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Self-assembled gold nanoparticle monolayers in sol–gel matrices: synthesis and gas sensing applications

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Gold nanoparticle monolayers have been deposited on amino-functionalized commercial glass and on sol–gel glass surfaces using a fast chemisorption protocol. The nanoparticle surface coverage could be tuned by varying the deposition conditions. The nanoparticle monolayers have been embedded into SiO₂ sol–gel matrices to study the feasibility of this approach for the engineering of sol–gel based nanocomposites. The same approach has been used for obtaining Au–NiO multilayer films which showed a reversible absorbance change when exposed to CO (100–10000 ppm) at 300 °C operating temperature.

Introduction

Nanocrystal electronics involves the incorporation of nanoscale inorganic materials into electronically addressable devices. The nanoscale components may be distributed within a matrix or need to be deposited at an interface. Homogeneous surface deposition is often difficult to achieve and chemically directed assembly (CDA) of nano-objects is therefore one of the key pre-requisites for scalable fabrication of such devices. In this work we consider the fabrication of a simple gas sensor comprising small gold nanoparticles (NPs) embedded in a conductive sol–gel matrix. The key issue in such a device is firstly that the sensor requires a high degree of matrix porosity. This is readily achieved using sol–gel techniques.^{1,2} Secondly, the active catalyst particles must be homogeneously dispersed for maximum sensitivity, *i.e.* they must not be aggregated. In CDA, a substrate is first patterned or decorated with molecules having specific functional groups capable of linking the desired target objects (the NPs in this case) in order to assemble them. The functional groups eventually guide the assembly of the NPs through specific chemical interactions to form a dense, homogeneous monolayer, which is stable in air under ambient room conditions. Once a substrate is functionalized with such a monolayer of particles it can itself be used as a regular substrate for sol–gel film deposition, allowing easy incorporation of NPs inside any hosting medium.

The present work explores the possibility of embedding NP monolayers inside SiO₂ and NiO films. Silica has been adopted as a reference matrix in order to study the feasibility of this fabrication method together with the eventual effect of the deposition/annealing procedure on the NP morphology. NiO has also been chosen because, when coupled with gold, it is capable of optical

detection and recognition of reducing species such as CO.^{3–6} The goal here is to demonstrate simple and scalable fabrication of a nanoparticle gas sensor based on CDA.

Experimental procedures

The multi-step procedure that has been developed to build the nanocomposites comprises: (1) synthesis of metal nanocrystal colloids, (2) deposition of a molecular monolayer of surface amino-terminated molecules, (3) self assembly of the nanoparticles on the molecular layer and (4) deposition of the sol–gel matrix.

(3-Aminopropyl)trimethoxysilane (APTMS) was chosen for SiO₂ surface functionalization. Substrate preparation prior to APTMS deposition was found to be critical for the fabrication of a homogeneous monolayer. Substrates were first cleaned to remove any organic residuals by immersion in dichloromethane (CH₂Cl₂) at room temperature for 15 minutes. This method was found to be as efficacious as cleaning with piranha solution (H₂SO₄:H₂O₂) and less dangerous. Subsequently they were immersed into a mixture of NH₃ (25% v/v aqueous solution), H₂O₂ (30% v/v aqueous solution) and distilled H₂O according to 1 : 1 : 5 volume ratio, at 70 °C for 20 minutes. The samples were then rinsed with distilled water and dried with a N₂ flux. The freshly cleaned substrates were then immersed into a 1% wt solution of APTMS in toluene and kept at 60 °C for 4 minutes, followed by a final rinse with toluene and drying using a stream of N₂.

Gold colloids were synthesized in water using citrate as reductant, then surface functionalized with 11-mercapto-undecanoic acid (MUA) and eventually concentrated according to a procedure described in detail elsewhere.¹ The deposition of a Au NP monolayer was performed by spin-coating the liquid suspensions directly onto the APTMS monolayers. NP monolayers were deposited at spinning rates in the 1500 rpm–4500 rpm range and starting from colloids with a particle concentrations ranging from 20 nM to 250 nM.

