Novel Photoluminescence Properties of Surface-Modified Nanocrystalline Zinc Oxide: Toward a Reactive Scaffold

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Nanocrystalline zinc oxide has been functionalized with 11-triethoxysilylundecal to introduce chemical reactivity for subsequent molecular attachment while preserving its unique photoluminescence (PL) properties. Silane bonding is confirmed using FTIR and photoelectron spectroscopy, with a total Si concentration of 3 to 4 atomic %. PL measurements demonstrate a 2-fold enhancement of its UV peak and maintenance of its visible peak compared to control samples. Enhancement of the UV peak is likely due to a decrease in the surface-dependent nonradiative recombination process. These results lay the framework for sensor fabrication, with the aldehyde groups available to bind analytes that would alter the PL spectrum.

Introduction

Nanocrystalline zinc oxide (nano-ZnO) is a wide band gap semiconductor possessing a large excitonic binding energy and a unique photoluminescence (PL) spectrum. These properties make nano-ZnO a promising material for use in the areas of photonics, electronics, and sensors. For example, the ability of nano-ZnO to act as a gas sensor has been demonstrated by utilizing changes in its electrical resistivity.[1,2] Our research focuses on the utilization of nano-ZnO as an optical sensing material. The unique PL spectrum of nano-ZnO consists of two emission peaks, one in the UV due to near-band-edge emission and the other in the visible (green) region due to oxygen vacancies caused by crystalline defects. The presence of these two PL emission peaks may allow for the use of nano-ZnO as a real-time optical sensing platform if changes (i.e., emission intensities, emission maxima shifts, and/or peak proportionalities) within the inherent PL spectrum can be induced upon a surface-binding event. However, to detect the binding of specific target ligands, the surface of the nano-ZnO must be functionalized with appropriate receptors. In the process of rendering the nano-ZnO surface reactive, it is quite possible that the inherent PL spectrum could be adversely affected. Previous studies have shown that surface alterations generally stabilize the UV emission but quench the visible emission.[3−9] The versatility of the two inherent emission peaks of the nano-ZnO is lost, and functionality as a sensor platform may be adversely influenced. Furthermore, those studies did not introduce any level of chemical functionality and therefore are not satisfactory techniques in the development of optically responsive nano-ZnO sensors. In this letter, we describe a surface-functionalization approach that, while generating nano-ZnO surface reactivity, maintains the inherent bimodal PL signal.

Experimental Section

Organosilane Surface Modification. Nanocrystalline ZnO nanorods (Nanocerox, Inc.) with a mean particle size of 10−20 nm wide by 100−300 nm long, as determined by TEM, were dried overnight under vacuum at 200 °C before use. The nano-ZnO was suspended by means of sonication via a Branson Cell Disruptor in 95% ethanol/5% H_2O at pH 5 (adjusted with acetic acid). The organosilane linker (11-triethoxysilylundecanal, Gelest, Inc.) was added, without purification, to achieve 1:2.5 w/w ZnO/silane and was allowed to react for 1 h at 75 °C. The powders were collected by filtration and washed extensively with 100% ethanol. The samples were cured at 110 °C for 10 min and stored in a desiccator.

FTIR Analysis of Surface-Modified Nano-ZnO. FTIR spectra of the powdered materials were acquired using a BioRad Fourier transform infrared spectrometer (model FTS-60A). Potassium bromide (KBr) pellets were prepared for FTIR analysis using 200 mg of KBr and 15 mg of sample. A background scan was performed using pure KBr and was automatically subtracted from the data. A total of 32 scans were averaged for each sample.

Optical Characterization. The photoluminescence spectra of the powdered materials were acquired using a Fluorolog 3 fluorescence spectrometer (Horiba Jobin Yvon, Inc.) equipped with a solid sample holder accessory at an excitation wavelength of 325 nm. Three scans were acquired and averaged together for each sample.

XPS Analysis. Samples for XPS analysis were prepared by suspending 60 mg of the unmodified nano-ZnO or the silane-modified nano-ZnO in 30 mL of the aqueous ethanol solution and sonicating for 3 min using a Branson Cell Disruptor. The resulting dispersion was poured over a small copper coupon (1 cm^2, cleaned with dilute hydrochloric acid and distilled water) in a Gooch crucible. Copper coupons were used as a means to fix the powders and to minimize surface charging that may occur as a result of uncompensated electron ejection during analysis. The solution was allowed to evaporate/drain through the crucible overnight at room temperature. This procedure resulted in a uniform coating of the nano-ZnO powder onto the copper coupons. The metal substrates were mounted as is on sample stubs using conducting silver paint on the back side of the substrate holder. The XPS spectra were acquired using 100 W Al Kα X-rays.

