Preparation of Hg^{2+} selective fluorescent chemosensors based on surface modified core–shell aluminosilicate nanoparticles†

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A synthetic procedure for the preparation of functional structured inorganic–organic hybrid materials consisting of boehmite-silica core–shell nanoparticles and anthracene-containing amines covalently attached to the nanoparticles surface is reported. The system functionalised with the monoamine chain shows a very high sensing performance for Hg^{2+} detection in pure water reaching a detection limit of 0.2 ppb. Two additional advantages of these systems are their stability over a wide pH window and the feasibility to be recovered by a simple procedure.

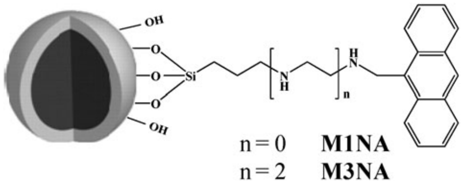
Introduction

Hg^{2+} is a very toxic chemical species dispersed in different strategic living resources such as water.[1] Various methods have been reported for sensing the presence of Hg^{2+} in aqueous solution, based mainly on electrochemical,[2] colorimetric[2,3] or fluorescence[4] approaches. In this respect, a few years ago we reported on a voltammetric method based on a Paraloid B72 film electrode modified with an aza-coronand macrocycle which permitted the detection of nanomolar amounts of Hg^{2+} in water.[5] In the search for increasingly lower detection limits, fluorescent methods are particularly attractive. The performance of the fluorescent chemosensor relies on the occurrence of a large variation of the emission of the fluorophore when the target species is bound to the complexing unit. Grafting of these molecular chemosensors to solid supports can provide some important advantages, such as the possibility of recovering the sensing system by filtration, centrifugation, *etc.*, and further reusing. Moreover, the solid support usually affords stability to the device.[6] Apart from displaying a large modification of the luminescence following the binding event, for having an efficient chemosensing performance in aqueous solution these grafted systems must have colloidal stability over a wide pH range. This very important feature permits recording neat emission spectra with negligible scattering. Small-sized non-aggregated particles would fulfil this requirement. However, as far as we know, there are not any reports regarding nanoparticles and complexing-fluorophore systems as efficient, recoverable, sensitive and selective Hg^{2+} chemosensing devices in aqueous solution.

Different types of nanoparticles have found applications after surface modification by covalently bonded ligand-fluorophore systems. For instance, modified silica, gold and boehmite nanoparticles have found applications in metal ion sensing.[7,8] We have also recently reported on surface-modified boehmite nanoparticles for MR imaging.[9] Similarly, lanthanide-grafted oxidic nanoparticles have been found to be effective contrast agents for cellular uptake imaging.[10] While the functionality of these structured hybrid materials is mainly dictated by the specific properties of the organic moiety, the performance of the device can be improved by the selection of a proper support. However, these systems have some drawbacks. Boehmite supports in aqueous solution tend to coagulate at pH values over 7. On the other hand, although nanometre-sized silica particles remain dispersed and non-aggregated in aqueous solution over a wide pH range, their preparation involves microemulsion media using surfactants.

In order to avoid these inconveniences and meet the advantages of both boehmite and silica nanoparticles we have prepared for the first time boehmite-silica core–shell composite nanoparticles improving the performances of both boehmite and silica nanoparticles, namely: (i) size control in neutral pH medium without using surface-directing agents, and (ii) colloidal stability over a wide pH range.

In this article, we report on the functionalisation of boehmite-silica nanoparticles with a couple of anthracene-amine systems (M1NA and M3NA, see Scheme 1). For achieving Hg^{2+} discrimination over other heavy metal ions, we have exploited the well-known preference of mercury for



Scheme 1 Anthracene-amine systems supported boehmite-silica nanoparticles.

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low coordination numbers. Indeed, at difference with other metal ions, two-coordinated linear Hg^{2+} complexes are quite stable and very frequent in the coordination chemistry of this heavy metal ion.[11]

Experimental section

Preparation of the materials

Composed core–shell nanoparticles were obtained by a sol–gel method consisting of the hydrolysis and condensation of tetraethylorthosilicate (TEOS) in a solution of $Al(NO_3)_3 \cdot 9H_2O$ in ethanol at 60 °C. The resulting solution was refluxed and aged for 1 week. Gels were dried at 60 and 120 °C and characterised by X-ray diffraction powder pattern (XRD), ^{27}Al and ^{29}Si nuclear magnetic resonance (NMR), infrared spectroscopy (IR), and transmission electron microscopy (TEM).

