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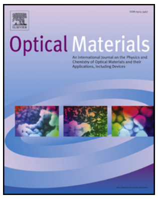

Albumin capped carbon-gold (C-Au) nanocomposite as an optical sensor for the detection of Arsenic(III)

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ABSTRACT

A sensitive arsenic (III) (As(III)) detection method based on the fluorescence quenching system using bovine serum albumin (BSA) capped carbon-gold composite (C-Au-BSA) was developed. BSA could attach to the surface of C-Au composite and increase the photoluminescence (PL) efficiency, As(III) could combine with BSA and remove it from C-Au composite to decrease the PL efficiency. A linear relationship was observed between (As(III)) concentration and PL quenching at low concentrations (5–50 ppb - for drinking and bore water detection) and high concentrations (100–800 ppb - sedimentary arsenic) of the metal. The limit of detection was more superior (low conc; $R^2 = 0.96$ with sensitivity 0.004 ppb, high conc; $R^2 = 0.98$ with sensitivity 0.0002) when compared to other techniques. Thus, this method can be applied to determine low levels as well as sedimentary levels of As(III).

1. Introduction

Arsenic (As(III)) is ranked first amongst the known toxicants and its contamination in drinking water is a major and serious global problem. It is known to be a poison, a co-carcinogen, and even in lower concentrations has been shown to be susceptible to brain, pitutary and cognitive dysfunction [1,2]. The most serious concern about arsenic is that it can cross the placenta and induce delayed growth and neural tube defects [3–5]. World Health Organization (WHO) has suggested worried that the maximum contamination limit (MCL) for arsenic in drinking water should be 10 ppb. It exists mainly in organic (As(III) and As(V)), and inorganic As(III) forms, however, inorganic As(III) is more stable in the environment. In our body, As(V) can be converted to As(III) by a few reducing agents including vitamin C, therefore, rapid and sensitive analytical methods to detect it in food products, drinking water and the environment are very urgently needed [6].

The present study demonstrates the detection of As(III) from contaminated sources both low as well as high concentrations using carbon nano dots (C-dots) coated gold nanoparticles (Au NPs) in combination with bovine serum albumin (BSA). In general, AuNPs can be synthesized using plant extracts and other biological methods, however, here C-dots were used as reducing and stabilizing agent for the synthesis of AuNPs [7–9]. This method involves two steps namely synthesis of carbon-gold (C-Au) composite followed by capping of BSA on it to form C-Au-BSA complex. In this complex, C-Au and BSA act as the energy donor and the energy acceptor, respectively. The photoluminescence (PL) spectra of this complex (C-Au-BSA) vary in the presence of As (III) and hence can be used to detect the amount of this metal. In this optical sensor, BSA acts as the sensing material. The proposed method can be used to detect the As(III) at low and high concentrations. The possible mechanism of the sensing is also discussed.

2. Materials and method

2.1. Materials

All the chemicals were of analytical grade and purchased from (Merck, Mumbai and Sigma, Chennai). HeLa cells were purchased from NCCS, Pune, India and were maintained in DMEM medium. Water was collected from the borewell, Velachery (12.9760° N, 80.2212° E), Chennai, India.

Synthesis of C-dots: C-dot were synthesized using our previous protocol [10]. In brief, 500 g of *Citrullus lanatus* pulp was added to 500 ml of double distilled (DD) water and ground. The pulp was filtered twice using Whatman paper (Grade 1) and heated in a domestic microwave oven (900 W, 2.45 GHz, LG MO- MC-767 W/WS) for 30 min at 1200 W. The obtained product was centrifuged at 5000 rpm for 10 min and the supernatant containing C-dots were freeze dried in a lyophilizer for 14 h.

C-Au NC synthesis: 200 µl of 1 mM of $HAuCl_4$ was added to a 10 ml

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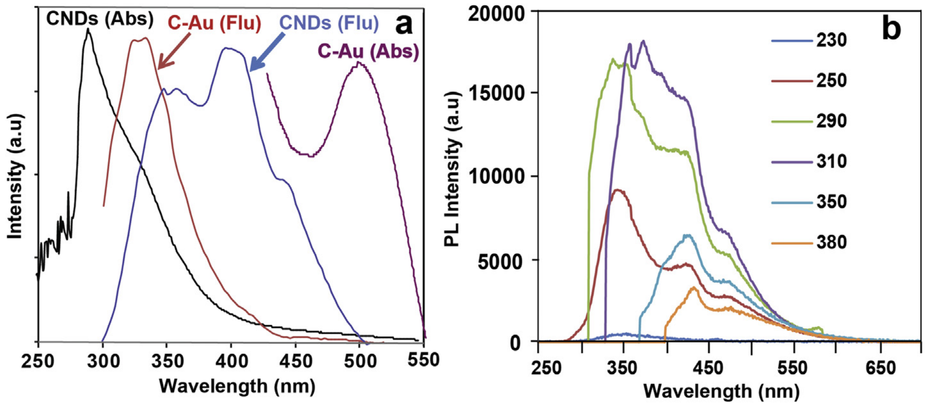

Fig. 1. (A) Absorption and PL emission spectra of C-dots and C-Au composite (b) PL of C-Au composite at different wavelength (nm).