The gold nanoparticle monolayers were subsequently covered with a SiO₂ or a NiO layer as follows. To deposit a pure silica layer, a standard solution of tetraethoxysilane (TEOS) in ethanol was used, containing TEOS : ethanol : H₂O : HCl = 1 : 4 : 2 : 0.01

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molar ratios. A solution of the silica precursors was first made with only 1/3 of the required ethanol and stirred for 30 minutes. Only prior to film deposition was the remaining ethanol added to reach the nominal sol composition. Silica layers were deposited by spin-coating at 3000 rpm and 6000 rpm under ambient conditions. To demonstrate the possibility of performing the complete procedure also on top of a sol–gel layer, an initial SiO₂ buffer layer was deposited on a silicon substrate and annealed at 700 °C for 30 minutes. Subsequently this layer underwent the cleaning–functionalization procedure described above, followed by deposition of a 10 nm size Au NPs monolayer. The latter was eventually coated with another silica layer and annealed at 500 °C for 30 minutes. In addition to silica films, NiO layers were also deposited. This was achieved by deposition with a NiCl₂·6H₂O solution in methanol (MeOH) containing N-[3-(trimethoxysilyl)propyl]ethylenediamine (DAEPTMS) with a molar composition Ni : MeOH : DAEPTMS = 1 : 33 : 0.3. Layers were spin-coated onto Au NP monolayers at 5000 rpm under ambient conditions and subsequently annealed at 500 °C for 30 minutes.

Absorption spectra of nanocrystal solutions and films were collected using a Cary 5 UV-vis-NIR spectrometer in the 200–800 nm wavelength range. Atomic force microscope (AFM) imaging was carried out in tapping mode on a Digital Instruments Dimension 3100 instrument. TEM measurements were taken with a field-emission FEI TECNAI F20 SuperTwin FEG-(S)TEM microscope operating at 200 kV. The films were characterized by X-ray diffraction (XRD) using a Philips diffractometer equipped with glancing-incidence X-ray optics. The analysis was performed using CuK_α Ni filtered radiation at 40 kV and 40 mA. Optical sensor functionality was studied by performing optical absorbance/transmittance measurements over the wavelength range 350 < λ < 800 nm with sample films mounted on a heater in a custom built gas flow cell. Transmission data were recorded with a Varian Cary1E spectrophotometer with films heated at temperatures between room temperature and 300 °C and CO concentrations ranging from 100 to 10000 ppm in dry air. The substrate size for these measurements was approximately 1 cm × 2 cm and the incident spectrophotometer beam was normal to the film surface and covering a 6 mm × 1.5 mm section area.

Results and discussion

Au NP monolayers

Surface silanization is a widely used technique for activating surfaces for anchoring proteins^{7,8} and polymers.⁹ The homogeneity of such layers strongly depends on deposition conditions. Other parameters are also important, with concentration, solvent quality, temperature and reaction time all playing key roles in determining the final morphology of the layers, on both silicon and silica glass surfaces.^{10–16} The first attempts to achieve surface modification with amino-terminated molecules were conducted in a special apparatus where silicon wafers were in contact with the vapour phase of a 5% (wt) solution of APTMS in toluene and refluxed for 16 hours at high temperature (≈ 120 °C).¹⁶ Cooper *et al.* used glass slides and the dip technique into a 2% (wt) solution of DAEPTMS in ethanol followed by annealing of samples at 110 °C for 10 minutes.⁹ The silanization method used in the present work was inspired by the work of Petri *et al.*¹⁷ and Barsotti *et al.*¹⁸ For the synthesis of CDA monolayers of NPs there are typically two approaches: one in which assembly is driven by ionic or weaker van der Waals attractions^{19,20–22} between surface ligands and NPs, and the other in which the formation of covalent bonds between them is the driving force. The binding of gold NP monolayers is driven by the electrostatic interactions between the carboxyl groups on the nanoparticles and the surface amine groups. In addition, short range hydrogen bonds anchor the particles to the surface after contact. Rapid chemisorption leads to fast coating but dictates against the formation of ordered particle monolayers. The methodology here is somewhat similar to the protocol reported by Natan and colleagues;²³ however they used dip coating rather than spin coating.