M1NA was prepared by reaction of 3×10^{-3} moles of 9-anthracene-1-carboxaldehyde and 3×10^{-3} moles of (3-aminopropyl)triethoxysilane in 150 cm^3 of dry ethanol. After one and a half hours, the yielded imine was reduced by addition of 794 mg of $NaHB_4$ in a dried atmosphere.[12] Following the same synthetic procedure, a modified fluorescent sensor (M3NA) with (*N*′-[3-(trimethoxysilyl)propyl]-diethylenetriamine, a triamine complexing unit, was also prepared.

Finally, the hybrid inorganic–organic systems were prepared by adding 1 g of boehmite-silica core–shell nanoparticles to an ethanolic solution of the functionalised anthracene-amine compound, keeping the samples under stirring for 3 h. The functionalised nanoparticles were collected by centrifugation, and the product was successively washed with CH_2Cl_2, EtOH and an EtOH–H_2O mixture (see ESI, Fig. 1*S*†). Anal. For M1NA: C 4.87%; N 0.30%; H 3.26%. M3NA; C 4.41%; N 0.70%; H 2.84%.

Materials and methods

X-ray diffraction analysis was performed on a Siemens D-5000 diffractometer using graphite monochromatic Cu-Kα radiation (λ = 1.5418 Å). Powdered samples were sprayed on glass sample holders and data collected in Bragg–Brentano geometry from 5 to 65° 2θ with a step-size of 0.02° 2θ and a counting time of 5 s per step.

Infrared transmission spectra were obtained with a Perkin Elmer spectrometer Model 882 in the 400–1400 cm^{-1} range using the KBr pellet method.

The morphology of as-prepared and polyamine containing boehmite particles was examined using a Jeol 1010 transmission electron microscope at an accelerating voltage of 100 kV and a field emission gun Tecnai F20 working at 200 kV. Samples were prepared by dispersing as-produced powders in absolute ethanol and setting dropwise on copper grids that had previously been coated with a holey thin carbon film.

^{29}Si NMR studies were carried out on a Varian UNITY 300 spectrometer at a resonance frequency of 59.59 MHz. The MAS NMR spectra were recorded with a 7 mm zirconium oxide rotor spinning at 4.5 kHz. A 90° single-pulse was used with an acquisition time of 0.08–0.1 s and a delay time of 30–60 s. Chemical shifts were measured relative to tetramethylsilane (TMS). ^{27}Al NMR spectra were recorded on a Bruker Avance 400 spectrometer at a resonance frequency of 104.26 MHz. Relaxation delay times of 1–5 s and acquisition times of 0.4 s were used.

The solvents used for spectrofluorimetric measurements were of spectroscopic or equivalent grade. Water was twice distilled and passed through a Millipore apparatus. All solutions were prepared in pure water. The pH values were measured with a Mettler-Toledo MP-120 pH-meter and adjustments of the hydrogen ion concentration of the solutions were made with diluted HCl and NaOH solutions. The emission spectra were recorded with a PTI MO-5020 spectrofluorimeter in the 380–580 nm range with excitation wavelength of 350 nm.

Results and discussion

Preparation and characterisation of materials

As commented above, the core–shell nanoparticle platform for grafting the fluorophoric amines was achieved by condensation of TEOS and $Al(NO_3)_3 \cdot 9H_2O$ in ethanol, followed by aging for one week. The nature of the prepared nanoparticles was assessed by different techniques. Results from X-ray powder diffraction indicates the presence of boehmite as a crystalline phase. The X-ray displays peaks at around 13.6, 28.3, 38.4 49.2 and 64.8° 2θ which can be attributed to a crystalline phase with the structure of boehmite. The formation of boehmite is further confirmed by ^{27}Al NMR and infrared spectroscopies. The second component of these synthesised nanoparticles, *i.e.* silica, which is amorphous, as evidenced by the absence of peaks corresponding to any crystalline form of silica, has to be as a coat of the boehmite nanoparticles. Unfortunately it is difficult to evidence the thin layer of silica by TEM examination.

