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A novel fluorescence enhancement probe based on L-Cystine modified copper nanoclusters for the detection of 2,4,6-trinitrotoluene

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ABSTRACT

The rapid development of fluorescent nanomaterials has broadened a new horizon for the design of easy-to-use and sensitive sensors. Herein, the stable, water-soluble and fluorescent L-Cystine modified copper nanoclusters (CuNCs) were prepared via size-focusing etching method. The maximum emission wavelength of the obtained CuNCs was 500 nm with an excitation wavelength of 396 nm. The as-prepared CuNCs can only emit faint light when dispersed in aqueous solution, but generate obvious fluorescence intensity enhancement after adding specific amount of 2,4,6-trinitrotoluene (TNT). Under the optimal conditions, the CuNCs were adopted as an effective fluorescence probe for the detection of trace TNT through fluorescence “turn-on” mode for the first time. The calibration curve of TNT was linear up to 4.8 μM, with a detection limit of 9.1 nM.

1. Introduction

2,4,6-trinitrotoluene (TNT) has been widely available in the military and mining industry. However, its residues left in the environment may induce various health problems in human and animals [1]. Fluorescence-based detection has been proved to be a sensitive and cost-effective method for the detection of TNT [2–4]. However, almost all of those designs focused on fluorescence quenching mechanism based on resonance energy transfer, which were unable to effectively overcome the error resulted from light bleaching.

Metal nanoclusters (NCs) have become important candidates for the application in chemical sensors, catalysis and biological imaging due to their excellent photostability and biocompatibility [5–7]. Owing to their lower toxicity compared with organic fluorophores and semiconductor quantum dots, gold and silver nanoclusters have been widely investigated in those fields. In contrast with the noble metals, gold and silver, copper is low-cost, relatively abundant, and readily available from commercial sources. In the past few years, series of fluorescent copper NCs (CuNCs) have been successfully synthesized and applied to many fields [8–11]. However, to the best of our knowledge, CuNCs have never been used for the detection of TNT.

In this work, the L-Cystine (L-Cys) modified CuNCs were synthesized via a size-focusing etching process and exhibited aggregation-induced emission enhancement effect through the induction of trace amount of TNT. Donor-acceptor interaction occurred between TNT and the amino groups in L-Cys [12], which subsequently resulted in the aggregation of CuNCs and the observable enhancement in the fluorescence intensity. Herein, the CuNCs were firstly used for the “turn-on” detection of trace TNT with highly sensitivity and selectivity, which is supposed to broaden the scope of the applications of CuNCs and provide a valuable reference in the detection of nitro explosives.

2. Experimental section

2.1. Chemicals

L-Cystine (L-Cys) was purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Ascorbic acid (AA) was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Cupric nitrate trihydrate was purchased from Chengdu Kelong Chemical Co., Ltd (Chengdu China). TNT (AR), 2,4-dinitrotoluene (DNT) (99% purity), and p-nitrotoluene (NT) were obtained from Aladdin Chemistry Co., Ltd. (Shanghai, China). 2,4,6-trinitrophenol (TNP) was purchased from J&K Scientific Co., Ltd. (Beijing, China). The deionized water used throughout the work was obtained from a Milli-Q water purification system (Millipore, Bedford MA).

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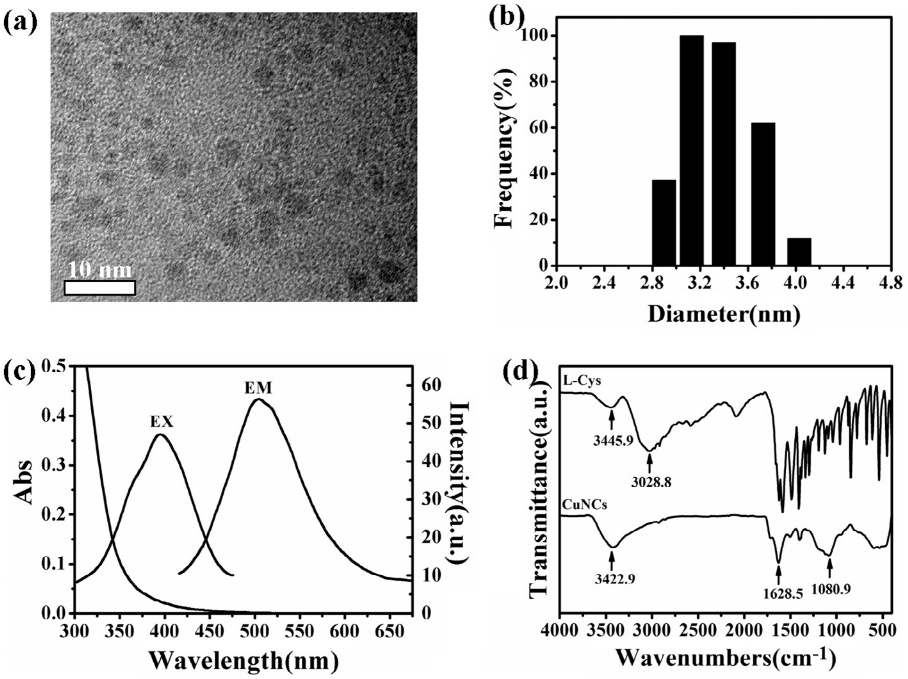

