Sensors and Actuators B 246 (2017) 680–685

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Differentiation and determination of metal ions using fluorescent sensor array based on carbon nanodots

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ARTICLE INFO

Article history:
Received 22 December 2016
Received in revised form 20 February 2017
Accepted 21 February 2017
Available online 24 February 2017

Keywords:
Sensor array
Fluorescence
Carbon nanodots
Principal component analysis
Metal ions analysis

ABSTRACT

In chemical and biological sensing research, design and preparation of various sensors is a question of first importance. Generally, fabrication of specific sensors always requirs amounts of time-consuming and low-efficient synthetic tasks. Herein, a novel sensor array based on carbon nanodots (CDs) was constructed to differentiate and detect metal ions (including Ag^{+}, Cd^{2+}, Cr^{2+}, Fe^{3+}, Hg^{2+}, and Pb^{2+}), which utilized non-specific collective recognition reactions between CDs and various metal ions. The convenient synthetic methods and abundant carbon source greatly simplified the constructing process of the sensor array. Moreover, the hexa-sensor array can be simplified into binary-sensor array using principal component analysis (PCA) method. The binary-sensor array can be constructed in less than 10 min with competitive working performance as before. The binary-sensor array has its most comfort pH zone of around 5–10 and can perform well in the metal ion concentration of 50–1600 μM, suitable for the differentiation and determination of metal ions. The sensor array can also realize qualitative detection of unknown metal ions under the interference of a specific environment, including fetal calf serum and local running water.

1. Introduction

The design and construction of highly selective chemical or biological sensors is always time-consuming and low-efficient. Inspired by our olfactory and gustatory systems [1,2], cross-reactive sensor arrays have attracted increasing interest [3–5]. Sensor arrays usually contain a series of nonselective sensors, and analytes can be differentiated and recognized through the cumulative non-specific responses from all the sensors [3–5]. Interestingly, using specific data processing method, such as principle component analysis (PCA) [6], the dimensionality of sensor array can be decreased, and a simplified sensor array with fewer sensors can work none the better for it [7].

Nowadays, various sensing materials have been applied to construct sensor arrays, including inorganic materials (metal oxides [8], semiconductor nanocrystals [9], etc), organic materials (fluorescent dyes [10], conductive polymers [11], molecularly imprinted polymers [12], etc) and nanomaterials [13,14]. However, synthesis for these sensing materials is time-consuming, especially for sensor arrays containing a set of sensors. Therefore, developing new sensing materials with simple synthetic method and excellent sensing performance can promote the development of sensor arrays. Carbon nanodots (CDs) are one of the most important and attractive carbon materials [15–17]. CDs can emit stable fluorescence and have already displayed encouraging performance in chemical sensing [18–21] and biological sensing [22–25]. It is worth noting that CDs can be prepared from extensive and low-cost carbon sources using simple and convenient methods, including microwave-assisted or solvothermal methods. These merits make CDs very ideal candidates for sensor array application.

Heavy metal accumulation can cause serious environmental and health issues [26]. Among various techniques to detect heavy metals, optical methods (via fluorescence changes or colorimetric changes) are the most convenient methods, along with high sensitivity and low detection limit [27,28]. Hydrophilic fluorescent CDs possess abundant functional groups with oxygen-nitrogen, which endow CDs with combining capacity with metal ions [29]. Through fluorescence inner filter effect (IFE) or electron/energy transfer effect, the fluorescence intensity of CDs will change quantitatively, making CDs candidates as sensors for various metal ions [30–35]. Recently, there have been several reports about applying CDs as sensor units to construct sensor arrays to differentiate metal ions [36,37].