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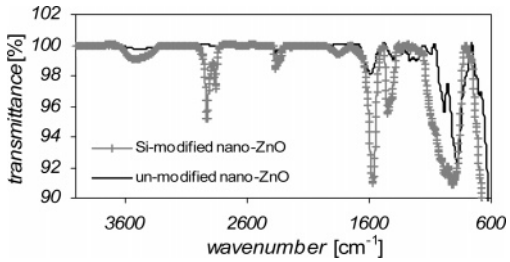

Figure 1. FTIR spectrum of the silane-modified nanocrystalline ZnO. The appearance of the C−H stretch at 2930−2858 cm^{-1} confirms the presence of the organosilane linker. The band centered at ca. 900 cm^{-1} indicates covalent attachment of the organosilane linker to nano-ZnO.

Results and Discussion

Nano-ZnO can be derivatized with a variety of surface modifiers to introduce the desired chemical reactivity for subsequent covalent attachment. In this case, we have surface-functionalized nano-ZnO powders using a silane cross-linking agent. Although the silylation of metal oxide surfaces has previously been achieved,[10] our approach brings together three aspects not previously considered concurrently, namely, (1) covalent attachment of the linker, which is required to prevent dissociation during subsequent interactions; (2) introduction of a chemical reactive group to allow for subsequent molecular derivatization; and (3) stabilization of both emission bands of the nano-ZnO inherent PL. The silane agent used in this work, triethoxysilylundecanal, forms a Zn−O−Si covalent bond at the nanopowder surface and introduces an aldehyde group at the other end of a 10-carbon spacer for the coupling of analytes, including biomolecules, containing primary amino groups. We have employed an aqueous alcohol deposition technique[11] to provide for simultaneous surface hydrolysis and organosilane condensation steps. The presence of the surface-attached cross-linking agent was verified through FTIR analysis (Figure 1). The aldehyde moiety is confirmed by the characteristic C−H stretching band at 2930−2858 cm^{-1} and the C═O stretching band at ca. 1600 cm^{-1}. The O−H stretch is present at ca. 3500 cm^{-1}, and the CH_2 bend of the aliphatic groups appears at ca. 1450 cm^{-1}. The formation of a covalent Si−O−Zn bond is evident by the broad band centered at approximately 900 cm^{-1}. FTIR validates not only the presence of the amine-reactive silane agent but also its covalent attachment. Analysis of the surface-modified nano-ZnO indicates that the complex is remarkably stable without silane dissociation after more than 12 months of room-temperature storage within a desiccator (data not shown).

X-ray photoelectron spectroscopy (XPS) was used to determine the changes occurring on the surface of the nano-ZnO powder as a result of silane treatment. For an untreated sample, measurement of the O/Zn atomic ratio by comparison of the areas of the O 1s and Zn 2p peaks, divided by their sensitivity factors, confirms a 1:1 stoichiometric ratio. For the silane-treated sample, the atomic percentage of Si in the sample (based on comparison of the Si 2p peak area to the areas of all other detected elements weighted by appropriate sensitivity factors) is 3% to 4%. The Si/Zn atomic ratio, obtained from the Si 2p and Zn 2p peaks, is 0.14. Note, however, that the *surface* concentration is significantly higher. As discussed previously, the typical length of the nano-ZnO particles is 100−300 nm, and the typical width is 10−20 nm. Assuming a 200-nm-long, 15-nm-wide ZnO cylinder, the surface area-to-volume ratio is 0.27. Combined with the measured Si/Zn atomic ratio, this indicates that approximately half of the Zn atoms on the surface are involved in Zn−O−Si bonding. Note that this is a very rough approximation because the ZnO particles are polydisperse, and XPS interrogates only 50−100 Å deep.