Fig. 1a reports the optical absorbance spectra of the Au NP suspensions used for monolayer deposition. The surface plasmon resonance (SPR) band due to Au NPs is evident and centred at 523 nm in both plots. The plots refer to the absorption of the NPs measured before (as synthesized) and after the separation/concentration protocol prior to the monolayer deposition. The mean diameter evaluated from TEM images was 9.8 nm with

Fig. 1 Optical absorbance spectra of Au NPs. (a) Spectra of as synthesized Au NPs (grey) and after the MUA functionalization and concentration protocol (black). SPR band of Au NPs is centred at λ = 523 nm. (b) Spectra of bare Au NPs monolayers deposited on soda-lime glass substrates at 2500 rpm spinning rate. The plots show absorbance of monolayers obtained using increasingly concentrated NP suspensions in the 20 nM–250 nM range. Grey plot (bottom curve) refers to APTMS functionalized substrates prior to NP deposition.

a standard deviation of 1 nm. The as-synthesized suspension had a NP concentration of $[Au] = 2.8$ nM, calculated according to the Lambert–Beer formula.^{24,25} After the concentration protocol, a 250 nM concentration of particles was obtained.

Five NP batches were prepared at decreasing concentrations (250 nM, 85 nM, 60 nM, 40 nM and 20 nM) and used for monolayer deposition under different conditions on pre-functionalized glass surfaces. Fig. 1b shows the absorption spectra of the monolayers obtained. A shift of SPR frequencies is detectable, due to plasmon coupling between neighbouring particles at higher packing densities.²⁶ The peak centred at about 380 nm is the absorbance signal arising from the APTMS layer, as it is possible to deduce from the grey curve (Fig. 1b), which is due to the APTMS functionalized substrate prior to any Au NP deposition.

Fig. 2 shows a collection of $1\ \mu\text{m} \times 1\ \mu\text{m}$ AFM images collected in tapping mode on as-deposited NP monolayers. The

Fig. 2 AFM scans of Au-MUA NP monolayers deposited on a SiO_2 substrate surface with decreasing Au NP concentration in the suspension used for deposition. (a) 250 nM, (b) 85 nM, (c) 60 nM, (d) 40 nM, (e) 20 nM. Image (f) is the calibration curve obtained from AFM scans to determine the NPs average inter-distance once the concentration of NPs in the deposition suspension is known. The scans and the calibration refer to the monolayers deposited at 2500 rpm. Scale bar in scan images is 200 nm.

Fig. 3 (a) Calibration curve for the determination of the final NPs surface coverage according to deposition parameters (concentration of colloidal suspension used for spin-coating and spin coating rate). The plot covers operative conditions in the 20 nM–250 nM NPs concentration range and 1500 rpm–4500 rpm spinning rate range at room temperature. (b) Surface coverage evaluated from AFM images (solid squares) and calculated from equation (1) (open circles) as a function of the solution concentration.

scans refer to NP layers deposited at 2500 rpm on pre-functionalized surfaces using colloidal suspensions with NP concentrations in the 20 nM–250 nM range. The thickness of the gold nanoparticle films was found to be in the 11 nm–13 nm range, consistent with monolayer coverage.¹ The apparent width of the individual nanoparticles was found to be about 45 nm; this broadening is a spatial aberration caused by the finite tip angle.²⁷ The single NPs are easily recognized in all cases, and a progressive decrease of the packing factor is evident with decreasing concentration. The average inter-particle distance was evaluated using ImageJ 1.38x Pictures Analyzer software²⁸ and the inter-particle distance is plotted as a function of the NPs suspension concentration in Fig. 2f. The inter-particle distance is found to obey an equation of the form: $D = A \log [Au]$, where D is the mean particle spacing between particles on the surface and A is a constant. In addition, the surface coverage of Au particles, Γ (NPs/cm^2), can be estimated from the optical absorbance spectra through the relationship:

$$A_{\text{surf}} = \frac{\Gamma \varepsilon_{\text{surf}}}{6.02 \times 10^{20}} \quad (1)$$

where A_{surf} is the absorbance of surface-confined species and $\varepsilon_{\text{surf}}$ is the surface extinction coefficient.^{18,25,26,29} A calibration plot to predict the surface coverage according to the main deposition parameters has been obtained from the optical data recorded from the deposited layers, and it is shown in Fig. 3a. The calibration is obtained for the same concentration range reported above and for deposition spinning rates from 1500 rpm–4500 rpm. The surface coverage obtained within this parametric range is from 4×10^{10} NPs/cm^2 – 2.1×10^{11} NPs/cm^2 . The effective surface coverage of Au particles, evaluated from AFM images, is in good agreement with the calculated values obtained from equation (1) (see Fig. 3b)

