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FUNCTIONAL NANOPARTICLES IN THIN FILMS AS SENSING MEDIA

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Abstract. The combination of unique properties offered by materials on the nanoscale with the increased role of surface chemistry in nanostructured solids makes core-shell nanoparticles extremely attractive for application to 'smart' thin-film coatings. Sensing properties of nanoparticle-based thin films were studied in several systems containing organic-coated semiconductor and metallic particles. In semiconductors, the interaction of organic shell and/or thin-film 'matrix' with the environment results in changes in the nanoparticle's surface states, altering the optical properties of the thin film. Measuring the electrical properties of thin films composed of metallic cores with hydrocarbon shells offers another mechanism to monitor the local environment through the swelling of the hydrocarbons in the presence of external compounds. These mechanisms and their potential application to novel sensors will be discussed.

1. INTRODUCTION

Sensors are a vital part of our lives. A humans' entire existence is based on interaction with the environment through our sensing organs: skin detects miniscule changes in temperature and pressure, eyes monitor the intensity and spectral properties of light, nose and tongue detect chemical composition of the surroundings through smell and taste. The human body is loaded with miniature micro- and nanoscale-size sensors and actuators connected through the brain, our main controller, and is the most complicated, efficient, durable, self-healing, and perfected machine ever created on earth. Exploration and development of sensing mechanisms analogous to naturally occurring sensors found in biological entities has been and continues to be a major focus of scientific endeavour.

Functional hybrid organic/inorganic core-shell nanoparticles offer the exciting combination of unique properties characteristic of materials on the nanoscale with controllable surface chemistry. With the growing demand for highly efficient miniature sensor networks capable of accurate, fast-response measurements, the multidisciplinary research of self-assembled nanostructured entities becomes more essential. This paper describes initial studies aimed at exploring the feasibility of two novel organic/inorganic nanoparticle thin-film systems as chemical sensing media. The first concept is based on the unique property of direct bandgap semiconductors to alter their optical response in the presence of a 'recognition element', the chemical adsorbent on the surface. This mechanism has a strong potential to find applications as an efficient opto-chemical sensor. The second concept utilizes metallic core/or-

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ganic shell nanoparticle-composed thin films and relies on the changes in the films' resistance induced by swelling of organics in the presence of external chemical compounds. This concept offers a capability to monitor the changes in electrical properties and can be applied to electro-chemical sensors. These two concepts and underlying mechanisms are considered below in more detail.

Opto-chemical sensing. A recent discovery has shown that some II-VI compound semiconductor nanoparticles synthesized in a liquid solution possess certain optoelectronic properties [1-3] that make them very promising for application to various optical sensors. Strong radiative transitions characteristic of these direct band gap compounds combined with quantum confinement effects inherent to particles on the nanoscale justified an extensive investigation of the photophysics of CdS nanoparticles. Moreover, these CdS nanoparticles exhibit very interesting photochemical properties when a foreign molecule adsorbs on the surface of such a particle under irradiation. Both absorption and luminescence kinetics undergo changes due to so-called interfacial reactions, i.e. electron transfer taking place between the electron-hole pair formed at the surface upon photo-excitation and the molecule adsorbed on the surface. This results in certain changes in the surface recombination velocity and electronic transitions between energy levels, which, in turn, leads to the respective changes in the emission properties and therefore offers an excellent mechanism for opto-chemical sensing. However, in order to utilize these nanoparticles in planar solid-state fiber optic sensors, these particles have to be immobilized on solid surfaces while maintaining their sensing capabilities. Although chemical quenching and enhancing of photoluminescence of CdS nanoparticles were studied in detail when suspended in a solution [4,5], very little work has been reported on the surface-analyte interactions of CdS nanoparticles incorporated in a solid matrix.

