Photofunctional hybrid ionogel prepared by doping the terbium complex covalently modified graphene within a stationary ionic liquid matrix

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Abstract. Ionogel is an emerging hybrid material which is usually constructed by confined an ionic liquid into some special matrices, and it is expected to have great potential applications in the field of electrolyte materials, optical-electric materials and so on. Here, a terbium complex covalently modified graphene was introduced into the 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ionic liquid based ionogel matrix. The resulted material is a kind of novel photoluminescent hybrid material which has a transparent appearance and shows strong green under the UV light. The photoluminescent properties of the ionogel has been measured in details, revealing a broad excitation spectra, line-like emission spectra and long luminescence lifetimes which make it great potential applications in the preparation of optical-electric devices, together with the intrinsic conductive property of the embedded ionic liquid.

1 Introduction

Lanthanide complexes functionalized hybrid materials have gathered lots of attentions from the material scientists over the past decades. It is mainly due to the combination of lanthanide complexes with various matrices would have promised a novel multi-functional materials that could be used in some emerging research areas such as biomedical imaging, optical-electrical devices or photoluminescent makers [1]. Duing to effective intramolecular energy transfer (the so-called “antenna effect”), the lanthanide complexes are characterized by long lifetime, narrow-width emission bands in the visible and near infrared regions, large Stokes shift, and it can be easily combined with the other host matrices through the ligand-derived conjugated molecular [2]. However, the poor thermal-stability, chemical-stability and low mechanical strength of traditional lanthanide complexes has limited its practical applications [3-4]. Thus, in order to improve the photo-stability, the lanthanide complexes have been introduced into various organic-inorganic systems to build the so-called lanthanide organic-inorganic hybrid materials which had been proven to have the potential applications for new developments [5-6]. The combination of lanthanide complexes with the other organic and inorganic components could integrate the merits of different matrices together, for instance, the processability, thermal and chemical stability, conductivity, bio-compatibility and even the second luminescence centers. Besides, most of the photosensitive ligands can be easily modified by some couple agent and then linked to the corresponding supported matrix, which

also makes the construction of lanthanide organic-inorganic hybrid materials feasible and variable. From this bases, the lanthanide complexes have been covalently grafted to various silicon-oxygen matrices, polymer matrices, carbon matrices etc. and formed numerous luminescent hybrid materials [7-11].

Recently, the nanoparticle composited gel materials which are built by incorporating a nanoparticle into the polymer networks derived gel systems have arouse the general attentions [12]. This combination may result in a synergistic property enhancement of each component, and even holds the promise of providing a multi-functional hybrid materials with applications in diverse fields such as nano-medicine, optoelectronic devices, drug delivery and so on. Especially the new developed ionogel has been put on lots of focus. Ionogel is an emerging hybrid material which is prepared by the confinement of ionic liquid in the well-designed three-dimension network usually comes from the cross-linking silica-oxygen, polymer or metal-organic matrices [13]. Because of the inherited ionic conductivity performance that comes from the stationary ionic liquid, it has been expected to have potential application in the fields such as electrochemical sensing, supercapacitor, luminescent hybrid materials and so on. It has been proved that the introduction of lanthanide complexes into an ionogel matrix would provide a new opportunity to design and synthesis novel hybrid materials, which is hoped to have the outstanding luminescent properties of lanthanide complex and the good ionic conductivity comes from ionic liquids [14-16].

Inspired by the above discussion, we have designed and synthesized a novel ionogel by doped the terbium

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complex covalently bonded graphene to a poly(methyl methacrylate) (PMMA) confined ionic liquid hybrid matrix. The photoluminescent properties of the hybrid ionogel had been measured in details.

2 Experimental sections

2.1 Materials

2,2'-Bipyridyl-4,4'-dicarboxylic acid (96%, BPC), N,N'-Dicyclohexylcarbodiimide (99%, DCC), 4-Dimethylaminopyridine (99%, DMAP), 1,6-Hexamethylenediamine (99%, HMEDA), azodiisobutyronitrile (98%, AIBN), Methyl methacrylate (99.5%, MMA) and Trifluoroacetylacetone (98%, TFA) were provided by Aladdin reagents Co. LTD. Graphene oxide (GO) was purchased from Shenzhen Turing evolutionary technology Co. LTD. 1-butyl-3-methylimidazoliumbis[(trifluoromethyl)sulfonyl]-imide (99%, [BMI][BTSI]) was provided by Shanghai Cheng Jie chemical Co. LTD (China). The $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ are prepared by dissolving Tb_4O_7 oxides in concentrated hydrochloric acid in our lab. While the other reagents are analytical pure and provide by China National Medicines Group.

