



Selective determination of Ag^+ using Salecan derived nitrogen doped carbon dots as a fluorescent probe



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ABSTRACT

We report that nitrogen doped carbon dots (N-CDs) represent a viable fluorescent probe for the determination of Ag^+ . The N-CDs can be fairly easily prepared by a hydrothermal treatment method using Salecan and dicyandiamide as the precursors, display excitation/emission maxima of 350/438 nm. The N-CDs have an average diameter of about 3.8 nm. The N-CDs exhibited blue fluorescence (quantum yield of 13.2%) and could response to Ag^+ selectively and sensitively. Other ions nearly had no interference. The probe has excellent selectivity, high sensitivity, and a linear response range that extends from 0 to 40 μM . The limit of detection is as low as 1.12×10^{-7} mol/L. The method was applied to the determination of Ag^+ dissolved in water.

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1. Introduction

In recent several years, as a late-model of fluorescent materials, quantum dots have aroused scientific attention [1–7]. CDs show distinguished features such as simple synthesis, low cost, low toxicity and good biocompatibility [8–11]. These particular characters endow CDs enormous potential applications, such as biomedicine, drug release and ions sensing [12–26]. Silver (Ag^+) is an essential precious metal. Over the past decade, it has been wide used in the photographic and imaging industry [27,28]. Nevertheless, Ag^+ as a heavy-metal ion could bring against effects to environment. Recently, selective determination of Ag^+ signaling used CDs has been attracting extensive research interest.

Normally, important efforts have been exerted on the synthesis of CDs from a variety of carbon precursors by various methods, such as hydrothermal method, microwave method, thermal method, and so on [29–39]. In the midst of them, hydrothermal method is considered to be a simple and efficient way to obtain CDs.

Several years ago, our group study found that Salecan is a new water soluble extracellular β -glucan (Cas.No.1439905-58-4) produced by fermentation from *Agrobacterium* sp. ZX09 [40]. This ZX09 was isolated from soil collected from the ocean coast of Shandong (China) by our group, and its 16S rDNA sequence was deposited in the GenBank database (accession number GU810841). Salecan consists of a linear backbone of β -D-glucan (GlcP) units linked by α -1,3 and β -1,3 glycosidic bonds [41–43]. In this article, we have reported a simple, but more effective strategy for the fabrication of blue-emitting N-CDs using Salecan

and dicyandiamide as the precursors through a simple hydrothermal process (Fig. 1). The obtained N-CDs exhibited well sensitivity of fluorescence quenching for Ag^+ . With the gradual addition of Ag^+ , the fluorescence color of the solution changed from blue to colorless which offers the possibility for us to detect the Ag^+ , other metal ions such as Fe^{3+} , Pb^{2+} , Cd^{2+} , Cr^{3+} , Mg^{2+} , Cu^{2+} , Zn^{2+} , Ca^{2+} , Na^+ , K^+ , Hg^{2+} , Ni^{2+} and Co^{3+} could not cause any interference. The detection limit for Ag^+ could achieve as low as 1.12×10^{-7} mol/L, which made this material a suitable candidate for environmental Ag^+ detection.

2. Materials and methods

2.1. Reagents and materials

Salecan was fabricated by Center for Molecular Metabolism, Nanjing University of Science & Technology. Dicyandiamide, AgNO_3 , $\text{CoCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, CdCl_2 , $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ZnCl_2 , CaCl_2 , NaCl , KCl , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, HgCl_2 and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were purchased from Energy Chemical (Shanghai, China). All reagents were of analytical grade and were used as received without further purification.

2.2. Synthesis of the N-CDs

First, 0.5 g of Salecan and 0.5 g of dicyandiamide were dissolved in 30 mL of water, and the solution was then transferred into a Teflon autoclave. After heating at 170 °C for 8 h, the autoclave was cooled down to room temperature naturally. After that, the solution was centrifugation at 4500 rpm and 12,000 rpm for 15 min and collected by filtration (0.2 μm cellulose membrane) respectively. The obtained N-CDs solution

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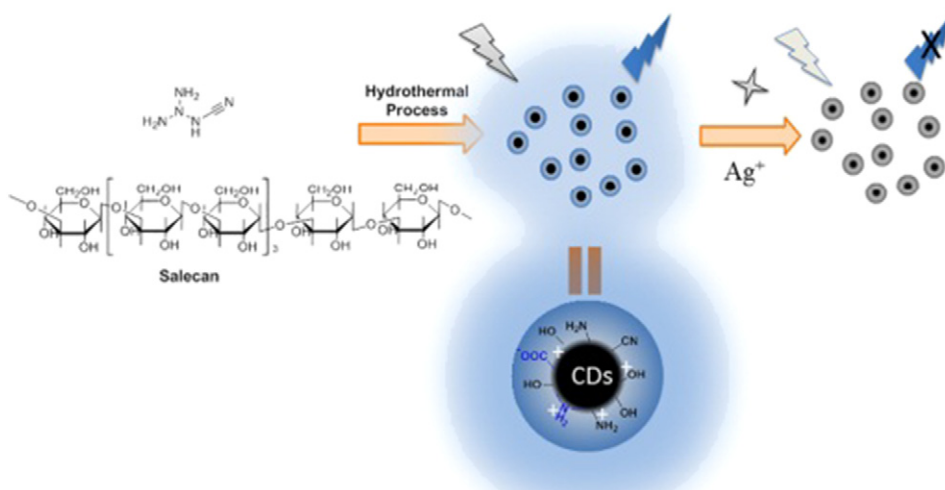


Fig. 1. Scheme of the Synthetic Strategy for N-CDs and the Principle of Ag^+ Sensing.

was subsequently dialyzed for 2 days to remove all kinds of inorganic ions.