Synthesis of CdS nanoparticles in reverse micelle solution using AOT surfactant as a stabilizer in this work has led to particles with relatively bright photoemission, which after a prolonged UV irradiation resulted in a luminescence quantum yield Φ_L of ~ 40% [6]. The biggest challenge in immobilizing the nanoparticles into films on solid surfaces was the choice of a matrix or capping material that does not cause any property deterioration of the nanoparticles as a sensing medium. These resulting nanostructured films cast into and capped with various porous polymeric and sol-gel protective coatings were exposed to a series of organic com-

pounds. Photoluminescence data collected for these samples served for identification of the compounds and their concentrations. This paper offers the discussion of photophysical response in CdS nanoparticle-based thin films with respect to development of novel nanostructured opto-chemical sensors.

Electro-chemical sensing. The first demonstration of electro-chemical sensors, or 'chemiresistors', was dated back to the 1960s but it was not until 1982 when a cross-reactive array of gas sensors based on tin oxide (SnO_2) crystals was fabricated to detect multiple chemical species [7]. The mechanism for gas sensing with tin oxide was explained by the changes in resistance due to reactions between the analyte and oxygen-derived adsorbants on the tin oxide surface, i.e. the chemisorption of the oxidizing gas. Although this sensing mechanism was later employed in a wide range of similar electro-chemical sensors, or 'electronic noses', they were not found efficient due to irreversibility of oxidizing reactions. A new era of chemiresistors has begun with conductive fillers such as carbon fibers incorporated in organic polymer matrixes such as polystyrene or polyethylene, in which an increase in resistance was attributed to vapour-induced swelling of the polymer [8,9]. An essentially new type of chemiresistor was first described by Wohltjen and Snow in 1998 [10], and later by Cai and Zellers in 2002 [11]. Both research groups had used gold (Au) nanoparticles coated in-situ with alkanethiols as metal-insulator ensembles for chemiresistor sensors. The sensors showed improved response time, reversibility, and sensitivity compared to the nanoparticles incorporated in polymer matrix after-the-fact. Although a few similar reports utilizing gold nanoparticles followed in the literature, no precedents were found for this mechanism applied to other metallic nanoparticles. This work describes the first attempt to employ the same concept using sonochemically synthesized zero-valent iron (Fe^0) nanoparticles coated in-situ with hydrocarbon acids. The results are described in the following sections.

2. EXPERIMENT

CdS nanoparticles were prepared using the reverse-micelle method described previously in detail elsewhere [12,13]. Briefly, the nanoparticles were prepared within the water core of dioctyl sulfosuccinate sodium salt (AOT) reverse micelles in heptane with a [water] to [AOT] ratio of 4 (w_o). Two separate preparations employing different solution volumes (all other parameters were kept constant) were investi-

gated for their impact on nanoparticle crystal structure. For thin film preparation, solutions of CdS nanoparticles in AOT were dried under vacuum and then redissolved in < 1 mL hexane. The highly concentrated solutions of nanoparticles were deposited on Si wafers by spin-coating at 2000 rpm for 30 seconds. In some experiments, polymethylmethacrylate (PMMA) in chloroform, and a tetraethyl orthosilicate (TEOS)-based sol-gel solutions were used as top coating (capping) materials.

The organic-coated iron nanoparticles were prepared by injecting 200 μ L of $\text{Fe}(\text{CO})_5$ into a solution of dodecane containing the organic capping agent hexanoic acid at a concentration of ~ 0.01 M. The solution was contained within a nitrogen purged sonochemical reaction vessel (total volume 14 mL). Sonication was performed for 15 min active time using a one-second-on, one-second-off procedure at a power of ~ 20 W/cm² per pulse. Excess heat was removed with the use of an ice bath. The action of the sonochemical process resulted in the formation of a black solution, that when dried, yields a black, powdery material. For testing of the chemiresistor sensors, the nanoparticles were redissolved in a small amount of chloroform and deposited onto interdigitated platinum electrodes embedded into aluminosilicate supports purchased from Synkera Technologies, Longmont, CO.