Fig. 1. HRTEM image (a), size distribution (b) of CuNCs, UV-vis, excitation (EX) and emission (EM) spectrum of L-Cys modified CuNCs (c), FTIR spectra of pure L-Cys and L-Cys modified CuNCs (d).

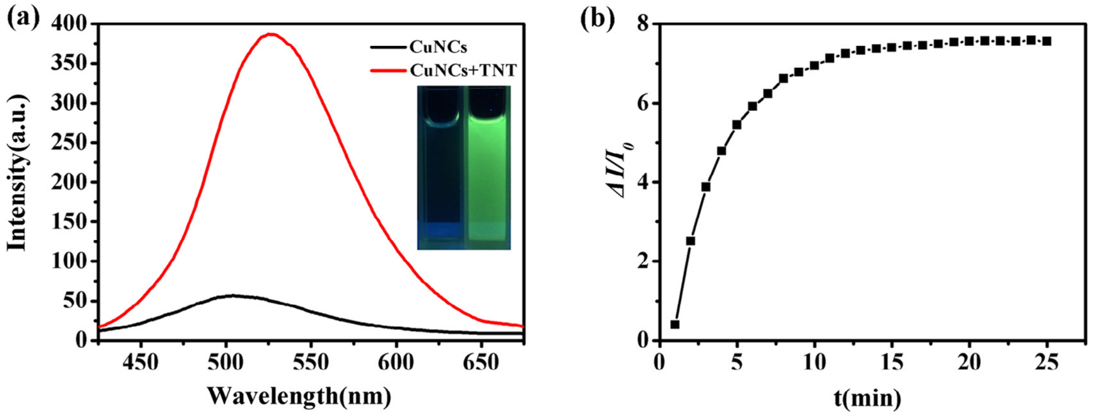

Fig. 2. Fluorescence spectra of CuNCs and CuNCs with TNT added (a). Influence of incubation time on the fluorescence change of CuNCs with TNT added (b).

2.2. Preparation of CuNCs

CuNCs were prepared according to the literature with some modifications [11]. Briefly, AA (0.1763 g) was dissolved in water (10 mL) to form a clear solution. Then the Cu(NO$_3$)$_2$ aqueous solution (0.1 M, 0.5 mL) was added into the AA solution under vigorous stirring. The reaction mixture was stirred for 1 h at room temperature, and get Cu nanocrystals. The as-prepared Cu nanocrystals solution (1.2 mL) was added to an L-Cys aqueous solution (0.1 M, 6 mL) containing 0.15 M of NaOH and kept for 5 h at room temperature under stirring. The prepared CuNCs were used for the detection of TNT after 7 days passivation.

2.3. Characterization of CuNCs

The UV–Vis absorption spectra and fluorescence spectra were recorded at room temperature on a UV 2800SPC spectrophotometer (Shanghai Hengping Scientific Instrument Co., Ltd., Shanghai, China) and an F97Pro fluorospectrophotometer (Shanghai Lengguang Technology Co., Ltd., Shanghai, China), respectively. The particle size distribution was measured on a BI-200SM dynamic laser light scattering (DLS) instrument (Brookhaven, USA). The Fourier transform infrared (FTIR) spectra were recorded on a Nicolet NEXUS 670 spectrometer. The morphology of CuNCs were characterized by a high-resolution transmission electron microscopy (HRTEM) on a Philips EM-420 with a 300 kV accelerating voltage.

2.4. Determination of TNT using CuNCs

Before use, the as-prepared CuNCs solution was diluted to 0.1 mM and adjusted to a pH value of 12.5. After that, 400 μL of the TNT solution was added into 3.6 mL of the CuNCs solution. The mixture was incubated at room temperature for 15 min and the fluorescence emission was detected at 500 nm with excitation of 396 nm.