Sensors and Actuators B 174 (2012) 102–108

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

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

Immobilization of phosphorescent quantum dots in a sol–gel matrix for acetone sensing

Emma Sotelo-Gonzalez, Ana M. Coto-Garcia, Maria T. Fernandez-Argüelles*, Jose M. Costa-Fernandez, Alfredo Sanz-Medel**

Department of Physical and Analytical Chemistry, University of Oviedo, Avda. Julian Claveria 8, E-33006 Oviedo, Spain

ARTICLE INFO

Article history:
Received 8 May 2012
Received in revised form 26 July 2012
Accepted 28 July 2012
Available online 21 August 2012

Keywords:
Quantum dots
Phosphorescence
Luminescence
Acetone sensing
Sol–gel

ABSTRACT

Quantum dots (QDs) are semiconductor nanoparticles (NPs) that are increasingly used in optical sensing applications due to their exceptional optoelectronic properties. When such nanocrystals are doped with certain metal impurities, a phosphorescence-like emission can be obtained, allowing the development of novel robust and highly selective sensing phases (it is possible to perform time resolved measurements enabling a simple discrimination between the luminescence emission from the QDs from the background fluorescence of the sample, in which luminescent lifetime is shorter).

In this context, a phosphorescent sensing material for acetone control in water media has been developed based on the immobilization of phosphorescent quantum dots in an inorganic sol–gel solid matrix.

For such purpose, colloidal manganese-doped ZnS nanoparticles (Mn:ZnS QDs) surface-modified with L-cysteine (for water solubilisation) were synthesised. The Mn:ZnS QDs exhibit an intense room temperature phosphorescence (RTP) emission in aqueous media even in the presence of dissolved oxygen. Further, a simple and general procedure is proposed to incorporate the colloidal L-cysteine Mn:ZnS QDs in a sol–gel matrix.

Application of the developed sensing material to analytical control of acetone dissolved in contaminated water samples was performed based on measurement of the quenching effect of the analyte on the QDs phosphorescence emission. The sol–gel procedure (e.g. nature and concentration of the silica precursors used) employed for immobilization of the QDs was optimized trying to obtain the best analytical features for detection of acetone. The optimized sensing material showed a high selectivity of the sensing material towards acetone. The linear range of the developed methodology turned out to be at least up to 50% acetone:water (v/v) with a detection limit (DL) for acetone dissolved in aqueous medium of 0.16% acetone:water (v/v). The developed sensing phase was finally applied for acetone determination in different spiked water samples, and the recoveries fall in the range of 93–109%.

1. Introduction

Quantum dots (QDs) are luminescent nanocrystals of semiconductor materials with diameter sizes between 2 and 10 nm with fascinating optical and electronic properties [1]. The quantum confinement effects are responsible for their remarkable properties that depend on their size and composition, allowing high fluorescent quantum yields and very large molar extinction coefficients, broad excitation coupled to narrow and symmetric size-tuneable emission spectra, high resistance to photobleaching and fluorescence lifetimes on the order of 20–50 ns [2–4].

Luminescence of quantum dots is very sensitive to their surface states. Therefore, eventual chemical or physical interactions between a given chemical species with the surface of the nanoparticles could result in changes of the efficiency of the core electron–hole recombination. This was the basis of the development of novel sensing approaches, based on QDs, for direct analysis of small molecules and ions. In fact, in the last years, the use of quantum dots has replaced conventional organic fluorophores in diverse applications such as direct sensing [5,6] of ions [7–10], gases [11] or other small molecules [12,13]. Unfortunately, although very simple and highly sensitive, very often, those "direct" sensing approaches lack of an appropriate selectivity. To improve selectivity of QDs based sensors, elimination of interferences from other concomitant fluorescent compounds emissions is a must.

In this context, recent investigations have demonstrated that, when certain metal impurities are incorporated during nanoparticles synthesis, phosphorescence-like emission quantum dots

---

* Corresponding author. Tel.: +34 985103000x5365.
** Corresponding author. Tel.: +34 985103474.
E-mail addresses: fernandezteresa@uniovi.es (M.T. Fernandez-Argüelles), asm@uniovi.es (A. Sanz-Medel).

0925-4005/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.snb.2012.07.107

could be obtained [14–18]. These QDs present features typically offered by phosphorescent compounds [19]. Moreover, since the excited states that are involved in the emission of phosphorescence when using nanoparticles which are different from those involved in conventional organic molecules, typical parameters that affect the emission of phosphorescence might not affect the emission of luminescence of the QDs, such as presence of heavy atoms or dissolved oxygen, necessity of a rigid environment, etc.

In this vein, Mn^{2+}-doped ZnS QDs have attracted considerable attention because doping Mn^{2+} ions may act as recombination centres for the excited electron–hole pairs and result in strong and characteristic luminescence at longer wavelengths. Upon Mn^{2+} doping, a characteristic emission band, centred at around 590 nm, is obtained for the well-known $^4T_1$–$^6A_1$ d–d transition of Mn^{2+} ions on Zn^{2+} sites of the QD (where Mn^{2+} is coordinated by S^{2-}) [17,18]. When compared with the traditional QDs such as CdSe or ZnS, the resulting Mn^{2+}-doped ZnS QDs exhibit both, longer Stokes shift between excitation and emission wavelengths and longer luminescent lifetimes (in the order of a few ms), properties which are typical from phosphorescent emission. Hence, it is possible to perform time resolved measurements allowing simple discrimination between the luminescence emission from Mn:ZnS QDs from the background fluorescence of the sample (in which luminescent lifetime is shorter). Such improved emission properties make the Mn^{2+}-doped ZnS QDs very exciting advanced nanomaterials as analytical luminescent labelling agents for sensing purposes.