The nanoparticles were then functionalized with the containing fluorophoric polyamines (see Scheme S1 in the ESI†) and were characterised by microelemental analysis, XRD, TEM, IR and NMR. The size of the synthesized boehmite-silica nanoparticles is in the 5–10 nm range as shown in TEM (Fig. 1). X-ray powder diffraction patterns and IR

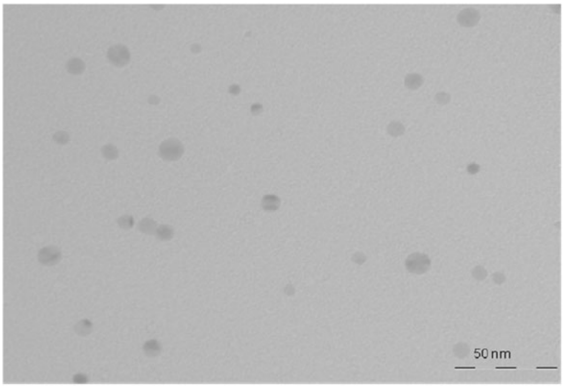

Fig. 1 TEM image of the synthesized boehmite-silica nanoparticles.

spectra are included in the supplementary information (see Fig. 2*S*).† The nitrogen and carbon elemental microanalysis indicates that the number of moles of attached polyamines per gram of material is 2.3 × 10^{-4} and 1.7 × 10^{-4} for M1NA and M3NA, respectively, which is in line with the numbers we have previously reported for boehmite nanoparticles functionalised with amines containing indol or naphthalene as fluorophores.[8]

With regard to their chemical and microstructural features, experimental results from XRD, IR, and ^{27}Al NMR studies reflect that the core–shell nature of these supports is maintained.

Chemosensing behaviour

The present systems have been checked for their ability to sense Hg^{2+} in pure water. Fig. 2 shows the fluorescence emission spectra of M1NA recorded at variable pH upon excitation at 350 nm. For M3NA system see Fig. 3S in the ESI.†

In both cases, the fluorescence intensity displays a clear diminution when the pH of the colloidal solutions varies from 2.0 to 11.0 (see ESI†, Fig. 4S and 5*S*), as a consequence of a photoinduced electron transfer from the amine lone pairs to the excited fluorophore due to deprotonation of the ammonium groups.

Fig. 3 plots the variation in the fluorescence intensity upon adding equimolar amounts of Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+} to colloidal water solutions of M1NA and M3NA at pH 5.

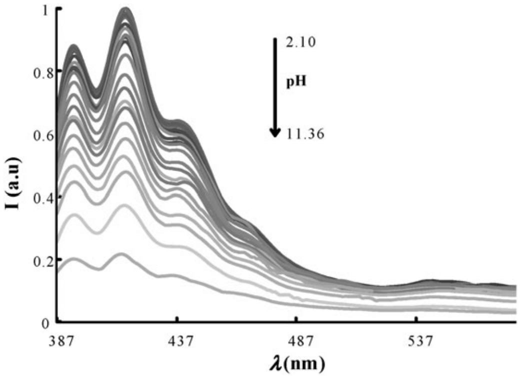

Fig. 2 Steady-state fluorescence emission for M1NA (λ_{exc} = 350 nm) recorded at 298.1 ± 0.1 K in pure water.

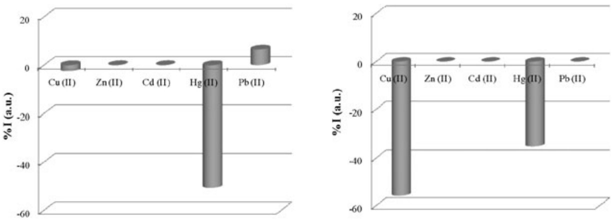

Fig. 3 Bar diagram representation of the % response relative fluorescence intensity of M1NA (left) and M3NA (right) upon addition of divalent metal ions in 1 : 1 M : L molar ratio at pH 5. The *y*-axes has been constructed so that the fluorescence of the free ligand is levelled to 0. Titrations performed in pure water at 298.1 ± 0.1 K, λ_{exc} = 350 nm.

