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Enhancement of hydrogen sulfide gas sensing of PbS colloidal quantum dots by remote doping through ligand exchange

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ABSTRACT

Colloidal quantum dots (CQDs) are solution-synthesized semiconductor nanocrystals with size typically below 10 nm. Their large surface-to-volume ratio and abundant active surface sites, combined with the grain size effect and solution-processability make CQDs promising building blocks for low-cost and high-performance gas sensors. Here we employed the ligand exchange strategy to develop low-power and highly sensitive H_2S gas sensors based on PbS CQDs. Following the layer-by-layer spin-coating of PbS CQDs capped with long-chain oleic acid ligands from synthesis, a surface treatment using different inorganic salts was conducted for ligand exchange in air ambient at room temperature. Upon exposure to 50 ppm of H_2S at 135 °C, the resistance of all those sensors decreased shown as the response and the $Pb(NO_3)_2$ treatment yielded highest response (4218 at 135 °C) with shortest response/recovery time. We tentatively proposed a H_2S-induced and temperature-promoted p-to-n transition of PbS CQDs as the sensing mechanism and the role of $Pb(NO_3)_2$ treatment was attributed to an n-type remote doping effect realized by the ligand exchange, which was further supported by the energy dispersive spectrometry (EDS) and ultraviolet photoelectron spectroscopy (UPS) analysis.

1. Introduction

Hydrogen sulfide (H_2S), a colorless, flammable and highly toxic gas with a strong odor of rotten eggs, often results from the bacterial breakdown of organic matter in the absence of oxygen and may cause a wide range of health effects [1,2]. Exposure to H_2S at low concentrations (e.g. 30–200 ppm) may cause loss of smell and server injury to eye nerves; high concentrations of H_2S gas (500–2000 ppm) can result in rapid unconsciousness with permanent brain damage and even instant death. For the detecting and monitoring of H_2S, chemiresistive gas sensors employing metal oxide nanostructures based on SnO_2 [3–7], ZnO [8,9] and WO_3 [10,11] have been intensely investigated. For example, SnO_2 nanofibers functionalized with reduced graphene oxide nanosheets exhibited a sensitive response of 35 toward 5 ppm of H_2S at 200 °C [6]. CuO-functionalized WO_3 nanowires were sensitive to a ppm level of H_2S at the operating temperature of 300 °C [11]. Overall, their sensitivity at lower operating temperature remains to be improved in order to achieve low-power and highly sensitive H_2S gas sensors.

We recently reported sensitive, low-temperature H_2S chemiresistive gas sensors based on PbS colloidal quantum dots (CQDs) [12], in which a ligand exchange treatment making use of $NaNO_2$ was conducted to ensure excellent access of gas molecules to PbS CQD surfaces and sensitive response [13]. Their extremely large surface-to-volume ratio and abundant active surface sites, combined with the grain size effect and solution-processability make CQDs promising building blocks for low-cost and high-performance gas sensors.

In this work, we rely on the ligand exchange strategy to enhance the H_2S-sensing performance of PbS CQD gas sensors. We applied screening techniques and focused mainly on simple inorganic salts for discovering appropriate ligand systems. We demonstrated that the H_2S-sensing of PbS CQD gas sensors could be significantly enhanced by a ligand exchange treatment using $Pb(NO_3)_2$ and the H_2S-sensing mechanism of $Pb(NO_3)_2$-treated PbS CQDs was

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discussed. The versatile ligand exchange may offer CQD materials desirable gas-sensing properties and thereby open up interesting opportunities to CQD gas sensors.

2. Experimental

2.1. Sensor fabrication and testing

The oleic acid (OA)-capped PbS CQDs were synthesized via an organo-metallic hot-injection route [12,13]. The average diameter of the cubic-lattice PbS CQDs was estimated to be 4.0 nm with a relative size dispersion of 7.5% [13]. Briefly, the lead precursor was prepared by heating 1.8 g (8 mmol) of PbO in a mixture of 6 mL of OA and 20 mL of 1-octadecene (ODE) at 80 °C for 8 h. Then the solution was heated to 120 °C under nitrogen, followed by the injection of the sulfur precursor formed with 720 μL (4 mmol) of hexamethyldisilathiane (TMS) and 10 mL of ODE. After injection, the reaction solution was cooled forcedly by a cold water bath. Finally, the products were rinsed and dispersed in octane at a concentration of 50 mg/mL. The layer-by-layer film deposition followed by the ligand exchange treatment was carried out inside a fumehood in air ambient at room temperature. We employed five different inorganic salts for comparison, resulting in the so-called $NaNO_2$-, $NaNO_3$-, $Bi(NO_3)_3$-, $Pb(NO_3)_2$- and NH_4Cl-treated PbS CQD gas sensors. 3-Mercaptopropionic acid (MPA), a commonly used short ligand in PbS CQD solar cells, was also included for comparison. Typically, three drops of the PbS CQD solution (50 mg/mL in octane) were dropped on the alumina ceramic substrate pre-patterned with interdigital Ag electrode and spun at 2500 rpm for 15 s. Five drops of the $Pb(NO_3)_2$ methanol solution (10 mg/mL) were dropped onto the PbS CQD film for the ligand exchange for ~45 s and then spun at 2500 rpm for 10 s to dry the solvent. This soaking-try treatment was repeated. The film was then washed by methanol flush and spun dry for three times. This film deposition and ligand exchange treatment process was repeated and resulted in two-layered PbS CQD films with a thickness of ~50 nm in the final sensor devices. The as-deposited PbS CQD film without the ligand exchange treatment which is termed as the untreated sample was also prepared for comparison.