Figure 2 shows the results of the O 1s, C 1s, Zn 2p, and Si 2p XPS scans. Because the peaks are not fully resolved as a result of inherent energy resolution limitations of the XPS technique, deconvolution of the O 1s peaks is included. As shown in Figure 2a, silane adsorption dramatically affects the O 1s spectrum, as evidenced by the growth of a high-binding-energy (BE) oxygen peak. The O 1s peak due to ZnO appears at a BE of 531.3 eV, and silane adsorption gives rise to an additional broad O 1s peak at 533.1 eV. The emergence of the high-BE peak is due to oxygen atoms present in Zn−O−Si and in the aldehyde groups because aliphatic carbonyl groups typically exhibit a value of 532.3 eV.[12] Mainly because of final state effects, the formation of a silane bond to the zinc oxide surface is also expected to shift the O 1s peak to higher BE, similar to the situation observed for silicon bonding to semiconducting titanium dioxide.[13] The two O 1s components in the silane-treated sample have approximately equal intensities. At first glance, this seems contradictory to the relatively small silane concentration. However, because the adsorption of a silane molecule occurs via Si−O−Zn bond formation, an increase in intensity of the higher-BE component occurs at the expense of the lower-BE one. Furthermore, each silane molecule has an oxygen-containing aldehyde group that is at the top of the ZnO−silane surface. Because of its surface sensitivity, XPS more efficiently detects the silane-induced O 1s peak compared to the bulk and surface ZnO oxygen atoms that are not involved in silane adsorption.

The C 1s peak at 285−286 eV in the untreated sample (Figure 2b) is due to adventitious carbon contamination that is almost always present for samples that are analyzed without in-situ sputtering or heating. The higher-BE C 1s peak at 290.1 eV is due to adsorbed carboxylate or carboxylic acid groups resulting from the acetic acid used in preparing the samples. Although the untreated and treated C 1s spectra are very similar, a comparison of the relative intensities of the two carbon peaks indicates that the lower-BE peak has increased in intensity relative to the higher-BE carboxylic acid peak in the case of the treated sample. This is consistent with silane adsorption because this molecule contains a long aliphatic carbon chain. The Zn 2p spectrum (Figure 2c) shows a decrease in zinc intensity after silane treatment. The decrease in zinc concentration is due to two effects. One is the fact that carbon, oxygen, and silicon are being introduced into the sample, and the other is that the silane is shielding the zinc by being adsorbed on top of it. Figure 2d shows the Si 2p region, confirming silane adsorption.

To probe the influence of the organosilane surface functionalization on the inherent optical properties of nano-ZnO, room-temperature PL spectroscopy was performed on both the silane-modified and control (unmodified) nano-ZnO powders (Figure 3). The presence of the cross-linking agent induces a stable, reproducible 2-fold enhancement of the UV emission while retaining the inherent visible emission intensity. The UV emission peak at 380 nm in the unmodified material exhibits an intensity of approximately 25 000 cps versus an intensity of approximately

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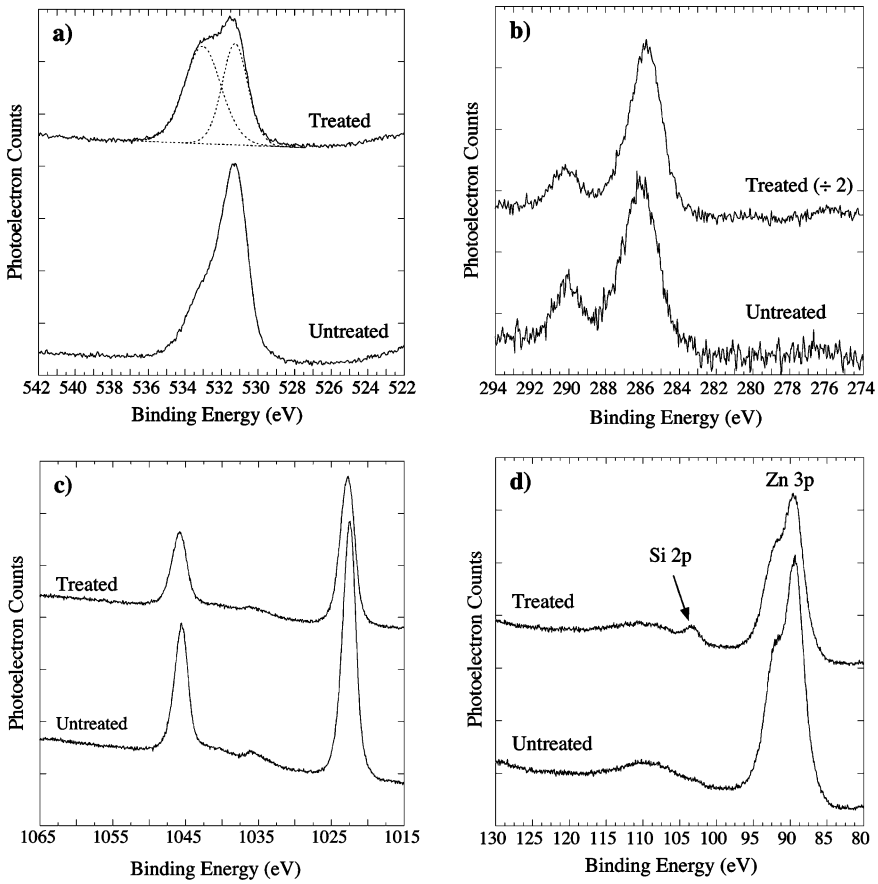

