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Nanocomposite of europium organic framework and quantum dots for highly sensitive chemosensing of trinitrotoluene

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ABSTRACT

Luminescent metal–organic frameworks (MOFs) are considered as next-generation sensor materials for small molecules and explosives. In the present work, a nanocomposite of luminescent europium organic framework (EuOF) and CdSe quantum dots (QDs) has been first time investigated for photoluminescence (PL) based highly sensitive detection of trinitrotoluene (TNT). The nanocomposite EuOF/QD has been synthesized by initiating the growth of EuOF in the presence of QDs. The successful synthesis of the product has been verified with the help of electron microscopy, X-ray diffraction analysis, and surface area measurements. Compared to EuOF alone, the EuOF/QD nanocomposite offers reproducible and stable measurements. The linear range of PL quenching based detection of TNT with EuOF/QD nanocomposite is 5–1000 ppb with the detection limit of 3 ppb. The detection of TNT with EuOF/QD is selective with respect to some other investigated aromatic compounds, such as phenol, *o*-cresol, toluene, benzene, nitrobenzene and nitrophenol.

1. Introduction

Metal–organic frameworks (MOFs) are microporous materials synthesized by the assembly of metal ions and organic ligands in appropriate solvents [1]. MOFs are crystalline structures in nature and generally characterized by large internal surface areas, and uniform but tunable cavities [2]. MOFs are utilized for a number of promising applications which include gas storage, chemical separation, catalysis, drug delivery and sensing [3–5]. Recently, MOFs have found new and interesting applications in the sensing of small molecules, solvents and explosives [6,7]. Detectable changes in luminescence of MOFs by tuning the host–guest chemistry along with their high surface area and tunable porosity make MOFs excellent candidates for sensing applications [8,9]. The pioneering work of Lan et al. [10] sparked research activities toward exploiting the potential of luminescent MOFs in explosives detection and small molecules sensing [11–15]. MOFs are reported to offer fast, highly sensitive, and reversible sensing in these cases.

MOFs are unique host matrices for various functional species and therefore opportunity lies in the development of new types of composite materials with enhanced gas storage capacities or introduction of new (catalytic, optical and electrically conductive) behaviors in comparison to the parent MOF counterparts [16,17]. The incorporation of nanoparticles in MOFs provides synergistic effect by combining chemical and physical properties of the nanoparticles. The preparation of nanoparticle–MOF composites has been reported through the use of MOFs as templates to generate nanoparticles within their cavities, encapsulation of the pre-synthesized nanoparticles and successive adsorption of nanoparticles onto the continuously forming surfaces of the growing MOF crystals [18–20]. An alternative approach of successive (or *in situ*) adsorption of nanoparticles onto the continuously forming surfaces of the growing MOF crystals has been reported with zinc imidazole framework, wherein significant advantages were mentioned [21].

MOFs with metal centers of europium, cadmium, zinc, lithium, iridium have been recently reported for the detection of nitro-aromatic explosives [22–26]. However, some of our tests on the nitro aromatic explosive sensing with MOFs revealed that, at times, it is difficult to obtain reproducible results in different sets of experiments. In the present study, we have incorporated small nanoparticles (CdSe quantum dots) in a europium MOF and studied the formed nanocomposite for the sensing of a representative nitro aromatic compound, trinitrotoluene (TNT). The results obtained were strikingly precise and we were able to reproduce the

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data. Moreover, it was also possible to detect the above analyte in a wide concentration range with detection limit of 3 ppb (~13 nM).

2. Experimental

2.1. Materials

All the chemicals and solvents used during the course of the study were high purity grade materials from Sigma Aldrich/Fisher Scientific/Merck.

2.2. Procedure

For the synthesis of CdSe quantum dots (QDs), 200 mg of $CdCl_2$ was first dissolved in 35 mL deionized water, followed by the addition of 160 μL of thioglycolic acid (TGA). The pH of the solution was adjusted to 11.3 by dropwise addition of 1 mol L^{-1} NaOH solution. A clear solution was obtained, which was subsequently bubbled with argon gas for 20 min (solution A). Separately, a 10 mL solution of NaHSe was prepared by mixing 125 mg $NaBH_4$ and 50 mg Se in water under oxygen-free environment (solution B). The synthesis of QDs was started by heating the solution A (60 °C, under argon environment), followed by a quick addition of 10 mL of solution B under vigorous shaking. The resulting reaction mixture was refluxed at 100 °C for 15 min. CdSe QDs were obtained by ethanolic precipitation, followed by centrifugation and washing steps.

Synthesis of europium MOF (EuOF) was carried out by following an established method with some modifications: 17.2 mg of europium (III) nitrate [$Eu(NO_3)_3{\cdot}5H_2O$] and 17.5 mg of 1,3,5-tris(4-carboxyphenyl) benzene [H_3BTB] were mixed in 30 mL methanol and stirred for 10 min. Triethylamine was dropwise added to the solution till the formation of the product. The reaction mixture was allowed to stand for 2 h at 25 °C, after which the contents were centrifuged to obtain the desired europium organic framework (EuOF) product. The synthesized material was purified by repeated washing, and finally it was dispersed in methanol.