2.2 Characterizations

Infrared (IR) spectra were obtained on Nicolet iS50. Luminescent excitation and emission spectra were recorded on Hitachi F-4600 instrument. Luminescent lifetime was obtained using the Edinburgh Instrument FLS920.

2.3 Preparation of terbium complex modified graphene

The $\text{Tb}(\text{TFA})_3(\text{H}_2\text{O})_2$ was prepared according to a modified method reported in ref. [17], typically as follows: 3 mmol TFA was dissolved in 15 mL boiling ethanol, and then a solution of 1 N sodium hydroxide was added, followed by the addition of 1 mmol $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ in 10 mL of ethanol in an hour. The mixture was refluxed and stirred for 2 h, and then stirred until cooled to room temperature. The NaCl precipitates was removed by filter and the residual solution was collected as the $\text{Tb}(\text{TFA})_3(\text{H}_2\text{O})_2$ solution which was used directly in future step without further purification.

The BPC modified graphene was synthesized from the GO as follows: Firstly, 100 mg GO was dispersed in 100 mL anhydrous solvent of DMF and dichloromethane (DCM) (v:v = 1:1) by means of supersonic vehicle, then, 1.5 mmol DCC and 1 mmol DMAP were added to active it for 1 h in ice bath. After that, 1 mmol HMEDA was added into the solution and stirred for 24 h at 40 °C. Subsequently, the amino functionalized graphene was collected by filtration with a microporous nylon66 membrane and washed with hot DMF repeatedly (Graphene- NH_2). Meanwhile, 1 mmol BPC was dissolved in anhydrous solvent of DMF and DCC, then, 1.5 mmol DCC and 1 mmol DMAP were added to active it for 1 h

in ice bath. In the following, the previously obtained Graphene- NH_2 was added into the mixture and treated with supersonic dispersion for 10 min, the resulting solution was then stirred for 24 h at 40 °C. Finally, the mixture was filtered by the nylon66 membrane and washed with hot DMF to obtain the Graphene-BPC.

The terbium complex functionalized graphene was synthesized as follows: 50 mg Graphene-BPC was then dispersed into the previously obtained $\text{Tb}(\text{TFA})_3(\text{H}_2\text{O})_2$ solution in ethanol and treated with ultrasound for 30 min, after the ligand exchange procedure in 48 h, the terbium complex functionalized graphene was obtained and collected by filtration with nylon66 membrane, which was denoted as Graphene-Tb.

2.4 Preparation of Graphene-Tb doped ionogel composite

Typically, 2 mg Graphene-Tb was evenly dispersed into 0.5 mL [BMI][BTSI] ionic liquid with the help of ultrasonic, followed by an addition of 0.5 mL MMA monomer and 25 mg AIBN. The mixture was kept in the ultrasonic bath and then raised the temperature to 75 °C to initiate the polymerization of MMA monomer until a transparent bulky-gel was obtained, the resulted composite was denoted as Graphene-Tb-Ionogel.

3 Results and discussion

Figure 1. Synthetic route for the ionogel and the photos of it under daylight (right) and 305 nm UV light (left). Step1: DCC, DMAP and HMEDA; Step2: DCC, DMAP and BPC; Step3: $\text{Tb}(\text{TFA})_3(\text{H}_2\text{O})_2$; Step4: MMA, ([BMI][BTSI]) and AIBN.

In this paper, we had introduced the terbium complex into an PMMA confined ionogel system through the supported graphene matrix. The detailed synthetic pathways to obtain the ionogel and the digital photos of it under daylight and UV lamp are shown in the Figure 1. The ionogel reported here is a transparent, flexible, viscous material, and shows strong green in appearance under the 305 nm UV light. Such material has well processability and excellent photoluminescent properties, the embed ionic liquid also ensure the ionogel a certain conductivity. It is a novel optical/electric dual-functional material which belongs to the field of nanoparticle

composited gel materials. The construction procedures of the ionogel had been confirmed by the FTIR spectroscopy (Figure 2). Here, the spectrum A shows a series typical adsorption peaks of graphene oxide. As show in the Figure 2B, the adsorption band around 1595 cm^{-1} and 1545 cm^{-1} are assigned to the -C=O stretching vibrations of the chelate ring of the lanthanide complex moieties and the ring breathing vibration of pyridine moieties, indicating that the surface modification of GO with terbium complex is successful. The spectrum C belongs to the Graphene-Tb-Ionogel, two obvious band at 1729 cm^{-1} and 1576 cm^{-1} are associated with to the -COO- stretching vibration of PMMA and the ring stretching of imidazolium moieties of the embed ionic liquid ([BMI][BTSI]), respectively.