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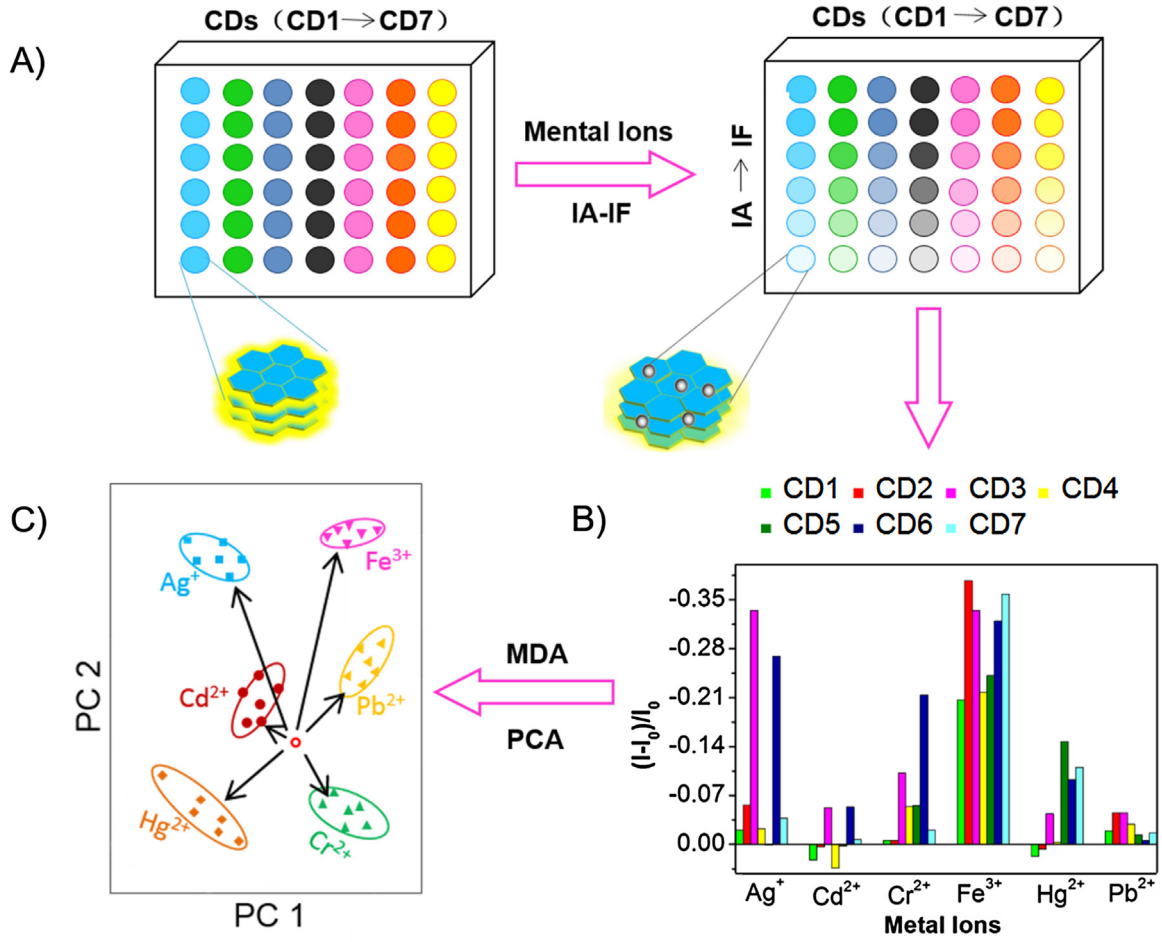
http://dx.doi.org/10.1016/j.snb.2017.02.132
0925-4005/



Scheme 1. The construction as well as the working mechanism of the CD sensor array. (A) Fluorescence responses of the sensor array towards six kinds of metal ions (IA, IB, IC, ID, IE and IF); (B) Fingerprints (response patterns) of various metal ions generated by the sensor array; (C) Discrimination of unknown metal ion through Mahalanobis distance analysis (MDA) using principal component analysis (PCA) scattergraph.

Here, we selected seven kinds of CDs and realized differentiation for six kinds of metal ions. Differing from previous reports, we took PCA to process the resulting data and succeeded to decrease the dimensionality of the sensor array from six to two units, which is less than the existing sensor array based on CDs. Moreover, the sensing performance of the two-sensor array was as excellent as before. The construction and working mechanism of the sensor array is shown in Scheme 1. For each metal ion, there exists a unique fingerprint or response pattern (Scheme 1B), containing all fluorescence intensity changing information from CD array (Scheme 1A). PCA was applied to process the response pattern including six repeated trails for each metal ions, and the first two principal components (PCs, describing at least 80% of the total variability) were taken as the horizontal and vertical coordinates to plot PCA scattergraph (Scheme 1C). Based on the PCA scattergraph, different metal ions can be differentiated, and unknown metal ions can be determined through Mahalanobis distance analysis (MDA).

2. Experimental materials and methods

2.1. Synthesis of carbon dots

In this paper, seven carbon nanodots (CDs) were prepared through microwave and hydrothermal methods. CD1, CD2, CD3, CD4 and CD5 were prepared through microwave reaction. CD6 and CD7 were prepared through hydrothermal reaction.

2.1.1. Synthesis of CD1

CD1 was synthesized following a typical procedure. 0.6 g asparaginic acid (4.5 mmol) and 1.2 g urea (20.0 mmol) were dissolved in NaOH solution (15 mL, 0.5 M) before the solution was heated in the microwave oven for 6 min. The resulted solid powder was dissolved with 10 mL ultrapure water. The supernatant was collected by centrifugation at 12 000 rpm for 5 min and then dialyzed against ultrapure water through a dialysis membrane for 48 h to remove the excessive precursors and small molecules. The resultant CD1 was maintained at 4 °C for further use.

2.1.2. Synthesis of CD2

0.5 g alanine (5.6 mmol) and 1.2 g urea (20.0 mmol) were dissolved in NaOH solution (15 mL, 0.5 M) and then the solution was heated in the microwave oven for 4 min. The resulted solid powder was processed using the same method as CD1.

2.1.3. Synthesis of CD3

CD3 was synthesized using 0.3 g lysine (2.3 mmol) and 1.7 g ethylenediamine (28.3 mmol) in ultrapure water (10 mL). The mixture solution was heated in the microwave oven for 4 min. The following processing method was similar to CD1.

2.1.4. Synthesis of CD4

CD4 was synthesized using 0.6 g alanine (4.5 mmol) and 1.0 g citric acid (5.2 mmol) in NaOH solution (15 mL, 0.5 M). The mix-