UV-VIS absorption spectra were obtained using a Perkin Elmer Lambda 900 spectrophotometer and luminescence spectra were recorded on a Spec Fluorolog-3 photon-counting emission spectrometer. All luminescence spectra were corrected for the nonlinear response of the instrument. Luminescence decays were obtained using a home-built system equipped with a nitrogen laser source, band-pass filters for wavelength selection, an R928p photomultiplier as the detector, and an oscilloscope for data acquisition. Electrical measurements of chemiresistor thin films were conducted using an SRS model DS345 functional generator as an a.c. square wave signal source with an SRS model SR850 lock-in amplifier at frequencies in the 10 Hz – 100 kHz range in order to study the feed frequency effect on the film sensitivity. The changes in the film resistance were monitored via changes in the voltage on a 100 M Ω resistor built into a voltage divider circuit with a chemiresistor sample.

3. RESULTS AND DISCUSSION

The emission spectrum of AOT-capped CdS nanoparticles suspended in hexane demonstrated a broad, Gaussian-like emission peak and was iden-

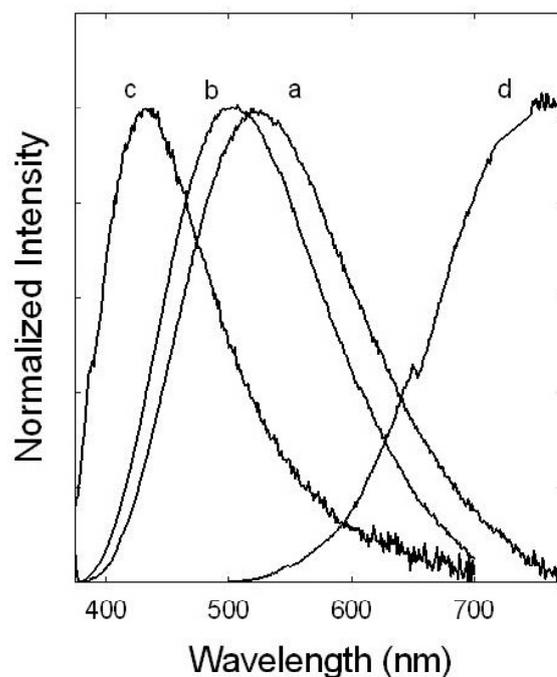


Fig. 1. Luminescence spectra of AOT-coated CdS nanoparticles in (a) solution, (b) thin film as is, (c) thin film PMMA-coated, and (d) thin film sol-gel coated.

tified as originating from trap states rather than from excitonic recombination due to the considerable red shift, broad transition distribution, and long decay [5,14]. The XRD analysis revealed the spectrum characteristic of a cubic crystal structure, and TEM was instrumental in determining the particle size which was relatively uniform and averaged around 3.8 nm [15].

As was mentioned earlier, II-VI compound semiconductor materials with trap-state emissions are well known for their sensitivity to their chemical environment [16]. Our solution studies using CdS/AOT nanoparticles demonstrated luminescence quenching by several sulfur-containing compounds (1-hexanethiol, dimethyl sulfoxide, and thiophene), which is in general agreement with other investigations of solution-based quenching of CdS nanoparticles [5,17]. The spectral properties CdS/AOT films prepared from a solution were found to be similar to those in solution (Fig. 1, spectra a and b). Since AOT alone is soluble in many organic liquids, the films were coated with protective top coatings for the PL quenching experiments. The PMMA coating was found to quench the CdS PL intensity and resulted in a noticeable blue shift of the PL peak com-