The PbS CQD gas sensors were tested following similar steps described in our prior work [12,13]. The static method where the gas concentration was determined by the volume ratio was employed and the gas-sensing tests throughout the work were performed on fresh-made sensor samples under atmospheric pressure with a relative humidity of 45 ± 1% at 25 °C. The accuracy of the temperature control is ±2 °C and the gas-sensing measurement was conducted until the temperature reaches steady state. It takes 2–10 min to reach a steady state depending on the temperature. The H_2S-sensing response is defined as the ratio of the larger value to the smaller value of the sensor resistances in ambient air (R_a) and in the H_2S gas (R_g). To be more specific, we defined the response signal direction as positive if the resistance decreases upon H_2S gas exposure shown as the n-type response (R_a/R_g). Otherwise, the direction of response signal is defined as negative in the case of p-type response ($-R_g/R_a$) where the resistance increases upon H_2S exposure. In both cases, the response time (T90) and the recovery time (T10) are the time for the sensor to reach 90% of its final response upon H_2S gas exposure and the time for the sensor response reduces to 10% of its maximal value after gas release, respectively.

2.2. Materials characterization

The Fourier transform infrared (FTIR) spectra and UV–Vis absorption spectra of the PbS CQD films deposited on quartz glass substrates were obtained using a Bruker Vertex 70 infrared spectrometer and a PerkinElmer Lambda 950 UV/Vis/NIR spectrophotometer, respectively. The transmittance in the low wavenumber range of FTIR spectra is not obtainable because of the absorption of quartz glass substrates. The compositions of the PbS CQD films were characterized by scanning electron microscopy (FEI Sirion 200) equipped with an energy dispersive spectrometer (EDS). The ultraviolet photoelectron spectroscopy (UPS) measurement was performed using an Omicron Nanotechnology system with a base pressure of 2×10^{-10} Torr. It was carried out by using an unfiltered HeI (21.21 eV) gas discharge lamp source with an energy resolution of 0.1 eV. The work function (W_s) was calculated by the difference of HeI and cutoff energy (E_{cutoff}). Similarly, the valence band energy (E_V) was calculated by the difference of Fermi energy (E_F) and the highest occupied molecular orbital energy (E_{HOMO}).

3. Results and discussion

3.1. Screening the short ligand for exchange

One of the distinctive properties of CQDs is the surface capping layer composed of long-chain organic ligands (e.g. oleic acid), which dynamically solvates nanocrystals and prevents further growth/aggregation in synthesis [14,15]. Attractively, these long-chain ligands are readily exchangeable with other short ligands, thereby allowing for a versatile manipulation of CQDs in many different environments through ligand exchange [16–18], for example, the ligand exchange making use of monovalent halide anions has led to reduced inter-quantum-dot spacing and enhanced charge-carrier mobility with controlled doping in PbS CQD photovoltaics [19,20]. In our OA-capped PbS CQDs, the OA ligands serve as metal coordinating groups as well as solvophilic groups, forming a tightly bound long-chain (18 carbons) organic shell which stabilizes the inorganic PbS core and ensures their solution processability in octane. This insulating organic shell on the other hand limits the gas adsorption as well as charge transfer and it has to be removed to allow for the access of gas molecules to CQD surfaces. According to the FTIR spectra (Fig. 1), the aliphatic C–H stretching bands at 2857–2920 cm^{-1} characteristic of the OA ligands as observed in the untreated PbS CQD film were significantly attenuated after the treatment using $NaNO_2$, $NaNO_3$, $Bi(NO_3)_3$, $Pb(NO_3)_2$, NH_4Cl and MPA respectively, suggestive of the removal of most oleate ligands. For an effective ligand exchange treatment, the OA ligands could be stripped off and replaced by ligands with strong affinity to CQD surface, such as the anions of the metal salts (such as NO_2^- and NO_3^-) or the thiol groups (—SH) of MPA in this study. The removal of OA ligand was considered as a perquisite to enable gas adsorption and charge transfer in PbS CQD gas sensors.

We then preliminarily compared the H_2S-sensing properties of PbS CQDs treated with different ligands (Fig. 2). Details of the

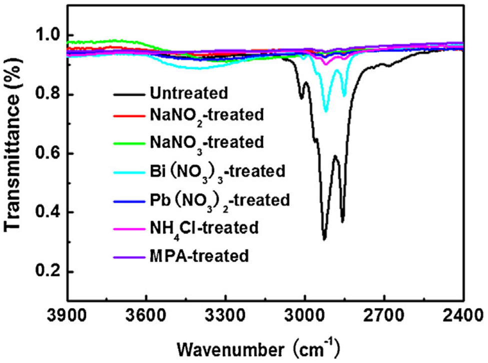

Fig. 1. FTIR spectra of the PbS CQD films treated with different short ligands.