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Research Paper

Facile fabrication of $\text{Ag}_2(\text{bdc})@\text{Ag}$ nano-composites with strong green emission and their response to sulfide anion in aqueous medium

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ABSTRACT

A novel composite constructed from MOF(s) and Ag nanoclusters, $\text{Ag}_2(\text{bdc})@\text{Ag}$ (H_2bdc is 1, 4-benzenedicarboxylate) has been simply fabricated through a solution strategy for the first time, and characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS). The as-prepared composite was found to be an effective material for the selective fluorescence detection of microgram levels of S^{2-} in aqueous solution based on fluorescence quenching effects. Under optimized experimental conditions, the probe exhibited a stable response for S^{2-} over a concentration range from 0.2 μM to 30 μM and a detection limit of 0.21 μM . The feasibility of the proposed method was further demonstrated through the detection of S^{2-} in real samples, with satisfactory recoveries in the range of 97.8–101.9%. The possible sensing quenching mechanism for the detection of S^{2-} could be attributed to the formation of Ag_2S during the addition of S^{2-} into the $\text{Ag}_2(\text{bdc})@\text{Ag}$ dispersion system. The proposed method for the detection of S^{2-} has potential application in the environmental pollutant analysis.

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1. Introduction

With the continuous development of society and economy, the degree of industrialization becomes increasingly higher and so do the requirements on environmental monitoring and management. In this way, the refuse with sulfur compounds has become one of the main pollutants, especially in fields like papermaking, petroleum cracking, printing & dyeing, process hides, electroplate and coking. The maximum allowable concentration of sulfide in wastewater stipulated in National Standard GB8978-88 is 1.0 mg/L. The sulfide in waterbody has a stronger chemical action on numerous metal ions necessary for living organisms and a stronger corrosion on plant roots and stems. For this reason, only 0.07 $\mu\text{g}/\text{L}$ of sulfide concentration in drinking water may also have an effect on the water taste. Hence, measuring sulfide contents in the pollutants under the environmental monitoring may act as a vital index.

At present, the commonly adopted methods for the sulfide measurement include capillary electrophoresis [1], fiber optical sensor [2], and gas chromatography [3], etc. All these analytical methods request for the complex instruments, highly demanded operation techniques or multifarious analytical procedures. Therefore,

developing a simple and practicable sulfide analytical method with low determination cost and good selectivity may have an important application merit. Due to its high selectivity and sensitivity, fluorescence analysis has become an all-important and effective spectrochemistry analysis method [4–7].

Metal-organic frameworks (MOFs) have recently emerged as promising materials for gas storage/separation, chemical sensing, catalysis, biomedicine, magnetism, clean energy technology and optoelectronics [8–12]. Especially, as fluorescence-based chemical sensors, MOFs offer great promise by virtue of their crystalline nature, permanent porosity, designable/modifiable pores, systematically tunable band gaps and electronic structures [13–15]. To the best of our knowledge, the detection with high selectivity and sensitivity for sulfide anion in solution over MOFs-based fluorescence probe has been seldom reported at present. On the other hand, as a kind of novel fluorescent nano-material, the metallic nanocluster has aroused more and more attention in the application of fluorescent sensor due to its small size, stability, higher quantum yield and low toxicity [16–18]. In order to explore nano-composites constructed from MOFs and metallic nanocluster in the application of fluorescent probe, a novel composite forming MOF(Ag) and Ag nanoclusters, that is $\text{Ag}_2(\text{bdc})@\text{Ag}$, was fabricated for the first time through a simple solution method and then established a recognition and detection for S^{2-} by the novel fluorescent sensor based on its strong fluorescence signal and obvious quenching effect on

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S^{2-} in solution. Under the optimum experimental condition, S^{2-} within 0.2–30 μM has a good linear response to the fluorescence quenching efficiency with a detection limit of 0.21 μM . The proposed method for the detection of S^{2-} has potential application in the environmental pollutant analysis.

