to size heterogeneity and distribution of different emissive sites on the carbon ribbons. Absolute photoluminescence quantum yield of IL-CNRs is measured to be 11.4%, which may be ascribed to the high crystallinity of IL-CNRs and the presence of BMIM+ on IL-CNRs surface which has electron-withdrawing nitrogen groups. The lifetime of B-GQDs is 5.9 ns (Fig. S3 in ESI†). The IL-CNRs also exhibits good photostability. As shown in Fig. S4 (ESI†), even after being illuminated for 4 h under UV light (365 nm), the fluorescent intensity remains 91%, indicating good anti-photo bleaching property.

3.3 Ion selectivity of IL-CNRs

Ionic liquids modified carbon materials have proven to exhibit anion exchange ability and have potential in direct detection of anion. Thus, the selectivity of the as-prepared IL-CNRs towards different anions were investigated. As revealed in Fig. 5a, the fluorescence of IL-CNRs is strongly quenched by $\text{S}_2^-$, but not the other physiologically or environmentally relevant anions (Fig. 5a). The lifetime of IL-CNRs in presence $\text{S}_2^-$ is also revealed to be 5.9 ns (Fig. S5 in ESI†). The unchanged fluorescence lifetime of IL-CNRs in the presence of $\text{S}_2^-$ indicates no charge transfer and exciton recombination process. Thus, the quenching might be ascribed to the ability of anion exchange originated from IL. As fluorescent carbon materials are usually easy to interact with metal cations and cause fluorescence quenching, the selectivity of IL-CNRs towards cations were also investigated. As demonstrated in Fig. 5b, $\text{Fe}^{3+}$ cause fluorescence quenching, while other common cations did not significantly affect the fluorescence intensity of the IL-CNRs. The interactions between IL-CNRs and $\text{Fe}^{3+}$ could be efficiently masked by ascorbic acid (AA). Thus, IL-CNRs have potential for direct and selective detection of $\text{S}_2^-$ ions.

3.4 Detection of $\text{S}_2^-$ ions using IL-CNRs as fluorescent probe

The detection of $\text{S}_2^-$ ions using IL-CNRs as fluorescent probe was investigated. To obtain the highest sensitivity, the detection conditions including pH and incubation time were optimized. As illustrated in Fig. 6a (ESI†), $\text{S}_2^-$ ions could quench the fluorescence of IL-CNRs very quickly. As the incubation time goes beyond 60 s, the fluorescence quenching reaches a plateau. Owing to the fast and sensitive fluorescence quenching of IL-CNRs by $\text{S}_2^-$ ions (insets in Fig. 6a), the fluorescent detection
was performed under the optimum conditions. As demonstrated in Fig. 6a, S²⁻ ions caused fluorescence quenching in dose dependent manner. Good linear correlation was found between \( (F_0 - F)/F_0 \) and the concentration of S²⁻ ions from 100 nM to 1 μM and 1 to 300 μM (Fig. 6b). The limit of detection (LOD) for S²⁻ ions is as low as 85 nM at a signal-to-noise ratio of 3. Thus, IL-CNRs based method is sensitive enough to detect the maximum allowable level of S²⁻ ions in drinking water recommended by World Health Organization.⁴⁴,⁴⁵ As shown in Table S1 (ESI†), the detection limit obtained with the present method was lower than those obtained by carbon dots (CDs)-Ag⁺,⁴⁴ covalent linking fluorescein isothiocyanate with branched-polyethyleneimine (PEI-FITC),⁴³ triarylimidazole chromophore (TPI-H)-Cu²⁺,⁴⁵ Au nanoclusters,⁴⁶ lysozyme-stabilized silver nanoclusters (Lys-Ag NCs),⁴⁷ graphene quantum dot (GQDs)-Cu²⁺,⁴⁸ but higher than that obtained using Cu nanoclusters,⁴⁹,⁵⁰ Au nanoclusters-Ce(III),⁵¹ and silver nanoparticles capped with carbon dots (AgNPs-CDs).⁵²

3.5 Real sample analysis

In order to demonstrate the practical application of the developed fluorescent sensor in detection of S²⁻ in real samples, tap water samples were analyzed by standard addition method. The recoveries ranges from 93.7–103.8% and the relative standard deviations (RSD) is less than 3.0% (Table S2†), indicating the potential for the detection of S²⁻ in complicated real samples.

4. Conclusions

Ionic liquid-functionalized carbon nanoribbons (IL-CNRs) were readily synthesized using one-step electrochemical exfoliation of graphite rod in water-IL biphasic system. The hybridization of IL with CNRs not only results in bright fluorescence of CNRs but also endows IL-CNRs with specific interaction with S²⁻ ions. Taking the advantages of bright photoluminescence and selectivity towards S²⁻, IL-CNRs are applied for fast, selective and sensitive detection of S²⁻ ion. In contrast with fluorescent detection of S²⁻ ion using turn-off-on mode, this IL-CNRs demonstrate its potential for practical use in direct detection of anions.

Conflicts of interest

There are no conflicts to declare.

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