The adsorption of molecules onto a surface from a solution is frequently described by the Langmuir equation

$$K[Au] = \frac{\theta}{1 - \theta} \quad (2)$$

where θ is the fractional surface coverage of Au particles and K is the equilibrium constant for surface binding.³⁰ Eq. (2) allows the

calculation of the equilibrium constant for adsorption of colloidal Au on the amino-derivatized surface knowing the fractional surface coverage and the concentration of NPs in the liquid suspension. However, the Langmuir isotherm is predicated on the following two assumptions: (1) a particle cannot bind at sites where other particles are already present (*i.e.* no NP multilayers) and (2) there are no interactions between particles. While the first assumption is fulfilled because it is confirmed by the AFM data reported above, the second one cannot be quantitatively fulfilled because Au-MUA NPs are known to be colloidally stable and hence there must be electrostatic repulsion between particles. An improved model is the Frumkin isotherm,³¹ a generalization of the Langmuir approach:

$$KC^* = \left(\frac{\theta}{1-\theta} \right) e^{(f\theta)} \quad (3)$$

in which f , the Frumkin parameter, describes the inter-particle repulsion (or attraction); this form assumes that the apparent free energy of binding to the substrate is linearly dependent on NP coverage. The equation describes repulsive forces between particles when f is positive and attractive forces when negative. When $f = 0$ eq. (3) simplifies to eq. (2). Values of K are expressed in M^{-1} while f is dimensionless. The θ value can be calculated from Γ/N , where N is the surface coverage (NPs/cm²) for a cubic close-packed monolayer of 12 nm Au particles (3×10^{11} NPs/cm²). It is thus possible to evaluate K and f from a nonlinear least-squares (NLS) fit of the experimental data to eq. (3). For the 2500 rpm deposition the equilibrium constant was found to be $K = 3.9 \pm 0.7 \times 10^6 M^{-1}$, and the Frumkin parameter $f = 1.3 \pm 0.5$. Data taken from the 3500 rpm deposition yielded $K = 7.6 \pm 1 \times 10^6 M^{-1}$ and $f = 4.8 \pm 0.6$. The positive value of f indicates the presence of inter-particle repulsive forces, and these K values are consistent with values reported in the literature³² for studies on protein–gold interactions. The large equilibrium constant observed for Au particle binding is expected, owing to the strong electrostatic attraction between the Au-MUA NPs and the positively charged glass surface.

Au NP monolayers coated with sol–gel films

SiO₂ film. A 3-layered structure was made with an Au NP monolayer deposited on top of a sol–gel SiO₂ buffer layer, and eventually coated with a further sol–gel SiO₂ layer. The objectives of fabricating such a multilayer were: (1) to evaluate the possibility of performing the silanization on a sol–gel layer, (2) to verify the structural continuity of the sol–gel matrix around the Au NPs, and (3) to test the degree of morphology control of the multilayered structure. The entire procedure proved to be extremely reproducible. The resulting multilayers were transparent and red coloured, as is typically associated with the presence of Au NPs. Fig. 4 shows the optical absorption spectra of the samples, taken after annealing at 500 °C. The SPR band of the Au NPs is detectable in the absorption band maximum centered at 527 nm, which corresponds to a medium refractive index value of 1.42. This value is lower than that of dense silica (1.459³³), indicating some residual porosity of the silica layer. This is consistent with the fact that sol–gel silica layers can be considered fully densified only after annealing at temperatures greater than 1200 °C.³³ The optical spectra confirm that Au NPs

Fig. 4 Optical absorbance spectra of SiO₂-Au monolayer-SiO₂ multilayered samples. Plots refer to NP monolayers deposited at 3000 and 6000 rpm spinning rates.

did not undergo structural or morphological modification during the thermal treatment at 500 °C.