2. Experimental section

2.1. Reagents and chemicals

1,4-benzenedicarboxylate (H_2bdc , $\text{C}_6\text{H}_4(\text{COOH})_2$), silver nitrate ($\text{Ag}(\text{NO}_3)$) were purchased from Sigma-Aldrich Co. LLC (USA). Double deionized water was obtained with a Pall Cascada laboratory water system. All other chemicals were of at least analytical grade and used without any purification.

2.2. One-pot preparation of $\text{Ag}_2(\text{bdc})@\text{Ag}$ composites (1)

An aqueous solution of H_2bdc was prepared by dissolving 0.16 g of TPA in 10 mL 1:1 DMF-water mixture, and metal ion solutions with 0.16 g (1 mmol) of AgNO_3 was prepared in 10 mL double deionized water. The prepared metal ion solution was transferred dropwise into the TPA solution in a beaker under constant stirring for 10 min. Black brown colored precipitate was observed upon complexing of TPA with Ag^+ ion and mixing continued for 20 min under 85 °C, the resulting product was filtered and washed with ethanol and water several times. The product was dried finally at 353 K overnight.

2.3. Detection methods

Na_2S was used as the S^{2-} source during the sensitivity studies. A S^{2-} stock solution (0.1 M) was prepared, and various concentrations were obtained by serial dilution of the stock solution. 0.1 g/L $\text{Ag}_2(\text{bdc})@\text{Ag}$ fluorescent sensor solution, phosphate buffer saline (PBS) solution with pH = 6.86, and 1×10^{-2} M stock solutions for other anions (I^- , F^- , CO_3^{2-} , N_3^- , SO_4^{2-} , Br^- , Cl^- , SO_3^{2-} , Ac^- , PO_4^{3-} , $\text{C}_2\text{O}_4^{2-}$, all anionic solutions were prepared by the relevant sodium salt or potassium) were prepared, respectively. To detect the S^{2-} , 5 mL of different concentrations S^{2-} were added to 8 mL of the obtained $\text{Ag}_2(\text{bdc})@\text{Ag}$ fluorescent probe solution and diluted to 50 L with PBS buffer solution, and then the mixtures were incubated at 28 °C for 80 min before measuring the fluorescence spectra. The fluorescence intensity (I) of the mixed system and fluorescence intensity (I_0) of the blank solution at the maximum emission wavelength were measured, respectively.

2.4. Characterization of $\text{Ag}_2(\text{bdc})@\text{Ag}$ composites

The X-ray diffraction (XRD) pattern of the sample was recorded using a Bruker D8 diffractometer in $\text{Cu K}\alpha$ -ray target ($\lambda = 0.1542$ nm) at a target voltage of 40 kV, target current 40 mA, scanning range of 2θ of 5°–80°, and scan rate of 6° min^{-1} . Scanning electron microscopy (SEM) images were obtained using a scanning electron microscope (S-4800) at an accelerating voltage of 5 kV. TEM images were obtained on a transmission electron microscope (Tecnai G2 F20, FEI company) equipped with an energy dispersive X-ray spectrometer (EDAX). XPS experiments were carried out in an ultrahigh vacuum using the ESCALAB Mark II X-ray photoelectron spectroscopy (XPS, VG Scientific, UK) with $\text{Mg K}\alpha$ radiation (1253.6 eV) from the Mg anode source. The high-resolution scans of core level spectra were recorded with an energy step of 0.05 eV and set to 15 eV pass energy. The binding energy was referenced to at 284.6 eV to the C1s peak. Experimental data were deconvolved by Gaussian-Lorentzian mixture peak-fitting software.

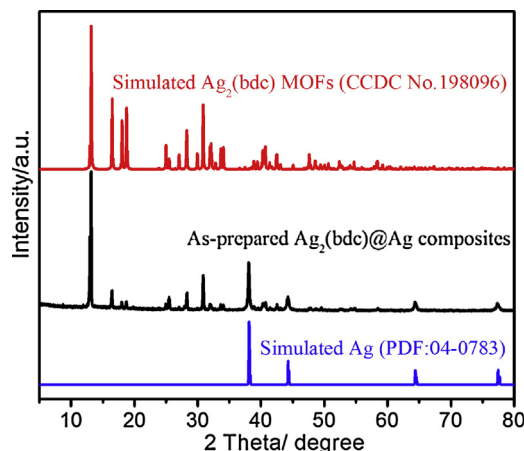


Fig. 1. XRD spectra of as-prepared $\text{Ag}_2(\text{bdc})@\text{Ag}$ composites, and simulated $\text{Ag}_2(\text{bdc})$ MOFs and Ag.