For the synthesis of EuOF/QD nanocomposite, a known volume of the ethanol dispersed CdSe QDs was mixed with the reaction mixture of $Eu(NO_3)_3{\cdot}5H_2O$ and H_3BTB and the above given procedure was followed to obtain EuOF/QD nanocomposite.

2.3. Characterization/equipment

X-ray diffraction (XRD, Shimadzu 6000), field-emission scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (FE-SEM–EDX, Hitachi 4300/SN), confocal laser scanning microscopy (CLSM, Zeiss LSM 510) and transmission electron microscopy (TEM, Hitachi H-7500) were used to confirm the crystal phase, lattice pattern and morphology of the prepared EuOF and EuOF/QD nanocomposite. Nitrogen isotherm analysis was done with Micromeritics ASAP-2020 sorptometer. Thermal stability was tested using a thermogravimetric analyzer (TGA, SDT Q600 thermal gravimeter). Photoluminescence spectra were measured by PL spectrophotometer (Varian). Time resolved decay of PL were measured by Edinburgh Instruments FLSP920 combined steady state fluorescence and phosphorescence lifetime spectrometer.

2.4. Sensing of trinitrotoluene (TNT)

Stock solution of TNT was prepared in ethanol. Known diluted volumes of the stock solutions were prepared and mixed with the homogenous ethanolic suspension of EuOF or EuOF/QD (5 mg/mL). The contents were thoroughly mixed and then incubated at 25 °C for 5 min. The PL intensity of the reaction mixture was measured and correlated with TNT concentration.

All the above experiments were done in triplicate and the average data value have been reported. Necessary corrections of dilution factors were incorporated while reporting normalized data. The detection limit was determined from the equation: Detection limit = $(K \times \text{s.d.})/S$. The value of K was taken as 3.3, s.d. was the standard deviation in the blank sample, and S was the slope of the calibration curve.

3. Results and discussion

3.1. Synthesis of Eu-MOF, QDs and EuOF/QD composite

The synthesized EuOF with Eu(III) as metal center and 1,3,5-tris(4-carboxyphenyl) benzene [H_3BTB] as organic linker, and the EuOF/QD nanocomposite were characterized with different instrumental techniques. Powder X-ray diffraction (XRD) pattern of the EuOF sample (Fig. 1a) was identical to the earlier reported data [27,28]. XRD pattern of the EuOF/QD nanocomposite (Fig. 1b) exhibits three additional peaks, which correspond to (1 1 1), (2 2 0), and (3 1 1) diffractions of cubic zinc-blend structure. However, these additional peaks are not very strong because of small fraction of QDs in the nanocomposite. The above observation suggests the inclusion of CdSe QDs in the EuOF structure. Nitrogen adsorption isotherms of the EuOF and EuOF/QD samples have been investigated at liquid nitrogen temperature. Samples were degassed at 120 °C for 18 h (at

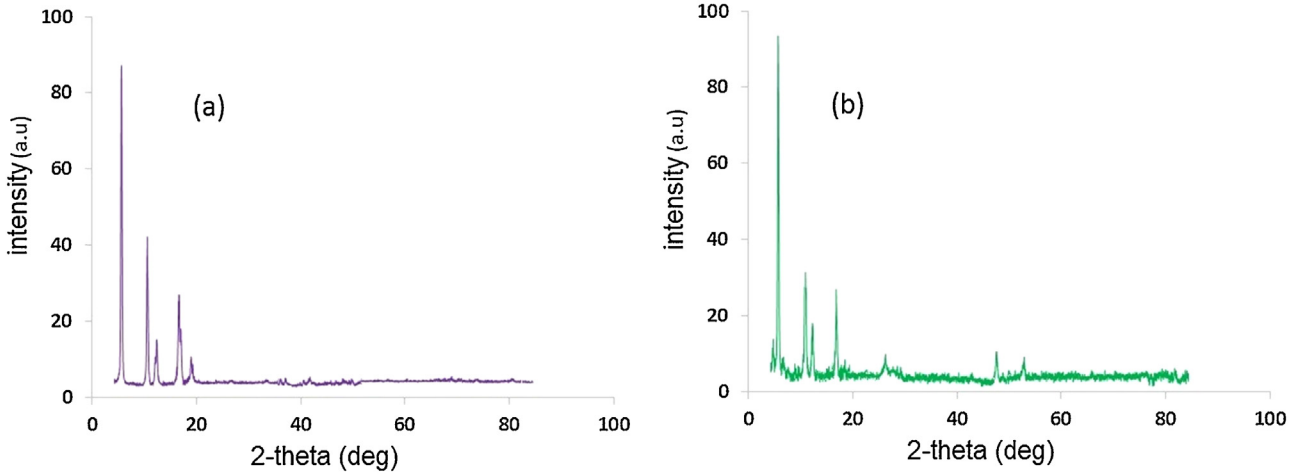

Fig. 1. (a) XRD spectra of EuOF, (b) XRD spectra of EuOF/QD.