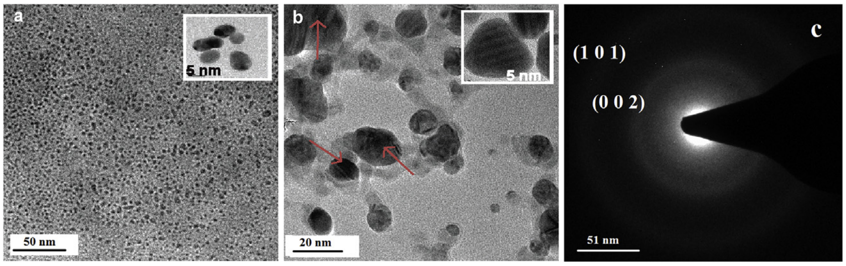

Fig. 2. TEM images of (a) C-dots (Inset: HRTEM) (b) C-Au composite (Inset: HRTEM and arrows marks indicate the adsorption of C-dots on AuNPs to form C-Au composite) (c) SAED pattern of C-dots.

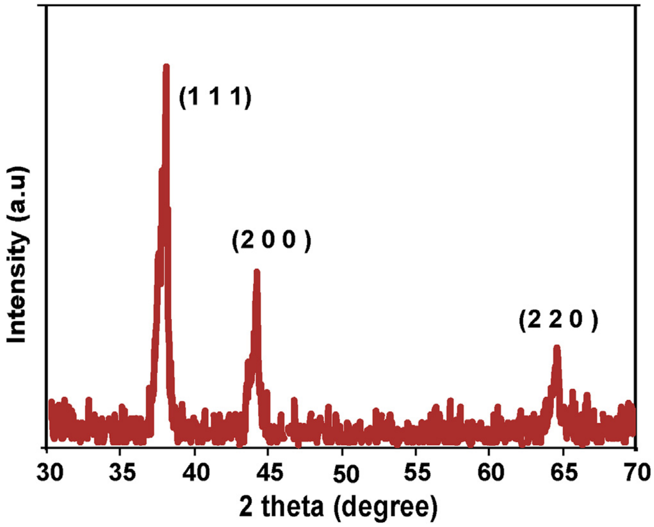

Fig. 3. XRD pattern of the C-Au composite.

reagent bottle containing 100 µl of C-dots (1 mg/ml) and the solution was finally made up to 2 ml by adding DD water. The resulting mixture was placed in a domestic microwave oven and irradiated for 5 min.

2.2. Synthesis of BSA capped C-Au composite followed by As(III) detection

100 µl of C-Au colloidal solution (1 mg/ml) and 500 µl of Bovine serum albumin (BSA: 1 mg/ml) were added to a series of centrifuge tubes. Various concentration of the As(III) (1 mg/ml) (ranging from 5 to 50 ppb and 100–800 ppb) were added to each of the tubes. The reaction mixture was made up to 2 ml by adding DD water and incubated for 10 min. PL spectra of the resulting solutions were read at a λ_{exi} of 280 nm using a EnSpire® Multimode Plate Reader (Model: 2300–0000, MA, USA).

2.3. Arsenic(III) detection in the borewell water

500 µl of Bovine serum albumin (BSA: 1 mg/ml) were added to a series of centrifuge tubes containing 100 µl of C-Au colloidal solution (1 mg/ml). The volume is made up to the 2 ml by suing borewell water and incubated for 10 min and see the reduction in the intensity of the PL.

2.4. Characterization of C-Au composites

UV–visible and PL spectroscopic measurements were carried out on EnSpire® Multimode Plate Reader (Model: 2300–0000, MA, USA). The morphology of the C-dots and C-Au composite were determined using the transmission electron microscope (TEM). C-Au-NC solution was placed on a microscope glass slide and allowed to dry in a hot air oven at 50 °C and the process was repeated to form a thin layer. The dried sample was analyzed with the help of an XRD instrument (Bruker Advance D8 XRD machine, Bruker, Madison,WI, USA) with a Cu source at 1.5406 Å wavelength in thin film mode. The elemental composition of the C-Au-NC was obtained by using an energy-dispersive X-ray spectroscope (EDX; LEO 1430 VP, Carl Zeiss AG, Oberkochen, Germany) at variable pressures and a scanning electron microscope equipped with INCA Oxford EDX facility at an acceleration voltage of 10 keV.

Cytotoxicity assay: Cytotoxicity studies were carried out on human cervical (HeLa) cancer cell lines as per a reported procedure [7]. After 24 h of C-Au (10–300 µg) treatment, viability of treated and untreated cells (control) was estimated by using the following equation.

$$\text{Cell viability (\%)} = A_{\text{treated}}/A_{\text{control}} \text{ X } 100$$

where $A_{treated}$ and $A_{control}$ are the absorbance of the treated and the untreated cells, respectively.