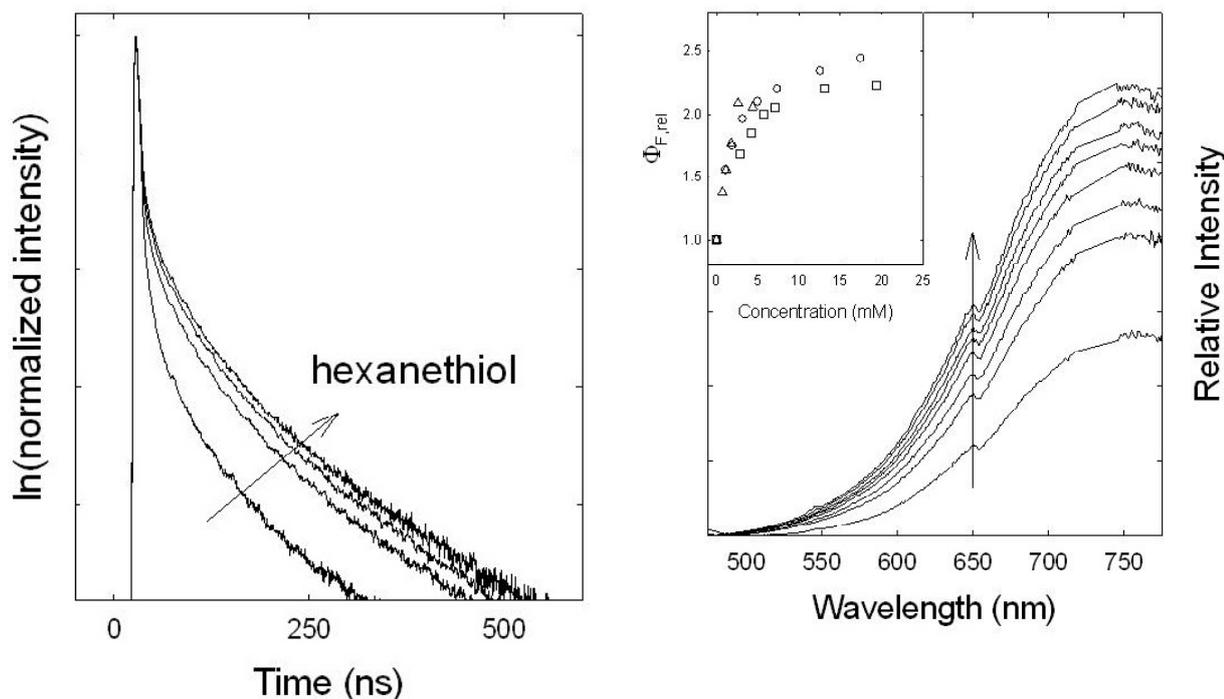


Fig. 2. (a) Luminescence decays obtained from PMMA-coated CdS/AOT nanoparticle films with hexanethiol; (b) Emission enhancement in sol-gel silica-coated CdS/AOT nanoparticle films with hexanethiol. Inset: Quantum yield results.

pared to uncoated CdS/AOT films (Fig. 1, spectrum c). PMMA-coated films were exposed to 1-hexanethiol, and the result was opposite to that in solution. While hexanethiol quenches CdS PL in solution, the films demonstrated longer PL decays (Fig. 2a) and an overall PL enhancement with an increase of hexanethiol concentration. However, the optical response was very slow, and most of the studied quenching compounds demonstrated a very low diffusivity in PMMA, which ruled out PMMA as a protective top coating for opto-chemical sensing applications.

Sol-gel coatings provided the best membrane characteristics with sufficient porosity and therefore high molecular diffusivity and fast response for the quenching studies. The presence of the sol-gel resulted in a considerable shift of the CdS PL peak toward longer wavelengths as well as the obvious peak broadening (Fig. 1, spectrum d). While the differences in the solution and solid spectra in Fig. 1 are within our experimental variance, PMMA and sol-gel had a well-pronounced effect on photophysics of CdS particles. Compared to PMMA chains, which diffuse into AOT micelles and passivate the shallow traps on the surface of CdS nanoparticles account-

ing for a more narrow distribution and higher energy of deeper emitting states, the sol-gel/CdS emission spectrum implies that the relaxation of deep trap states now occurs via carrier hopping to and between newly-created and broadly distributed shallow (low-energy) levels. As in the case of PMMA, exposure to hexanethiol has led to an increase in the PL intensity in sol-gel-coated CdS nanoparticle films (Fig. 2b). Since this phenomenon is contradictory to previous studies on the effect of hexanethiol on CdS luminescence in solution and makes the chemistry more complicated with the involvement of the coating materials, further studies are necessary in order to provide more detailed insights into the PL enhancing mechanism. PL quenching was observed with film exposure to dimethyl sulfoxide (DMSO). More studies are underway.

