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Development of highly selective novel fluorescence quenching probe based on Bi_2S_3-TiO_2 nanoparticles for sensing the Fe(III)

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ABSTRACT

In the present paper, hetrostructured Bi_2S_3-TiO_2 (BST) nanoparticle (NPs) was synthesized by modified hydrothermal technique using titanium butoxide as precursor of TiO_2 and $Bi(NO_3)_3$ and thiosemicarbazide as precursors of Bi_2S_3. The synthesized BST NPs was characterized by using XRD, TEM and FTIR spectra. BST NPs form stable dispersion and displays high fluorescence emission at 818 nm. The synthesized nanoparticles show excellent fluorescent property and highly selective for Fe (III) ions due to binding affinity of the BST NPs with Fe (III) ion as evident from the higher value of Stern-Volmer constant ($K_{sv} = 7859\ M^{-1}$). The number of binding sites of BST NPs was evaluated from the double logarithm regression method and was found to be 0.948. The intensity of the fluorescence emission drop linearly in concentration range from 15 μM to 5000 μM and linear plot of the Stern-Volmer confirmed the static quenching of BST. The optimum pH obtained was 3.35. The detection limit of the synthesis BST sensor was 0.1173 μM.

1. Introduction

Many transition metal ions (like Fe, Mn, Co, Ni, Cu, Zn, Mo etc.) are essential for living organisms. Among these metals, iron is most essential trace heavy element vital for many physiological processes and plays dominant role. The versatility of iron extends from its role as structural component of life molecule, haemoglobin to iron storage proteins, myoglobin, cytochromes as electron carrier and also part of enzyme catalysis for many metabolic reactions. The extensive repertoire of iron involvement in biological processes include oxygen transportation, transcriptional regulation, oxygen metabolism and electron transfer [1,2]. It also helps to prevent diseases such as Pancreas, heart, Alzhemier, Penkinson and liver [3–5]. The low solubility of hydrated Fe(III) (approximately 10^{-18} M) at physiological conditions emphasizes the difficulty of acquiring sufficient iron. On the other hand, excess of Fe (III) intake leads to adverse effects such as tissue damage due to the formation of free radicals. Therefore, iron concentrations in living organisms must be tightly regulated to control the disorders of iron metabolism leading to broad spectrum of diseases from anaemia to iron overload. Furthermore, the enormous variation in concentration of iron in different sources of water was observed and in particular the concentration of free ferric ion is extraordinarily low at neutral pH whatever may be the source of water. The maximum permitted limit of Fe (III) in drinking water is 5 μmol L^{-1} [6]. Therefore, the monitoring of iron levels has been an active issue in environmental analysis. But the lower concentration of Fe (III) ion limits its sensitivity and selectivity for practical analysis. Different methods have been adopted for the sensing of Fe (III) ions such as colorimetric analysis [7], mass spectroscopy [8], electrochemical [9,10], amperometeric [11,12] and florescence spectroscopy analysis [13–19]. Many research findings were devoted to the sensing of metal ions and other pollutants [27,28,44–53]. Megan et al. [20] differentiated Fe (II) and Fe (III) ion using fluorescence conjugated polymers as chemosensors. Raji et al. [21] synthesized nitrogen doped carbon dots for the detection of Fe (III) ion in water. Hani et al. [22] reported the fluorimetric sensing of the ferric ion by water soluble lanthanide metal organic framework. Jingshuai et al. [23] detected Fe (III) ion by the combination of fluorescent Fe_3O_4 –ZnO with L-cysteine. Natalia et al. [24] designed a coumarin- based turn-off fluorescent probe selective for ferrous ion. Jia et al. [25] synthesized photoluminescent nitrogen doped phenol formaldehyde resin polymer for detection of Fe (III) ion. Sharma et al. [26] synthesized CdS nanosheets for sensing of picric acid. Wang et al. [54] achieved the high selectivity and sensitivity for sensing Fe(III) using fluorescent organic nanoparticles. Yang et al. [55] slectively sense the Fe(III) ion by using fluorescence organic material.

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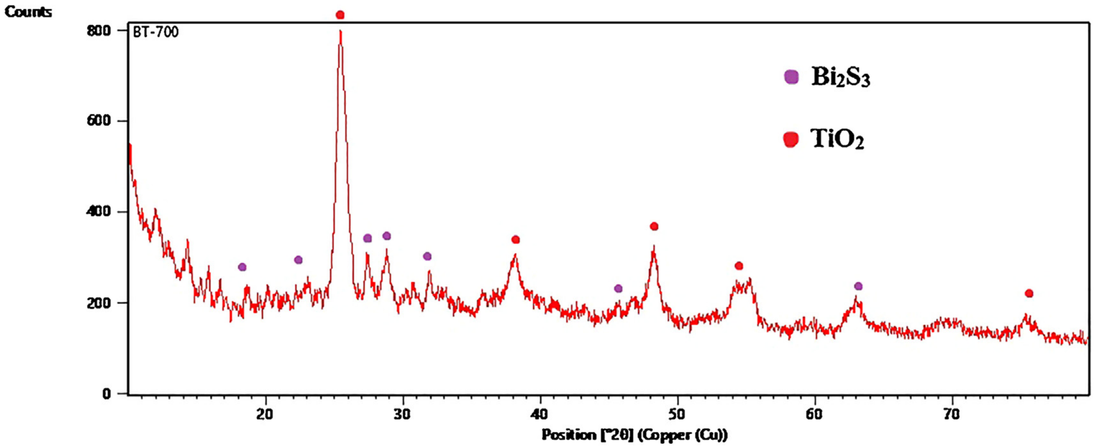

Fig. 1. XRD spectra of Bi_2S_3-TiO_2 nanoparticle.