The TEM results on the multilayer sample annealed at 500 °C are shown in Fig. 5. The bright-field cross-section in Fig. 5a shows the planar configuration of the Au NPs monolayer, separated by 10 nm from the silicon substrate surface by the SiO₂ buffer layer, and coated with a 100 nm thick layer of pure SiO₂. The continuity of the Au NP monolayer is retained, and the morphological configuration of the overall film structure designed prior to sample realization was precisely retained. Moreover, the cross-sectional image of the sample shows that the sol–gel matrix homogeneously surrounds all the NPs. In Fig. 5b the planar view of the sample demonstrates that the Au NPs did not undergo major structural changes during annealing at 500 °C (see the high-resolution TEM image in Fig. 5c), and that they remained separated and homogeneously distributed inside the SiO₂ matrix. The TEM measured average cluster size is $D = 9.1$

Fig. 5 TEM results on the SiO₂-Au monolayer-SiO₂ multilayer film annealed at 500 °C: (a) cross-sectional bright-field TEM image, pre-set layers thickness of 10 nm (buffer layer) and 100 nm (cover layer) is retained; (b) planar view; (c) high-resolution image of a single Au NP and (d) histogram of the size distribution.

nm with a standard deviation of the experimental distribution $\sigma = 2.6$ nm. From the TEM image a nanoparticle coverage of about $(9.8 \pm 1.0) \times 10^{10}$ NPs/cm² can be estimated, in agreement with the value calculated using formula (2).

The TEM characterization is a confirmation of the degree of configurational control offered by this straightforward synthetic approach. It opens up the appealing possibility to design more complex multi-layered structures, and virtually any kind of sol-gel matrix can be employed in such systems since the problem of the chemical incompatibility between NPs and sol-gel precursor solutions is here completely bypassed. Moreover, any type of NP can be deposited, as long as the particles are capped with a carboxylic acid or other anionic headgroup. Separation of the NPs chemistry from that of the sol-gel, together with the good morphological control of the final multi-layers, are favorable points in terms of material design and engineering, which could eventually facilitate the scaling up of the whole synthetic process.

NiO film. Optical recognition of CO and H₂ using NiO and Au nanoparticles inside porous SiO₂ matrices has already been demonstrated.³⁻⁶ In this work reproduction of the Au/NiO coupling by using the bilayer composite architecture was explored. A NiO layer was deposited on top of a uniform Au NP monolayer, and tested as an optical gas sensor. The resulting multilayer film appeared homogeneous and optically transparent with a reddish colour indicating the presence of Au NPs. This was confirmed by the optical absorption analysis reported in Fig. 6. The SPR band due to Au NPs is centered at 531 nm, and the refractive index calculated from the plasmon frequency was calculated to be 1.48. This value is lower than those reported for crystalline NiO, which are typically in the 2.35–2.45 range.³⁴

XRD confirms that NiO layers deposited from the same solution on top of a silicon substrate, and in the absence of the Au NP monolayer are already crystalline after annealing at 500 °C for 30 minutes, as shown in Fig. 7.

Fig. 8 shows the TEM image of the Au NP monolayer coated with a NiO film. In this case it is more difficult to distinguish the Au monolayer from the NiO film as each are crystalline. From Fig. 8a it is clear that the thickness of the NiO layer is not uniform. The NiO layer shows larger pores (Fig. 8a) as well as

Fig. 6 Optical absorption spectra of NiO film and Au NP monolayer covered with NiO film measured at room temperature.

Fig. 7 XRD spectrum (monochromated Cu-K α radiation) of a NiO layer annealed at 500 °C for 30 minutes. The pattern presents signals associated to (111) and (200) lattice planes of NiO.

Fig. 8 TEM results on the Au monolayer–NiO film annealed at 500 °C: (a) cross-sectional bright-field TEM image; (b) enlargement of the region close to the substrate; (c) high-resolution (HR) image of Au NP and (d) Fourier transform (FT) of the HR image in (c) showing the presence of Au (111).

smaller pores between the crystalline grains (see Fig. 8b), and this is in agreement with the low refractive indices measured from the SPR peak position. HRTEM images showed the presence of Au nanoparticles to be mainly located close to the substrate (Fig. 8c).