As a proof-of-concept for a Fe^0 nanoparticle – based chemiresistor, several films deposited onto interdigitated electrodes using the same procedure were stabilized at a.c. current and then exposed to nitrogen gas. The electrical response of one of the samples to three ~ 50 s N_2 gas exposure/purge cycles is shown in Fig. 3. The voltage samples were

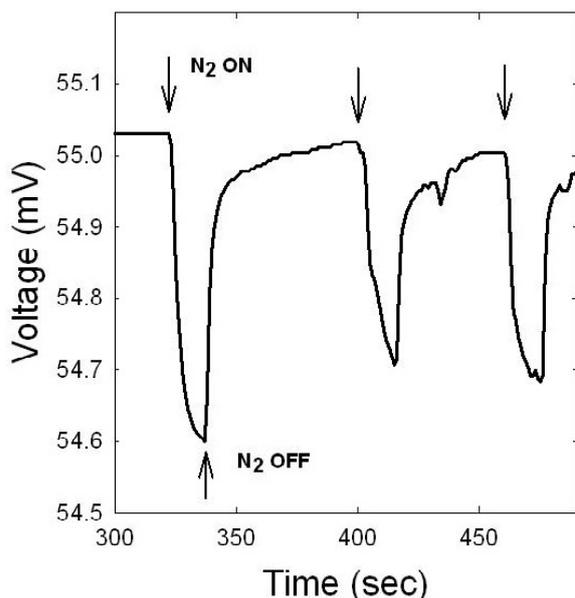


Fig. 3. Electrical response of Fe⁰/hexanoic acid nanoparticle thin film to exposure to N₂ gas under 0.5 Vpp 500 Hz feed square wave. The voltage drop on the voltage divider built-in resistor indicates an increase in voltage on a chemiresistor film.

collected at time intervals of 1 s (1 Hz sampling rate), with the 0.5 V peak-to-peak input signal locked with the output at 500 Hz. As seen in the figure, the electrical response saturates at a certain value, reaching its maximum change within approximately 10 s, which is comparable to the response of gold nanoparticles previously reported in [10,11]. It further returns completely to the baseline in ~ 20 s, indicating the 100% reversibility of the process. In order to achieve a maximal sensitivity of such a chemiresistor, the frequency of operation has to be adjusted to satisfy the requirements for charge/discharge time of the total circuit capacitance, formed by both the Fe core – insulative shell – Fe core structures within the film and parasitic capacitance of the a.c. circuit. While reducing the resistance to the electrical current and therefore improving the sensitivity of the film, higher frequencies do not allow a complete discharge of these natural capacitors and considerably affect both sensitivity and the response time. Furthermore, the electron transport in such chemiresistor sensors can be separated into two components: the transport through the metallic core which most likely follows the physics of electronic gas in conductors, and the transport inside the insulative shells. The latter can be attrib-

uted to either tunnelling through the shell barriers in case of sufficiently thin hydrocarbon coatings or electron hopping over the potential barriers between the states within the coatings at higher electric fields. Both mechanisms can definitely influence the overall film sensitivity and are worthy of further investigation.

4. SUMMARY

In this paper, we presented the results of our initial studies of two novel and essentially different core-shell nanoparticle systems incorporated in thin films and demonstrating sensitivity to external chemical species. AOT-capped CdS nanoparticles synthesized in reverse micelles were spin-coated on Si wafers and capped with thin layers of PMMA and TEOS-based sol-gel. The CdS/AOT films were found to undergo sufficient photophysical changes with both the presence of coating materials and the exposure to hydrocarbon compounds, which makes CdS nanoparticles attractive for thin-film opto-chemical sensing applications. Zero-valent iron nanoparticles capped with hexanoic acid were synthesized using a sonochemical approach and cast into thin films on interdigitated electrodes. The films' resistance was monitored under the a.c. signal and was shown to undergo sufficient changes under exposure to foreign gas species, making the films applicable to electro-chemical, or chemiresistor, sensors. In conclusion, both concepts were shown to be very promising for novel type chemical sensors.

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