Figure 2. FTIR spectra of GO (A), BPC modified Graphene (B : Graphene-BPC) and the ionogel (C: Graphene-Tb-Ionogel).

Figure 3. The excitation (left) and emission (right) spectra of the Graphene-Tb-Ionogel.

The excitation and emission spectrum of the ionogel were recorded in room temperature on the Hitachi F-4600 spectrophotometer and shown in Figure 3. The excitation spectrum was measured by monitoring the characteristic emission of terbium ion at 547 nm, which has a broad adsorption peak centered at about 308 nm, suggesting that the combination of TFA and the ionogel system can sensitize the transition of terbium ions effectively. Then, the emission spectra of ionogel was obtained by using the most appropriate wavelength (308 nm) as the excitation wavelength based on its excitation spectra. Subsequently,

the corresponding emission spectrum was obtained and found to have four peaks between 450 and 650 nm, which were associated with to the $^5\text{D}_4 \rightarrow ^7\text{F}_6$ (489 nm), $^5\text{D}_4 \rightarrow ^7\text{F}_5$ (547 nm), $^5\text{D}_4 \rightarrow ^7\text{F}_4$ (585 nm) and $^5\text{D}_4 \rightarrow ^7\text{F}_3$ (622 nm) respectively. The most intense peak appearing at 547 nm can be ascribed to the magnetic dipole transition of terbium ions, which results in the bright-green luminescence, and that is why the sample glowing strong green luminescence when it's exposed to the UV lights (see Figure 1). It's clearly that the emission spectrum is a typical ligand-based emission, meanwhile, there is not apparent f-f transition peaks in the excitation spectrum, indicating that efficient intramolecular energy transfer took place between the TFA ligands and the Tb^{3+} ions, and this makes the ionogel an efficient light conversion material. According to the Dexter's [18] theory, the suitability of the energy level between organic ligand and the corresponding lanthanide ions is critical for energy transfer. Thus, according to the above analysis, the ligand TFA used in our system can transfer energy efficiently to the $^5\text{D}_4$ energy level (21000 cm^{-1}) of the Tb^{3+} ions, indicating that the ligand used in our ionogel system and the terbium ions match very well.

Figure 4. Luminescence decay curve for the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition (545 nm) of the Graphene-Tb-Ionogel.

In order to further explore the photoluminescent properties of the terbium functionalized ionogel, its photoluminescent decay curve was measured by detecting the $^5\text{D}_4$ transition of Tb^{3+} on the FLS 920 fluorescence spectrometer. As shown in the Figure 4, the decay curve can be fitted to an exponential formation $\ln(S_t/S_0) = -k_1t = -t/\tau$, indicating that the Tb^{3+} ions within the ionogel has similar coordination environment. The photoluminescent lifetime value of Graphene-Tb-Ionogel was determined to be 0.694 ms. The above experimental results indicate that ionogel matrix could serve as an excellent host for lanthanide complexes when constructing the luminescent lanthanide hybrid materials.

4 Conclusions

In summary, a novel terbium complex modified graphene doped ionogel was prepared and characterized. This was achieved by firstly modified the GO with terbium complex via a three-step procedure: the GO was modified

with HMEDA and BPC subsequently through carboxyl amino coupling reaction with the help of DCC and DMAP, and then introduced the terbium complex onto its surfaces through a ligand exchange procedures. Second, the terbium complex functionalized graphene was doped into a stationary ionic liquid system, which was confined by the PMMA networks. The resulted material is a kind of composite gel of ionic liquid, polymer, terbium complex and graphene, which has been proven to have outstanding photoluminescent properties. In addition, the methods used for modifying graphene and preparing ionogel are very simple and convenient, it can be easily extended to other nanoparticle composited gel system. Furthermore, the ionogel reported here has viscous, flexible and conductive proprieties, which brings it opportunity in the application of optical-electronic device.

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