2.3. Detection of Ag^+ using N-CDs

The detection of Fe^{3+} was conducted in Tris-HCl (10 mM, pH = 7.4) buffer solution at room temperature. In a typical assay, 50 $\mu\text{g}/\text{mL}$ of N-CDs dispersion was added into PBS, followed by the addition of Ag^+ standard with various concentrations. The selectivity of Ag^+ sensing was confirmed by adding other common metal ions stock solutions (Ag^+ , Fe^{3+} , Pb^{2+} , Cd^{2+} , Cr^{3+} , Mg^{2+} , Cu^{2+} , Zn^{2+} , Ca^{2+} , Na^+ , K^+ , Hg^{2+} , Ni^{2+} and Co^{3+}) instead of Ag^+ and determining in the same way.

3. Results and discussion

The N-CDs were synthesized by hydrothermal treatment of the compound of Salican and dicyandiamide. HRTEM characterizations were carried out to authentication our successfully obtaining N-CDs. HRTEM image of N-CDs shows well-dispersed in water solution. The particle size histogram shows the sizes to be around 2.5–5.5 nm with an average size of 3.8 nm and possess almost globosity. The inset in Fig. 2a showed the lattice spacing of 0.20 nm. The typical XRD patterns of the N-CDs (Fig. 2b) display only one broader diffraction peak centered at $2\theta = 25.1^\circ$, which is also assigned to highly disordered carbon structure.

The chemical structure of N-CDs was further characterized by XPS. The XPS survey spectrum showed that C 1 s, N 1 s and O 1 s signals

appeared at 284.3, 399.2 and 531.0 eV, respectively (Fig. 3a). Moreover, quantitative analysis of the N-CDs elements showed the following elemental composition: carbon (53.2%), nitrogen (10.6%) and oxygen (36.2%). The C 1 s spectrum can be resolved as follows: C—H at 283.34 eV, C—C/C—N at 284.94 eV, C—O at 286.33 eV and O—C=O at 287.60 eV. The two fitted peaks at 529.82 and 531.26 eV in O 1 s spectrum were assigned to C—OH and C=O groups, respectively. The N 1 s peaks at 399.31 and 401.26 eV indicated that nitrogen existed mostly in the form of N—H and C—N/N—N, respectively. Simultaneously, the FTIR spectrum of N-CDs demonstrates the presence of the same groups as indicated by the XPS results. The peak at 1007 cm^{-1} was ascribed to the C—O bonds. The peak at 1417 cm^{-1} can be ascribed to the C=C group while the peak at 1663 cm^{-1} was ascribed to the C=O stretching vibration. In addition, the broad band at 3277 cm^{-1} corresponded to the stretching modes of N—H and O—H. All results of XPS and FTIR spectra clearly substantiated that N atoms had perfectly doped in N-CDs.

In the fluorescence spectrum, the optimal excitation and emission wavelength are at 350 and 438 nm. Excitation-dependent Fluorescence intensity behavior is observed, which is common in fluorescent carbon materials. The emission wavelength shifts from 430 to 510 nm when the excitation wavelength increases from 280 to 460 nm. The fluorescence intensity strengthened when the excitation wavelength increases from 280 to 350 nm. The fluorescence intensity receded when the excitation wavelength increases from 360 to 460 nm. (Fig. 4b). The QY of N-CDs is determined to be 13.2% by selecting the quinine sulfate as standard. The stability of both N-CDs under various conditions has also

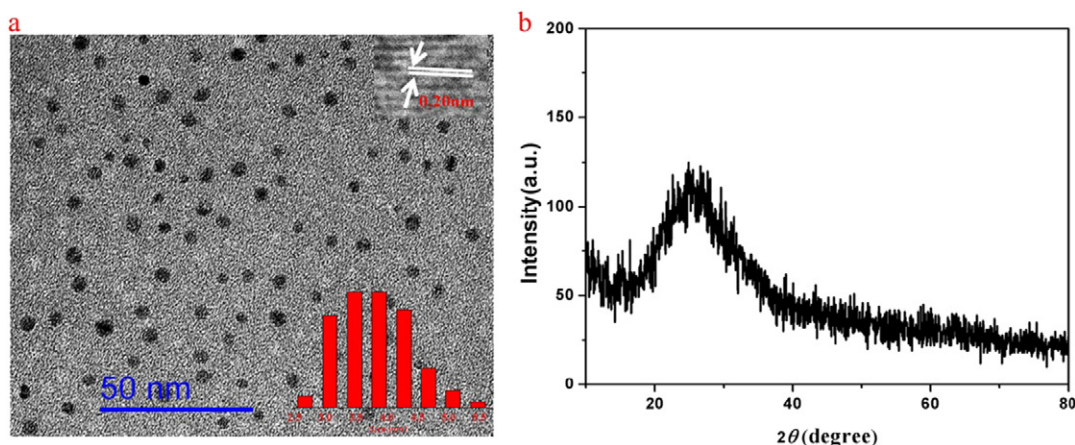


Fig. 2. (a) HR-TEM image and diameter distribution, (b) XRD spectrum of N-CDs.

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