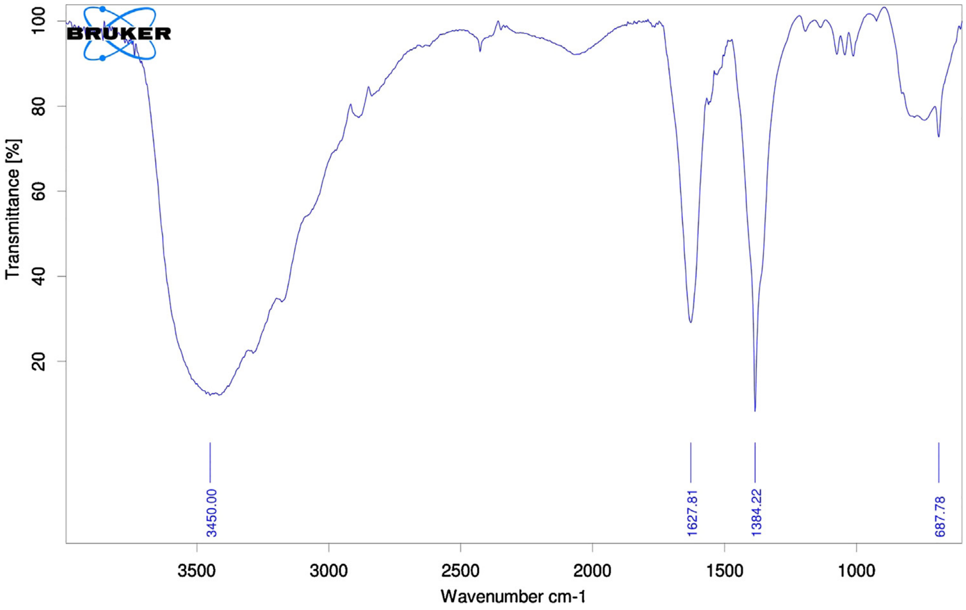

Fig. 2. FTIR Spectra of Bi_2S_3-TiO_2 nanoparticle.

The finding of these literature studies confirmed that fluorimetric spectroscopic technique is a favorite method due to its potential to offers higher sensitivity and selectivity. But complicated synthetic route needed for fluorescence organic dyes, their poor photo stability and toxicity of quantum dots in biological system are the major issue of concern. Keeping in mind these, the presentatier study reports the simple ultrasonicated assisted hydrothermal synthesis route of metal oxide showing highly sensitivity and selectivity. Further, to the best of our knowledge, most of the reported studies of sensing Fe (III) ion are restricted to dyes or biomolecules based fluorescence, quantum dots, chelate based sensor, etc. Sensing of Fe (III) by heterostructured Bi_2S_3 $-TiO_2$ nanoparticles has not been reported yet. The sensitivity and selectivity of ferric ion are examined by varying the concentration of ferric ion and in the presence of other metal ions respectively.

2. Experimental

2.1. Chemical

Titanium Butoxide, Bismuth Nitrate, Thiosemicarbazide, $CdCl_2$, $CuCl_2$, $SnCl_2$, $PdCl_2$, NH_4Cl, KCl, NaCl, $FeCl_3$, $HgCl_2$, $ZnCl_2$, $AlCl_3$, $NiCl_2$, HCl, $MnCl_2$ and $FeCl_2$ were purchased from Sigma Aldrich. Ethanol and Isopropanol were used by the analytical grade.

2.2. Synthetic procedure

2.2.1. Step 1: synthesis of TiO_2

TiO_2 was synthesized as per reported in our previous paper [38]. Titanium (IV) *n*-butoxide was magnetic stirred in 20 ml of ethanol for two hours. After the addition of NH_4OH, the jelly white precipitate was formed. Which were further stirred for two hours. The obtained precipitates were filtered by vacuum filtration, crystallized and dried in oven at 100 °C for two hours to get yellow color product.

2.2.2. Step 2: synthesis of Bi_2S_3

Bismuth nitrate and thiosemicarbazide (mole ratio 1:3) were mixed with isopropyl alcohol: ethanol (1:1) solvent mixture and then was ultrasonicated for 40 min. The obtained dark brown precipitate of Bi_2S_3 was washed many times with ethanol: water (1:1) to remove impurities. The precipitate was dried for 2 h at 80 °C.