The corresponding intensity variation at pH 7.5 is included in the supplementary information (see Fig. 6S in ESI†). From these results, the high selectivity of the system M1NA for sensing Hg^{2+} cations in aqueous solution in a pH window around 5 can be remarked. This quenching of the emission intensity (CHEQ effect) begins at very acidic pH yielding to a sharp decrease of the luminescence. The change in fluorescence with pH for the different M^{2+}-M1NA and M^{2+}-M3NA systems is shown in the ESI† (Fig. 7*S*). The remarkable efficiency and selectivity for Hg^{2+}-M1NA at pH 5 can be ascribed to the ability of Hg^{2+} to form stable complexes with low coordination numbers.[11] For instance, while 1 : 1 Cu^{2+}–CH_3NH_2 complex has a stability constant of *ca.* 4 logarithmic units, the corresponding complex for Hg^{2+} has a constant of 7 logarithmic units.[13] Although it is difficult to know the exact stoichiometry of the Hg^{2+} complexes in the grafted material, the fluorescent response and the degree of functionalisation of the materials permits to establish quite safely that Hg^{2+} can only bind to one organic residue and therefore to only one amine nitrogen. This higher stability of low-coordinated Hg^{2+} complexes permits to have a pH window (3.5–5.5) where Hg^{2+} can be selectively detected over the other metal ions. In the case of M3NA, this does not hold due to the larger number of nitrogen atoms present in the polyamine chain (3 instead of 1). It has to be also remarked that addition of over 1000-fold excesses of Na^+ or K^+ did not alter this behaviour.

In addition to this outstanding selectivity for Hg^{2+}-M1NA, a remarkable feature of this sensing system is its sensitivity. The detection limit depends on the instrumentation (*i.e.* the Signal-to-Noise Ratio gives you a quantitative indication of the sensitivity, in this case 230) and on the sensitivity of the ligand defined as the d(luminescence)/d[cation] (Fig. 4). Using these two parameters, the limit of detection can then be calculated as 3* SNR/sensitivity.

The mean values obtained from three independent measurements 0.19 ± 0.01 ppb for M1NA and 0.37 ± 0.03 ppb for M3NA lie far below the 2 ppb limit, which is the maximum permitted Hg^{2+} amount in drinking water following the USA Environmental Protection Agency (EPA) criterion.[14]

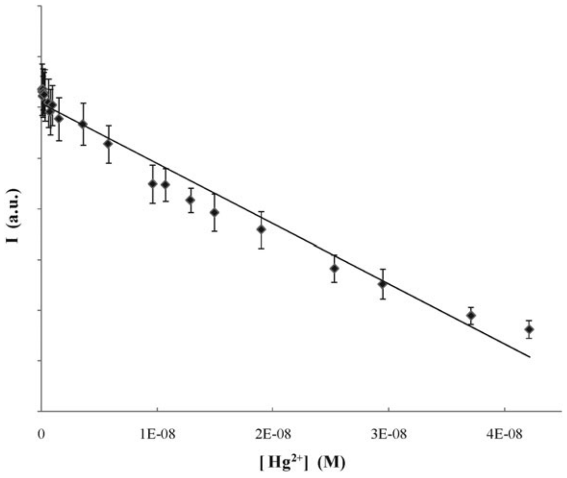

Fig. 4 Plot of the fluorescence intensity vs. [Hg^{2+}] for the M1NA system.

Conclusions

The systems here presented show important properties that can be advantageously used in the design of Hg^{2+} chemosensors in aqueous solution. These properties are related with both the simplicity of the combined chemosensor molecule, an amine nitrogen linked to a fluorophore, and to its covalent grafting on very small sized silica-coated boehmite nanoparticles. These properties along with the pH stability of the particles over a wide pH range help, on the one hand, to magnify the fluorescence signal. On the other hand, the gelification that occurs when the pH is brought to 11 permits the recovery of the nanoparticles by a simple centrifugation procedure.

Acknowledgements

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