A step further towards the development of QD-based sensing materials requires the immobilization of the QDs in an adequate solid supports in order to obtain an active solid sensing phases [6]. For this purpose, it is known that sol–gel based technology might be an outstanding method to entrap the nanoparticles inside a solid matrix due to the simplicity of the sol–gel preparation, the chemical inertness of the matrix, the tuneable porosity achieved by changing the amounts of silica precursors, the mechanical stability and the negligible swelling behaviour. In addition, the optical transparency offered by sol–gel materials makes them an excellent option for the development of optical sensing phases [20].

In the present work, incorporation of colloidal phosphorescent Mn:ZnS QDs in a sol–gel matrix has been carried out in order to fabricate “active” solid phases for acetone determination. Acetone, a highly volatile chemical reagent which is commonly analysed in environmental samples, was used as model analyte. Acetone, along with formaldehyde and acetaldehyde are the most abundant representatives of low molecular weight carbonyl compounds in water samples, representing more than 90% of total carbonyl content. Short-chain carbonyl compounds can appear in drinking water as pollutants due to the wide variety of their sources, mainly after disinfection treatments of natural waters or from migration from plastic containers into bottled water. Although the maximum contaminant levels in drinking water are still not applicable by the International Advisory Committees, the development of screening methods to test water samples is a necessity in order to control these compounds which can produce adverse health effects (from irritation of mucous membranes to problems in the central nervous system) and also organoleptic alterations [21–24].

Entrapment of the QDs in the sol–gel matrix was performed by incorporation of the nanoparticles in the precursor's mixture during the polymerization procedure. The sol–gel process was optimized to ensure that the QDs optical properties are retained (avoiding degradation or easy leaching into the solution) while maintain appropriate acetone sensing features.

2. Material and methods

2.1. Reagents

All chemical reagents used were of analytical-reagent grade and without further purification. Zinc sulphate heptahydrate, manganese chloride tetrahydrate, L-cysteine hydrochloride monohydrate and 2-propanol were obtained from MERK (Darmstadt, Germany). Sodium sulphide nonahydrate, sodium hydroxide, and methanol were purchased from Aldrich (Milwaukee, WI, USA). Acetone, methanol, ethanol and acetonitrile HPLC gradient grade were purchased from Prolabo (Leuven, Belgium). Sol–gel silicate precursors, tetramethoxysilane (TMOS) and 3-aminopropyltrietoxysilane (APTES) were obtained from Fluka Chemie (Steinheim, Germany) and N-ethyl-N-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) was purchased from Fluka (Basel, Switzerland). Freshly prepared ultrapure deionized water (Milli-Q3 RO/Milli-Q2 system, Millipore, UK) was used in all the experiments.

2.2. Synthesis of aqueous ZnS and Mn^{2+}-doped ZnS quantum dots

Colloidal water-soluble Mn^{2+}-doped ZnS quantum dots were synthesised in our laboratory via the procedure described by He et al. [25] with some slight modifications.

Mn^{2+}-doped ZnS QDs show both phosphorescence and fluorescence emission that are affected by the manganese stoichiometry. Thus, based on previous studies carried out in our laboratory to optimize the amount of dopant added for the synthesis of the QDs, a 3% Mn:ZnS QDs (% molar ratio Mn/Zn) was selected, which was found to be the molar ratio of precursors that gives rise to the best phosphorescence emission.

Briefly, the following procedure was then used: 50 mL of 0.02 M L-cysteine, 5 mL of 0.1 M $ZnSO_4$, and 0.15 mL of 0.1 M $MnCl_2$ were mixed in a beaker and pH was adjusted with NaOH 1 M to pH 11. The mixture of the precursors was placed in a three-necked flask and deoxygenated in an argon atmosphere under continuous stirring for 30 min. Then, 5 mL of 0.1 M Na_2S was swiftly injected into the solution to allow the nucleation of the nanoparticles. The mixture was stirred for 20 min, and then the solution was aged at 50 °C under air for 2 h to improve the crystallinity of the L-cysteine capped Mn^{2+}-doped ZnS QDs. Purification of the QDs was carried out by precipitation of the nanoparticles with ethanol in a centrifuge at 5000 rpm for 5 min (the procedure was repeated for 3 times). Finally, the QDs were dried under vacuum and stored under inert argon atmosphere as a water-soluble brown solid powder.

2.3. Sol–gel synthesis procedure for Mn:ZnS QDs immobilization

Based on previous studies carried out in our laboratory [26,27], sol–gels were synthesised by trapping QDs into the sol–gel matrix during the polymerization process. For this purpose, sol–gels were prepared by using different ratios of (3-aminopropyl)triethoxysilane (APTES) and tetramethoxysilane (TMOS) as silica precursors, ethanol and water as solvents, N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC) to retain the nanoparticles covalently bound to the sol–gel matrix, and sodium hydroxide as catalizer for the polymerization process.

Reagents were added under constant stirring in the following order: 2.5 mL of ethanol was mixed with 1 mL of Mn:ZnS QDs in aqueous phosphate buffer pH 7.4. Then, 750 μL of APTES was added, and immediately afterwards 100 μL EDC was added. Finally, 750 μL of TMOS and 50 μL of sodium hydroxide 0.1 M were added to the recipient. After homogenization of the mixture, the polymerization process takes place and the mixture was left to dry for 2 weeks, until a constant weight is achieved. The xerogel obtained is grinded in