The effect of high temperature exposure to different concentrations of CO in air upon the optical absorbance of the double layer films has been studied. Absorption spectra of films measured in air alone have been compared to those acquired while flowing the target gases inside the measuring chamber, and the resulting plots are shown in Fig. 9 for a testing temperature of 300 °C. Reversible gas-induced variations in the film absorption spectra were observed for all the tested concentrations.

Fig. 9 Absorption spectra of NP monolayer covered with NiO film in air (light grey line) and in 1% v/v CO (black line) measured at 300 °C.

The sample was dynamically tested at 610 nm at 300 °C and the results are shown in Fig. 10. The gas was introduced into the testing chambers at increasing concentrations in the 0.01%–1% v/v range and the concentration was subsequently decreased stepwise. The data clearly demonstrate a fast response rate for all gas concentrations, and that an easily measurable transmittance increase is detected even at the minimum gas concentration that was used. A detection threshold below 0.01% v/v CO is therefore established. The average response time was $\tau_{90} \sim 29$ seconds (τ_{90} = time to reach 90% of saturation signal after gas introduction into the testing chamber). The gas-to-air transient however was not ideal and clear hysteresis was observed. This can be related to slow desorption of intermediate carbonate adsorbates (CO_3^{2-} species) and is frequently invoked to explain variations in gas sensing behaviour of metal–metal oxide systems such as NiO–Au, ZnO–Au and TiO_2 –Au.^{35–37} The mechanism of CO induced optical transmittance change is considered to be related to a decrease in the activated oxygen concentration on the NiO particles surface which occurs when CO is oxidised to CO_2 . The consumption of activated oxygen (O^{2-}) on the NiO surface³⁸ during the oxidation process of CO results in a decrease in the positive hole density in the valence band of NiO lattice atoms.³⁹ This mechanism is known to be activated at temperatures higher

Fig. 10 Optical transmittance data: dynamic step-like response of the NiO–Au double layer to CO gas exposure; concentrations in air as shown. Data collected at $\lambda = 610$ nm and $T = 300$ °C.

Fig. 11 Comparison between CO detection levels (sensitivity) of NiO–Au double layer and of a NiO film with respect to CO concentration.

than 100 °C⁴⁰ and does not involve any catalytic oxidation of the target gas on the oxide surface.

A comparison of the sensitivity toward CO of the NiO–Au double layer film and that of a bare NiO film annealed at the same temperature (500 °C) was performed. The pure NiO film shows good response dynamics with an average τ_{90} of 34 seconds in the air-to-gas transient, slightly higher than the value measured for the NiO–Au film annealed at the same temperature. As is clear from the data presented in Fig. 11, where the change in normalized transmittance (*i.e.* $\Delta\text{Tr} \% = [\text{Tr}(\text{CO}) - \text{Tr}(\text{Air})]/\text{Tr}(\text{Air}) \times 100$) is shown, the Au–NiO films are at least a factor of two more sensitive to CO. The CO induced transmittance change is more pronounced for the NiO–Au system for all gas concentrations (filled data points). The optical signal-to-noise ratio is excellent despite the fact that the films are 400 nm thick, as measured by TEM (Fig. 8).

Conclusions

The objective to further improve sol–gel–NPs composite films by structural engineering has led to the design of a multi-step procedure to embed self-assembled monolayers of NPs inside different types of sol–gel matrices. Au NP monolayers have been deposited on silica and silicon substrates through surface silylation using APTMS molecules, which are capable of covalent attachment onto the substrate surface and to drive the NPs monolayer formation through specific interactions with the NPs surface. The obtained monolayers were successfully covered with SiO_2 and NiO coatings. This multi-step method allowed us to straightforwardly bypass the aggregation issues that can arise when mixing a NP suspension with sol–gel precursors solution, furthermore opening the possibility for controlled multi-layered nano-materials synthesis. NiO–Au film systems have been characterized as an optical CO gas sensor. The functional characterization revealed that the layers are optically sensitive to the target gas, showing good sensing dynamics and fast response/recovery kinetics. A sensing comparison between a NiO–Au layer and a pure NiO film permitted us to demonstrate the sensitivity-enhancing effect of Au NPs in the sensing performance of these materials.

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