3. Results and discussion

Fig. 1 shows the XRD patterns of as-prepared $\text{Ag}_2(\text{bdc})@\text{Ag}$ composites, simulated $\text{Ag}_2(\text{bdc})$ complex and Ag. From the as-prepared $\text{Ag}_2(\text{bdc})@\text{Ag}$ composites, the peaks at 10.6, 13.2, 16.5, 18.1, 23.9, 25, 30.9, 32.6, 33.8, 34.1, and 40.8° are assigned to diffractions of the complex $\text{Ag}_2(\text{bdc})$ (CCDC No. 198096) [19]. The four additional peaks at 38.2, 44.5, 64.5 and 77.7° can be indexed respectively to (111), (200), (222) and (014) planes of face-centered-cubic metal Ag (JCPDS card no. 04-0783). Those results indicated that the composites contain two material compositions, compound $\text{Ag}_2(\text{bdc})$ and metal Ag.

The morphology and microstructure of the as-prepared $\text{Ag}_2(\text{bdc})@\text{Ag}$ powders were examined by SEM and TEM, as shown in Fig. 2. The SEM image (Fig. 2a) reveals that the morphology of $\text{Ag}_2(\text{bdc})@\text{Ag}$ consists of irregular blocks with some spherical particles covered on surface. The high resolution TEM of product clearly indicates that these blocks were made up of 4–5 nm Ag nano-cluster and 50 nm spherical MOFs(Ag) nanoparticles covered on the surface were reunited by some $\text{Ag}_2(\text{bdc})@\text{Ag}$ composites.

In order to determine the chemical composition of $\text{Ag}_2(\text{bdc})@\text{Ag}$ composites and further identify the chemical state of the Ag element in the sample, XPS characterization was performed as shown in Fig. 3. In the XPS experiment, the samples are exposed to monochromic X-radiation, and the properties of inner-shell electrons are to be probed. According to the XPS survey spectrum of $\text{Ag}_2(\text{bdc})@\text{Ag}$ sample (Fig. 3(a)), three kinds of elements, that is Ag, O, and C were detected in the sample, in which the peaks at 573, 604, 1130 eV can be attributed to characteristic peak of $\text{Ag } 3p_{3/2}$, $\text{Ag } 3p_{1/2}$, Ag(A), respectively.

Fig. 3(b) displays the Ag 3d level spectrum. The $\text{Ag } 3d_{3/2}$ and $\text{Ag } 3d_{5/2}$ spin-orbital photoelectrons were located at binding energies of 368.3 eV and 374.4 eV, respectively. According to the previous report [20,21], the peaks at 368.3 and 374.4 eV were attributed to metallic silver, and these two peaks with a spin energy separation of 6.1 eV further indicated that the Ag^0 existed in the $\text{Ag}_2(\text{bdc})@\text{Ag}$ composite. The C1s emission spectrum can be divided into three main peaks, as shown in Fig. 3(c). The binding energy in 284.8 eV was obtained in the XPS analysis is standardized for specimen charging using C 1s as the reference. The peak in 289.4 eV was attributed from the carboxylate carbon in $\text{O}=\text{C}-\text{OH}$, while the peaks in 288.3 eV are associated with the aryl carbon from benzene ring. By using a Gaussian fitting method, the O 1s emission spectrum (Fig. 3(d)) can be divided into three main peaks. The component at 531.5 eV is typical of metal-oxygen (Ag–O) bonds, and 532.3 eV perhaps comes from $\text{O}=\text{C}-\text{O}$ bonds in the organic ligand, while the

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