Figure 2. Al Kα XPS spectra of silane-modified and unmodified nano-ZnO: (a) O 1s, (b) C 1s, (c) Zn 2p, and (d) Si 2p. The results of peak fitting are included (dashed lines) for the treated O 1s spectrum.

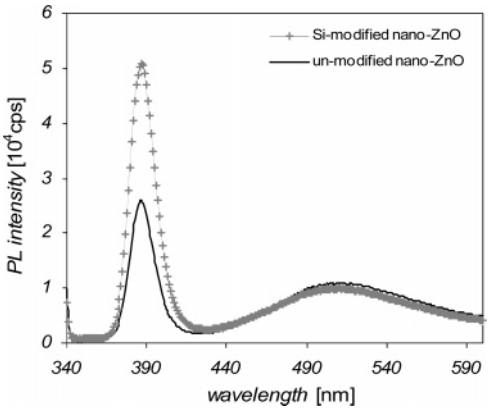

Figure 3. Photoluminescence (PL) spectra of silane-modified and unmodified nano-ZnO. Silane treatment results in a marked enhancement of the UV emission peak while maintaining the visible emission peak.

50 000 cps in the silane-modified ZnO. The intensity of the visible emission peak at 510 nm is essentially unchanged in the control and modified nano-ZnO. These results differ from recent surface modification approaches that have focused on polymer capping,[5,7,14] modified annealing procedures,[9] and the incorporation of adsorbed ions.[4,6,8] These techniques stabilize the UV emission at the expense of a quenched visible emission peak. However, in one study, the retention of a bimodal response has been demonstrated by surface capping with an alkyl-amine compound during the growth process, resulting in a UV emission of low intensity accompanied by a predominant visible emission, with each being dependent upon growth temperature conditions.[15]

By combining the surface chemistry and photochemistry knowledge that we have gained with a model proposed in the literature by van Dijken et al.,[16] we can hypothesize as to why the induced changes in the inherent PL spectrum occur. The van Dijken model consists of three general processes that competitively contribute to the relaxation of a photoexcited nano-ZnO molecule. Two of the processes are radiative in nature, resulting in the UV and visible PL emission peaks, and one process is nonradiative in nature. The radiative process that is responsible for the production of the UV PL peak results from the excitonic recombination of an excited electron and its hole, excited from the conduction band to the valence band, and does not involve surface trapping of the excitonic pair. The radiative process that is responsible for the visible PL emission results from the excitonic recombination of an excited electron that has been trapped at the surface and tunnels back into the molecule to recombine with its hole in a non-surface-related manner. The nonradiative process results from the recombination of a hole and an electron trapped at the surface. Because our silane treatment of the nano-ZnO results in changes to the surface, the occurrence of the entirely surface-dependent nonradiative process is reduced, and the relaxation process is forced to proceed via the non-surface-dependent (UV) and the less-surface-dependent (visible) radiative pathways. The enhancement of UV emission occurs because it is the higher-energy process and therefore energetically less stable. The visible emission is maintained by the nonpassivation of

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lattice defects (i.e., oxygen vacancies that can serve as deeply trapped holes). This varies from other surface-modification approaches explored to date. For instance, Usui et al. performed a detailed investigation regarding the influence of particle size and charged surfactants on the optical properties of nano-ZnO crystals that were synthesized in the presence of surfactants.[17] A surfactant molecule with a relatively high local negative charge passivated the defect (green) emission due to oxygen ions, during micelle formation, occupying vacancies on the positively charged nano-ZnO surface. This is not expected to occur within our surface-modification approach where the nano-ZnO particles are being modified in the bulk state, not during the growth process. When the modification occurs concomitantly with the growth process, the defects are more available for passivation because they are formed in the presence of the charged modifiers, and the nanoparticle size distribution can be controlled. Given the dimensions of the nanorods used in our studies, it is expected that a large portion of the defect sites will be inaccessible to the somewhat bulky organosilane surface modifier. Additionally, the largely aliphatic modifier is not favorable for effective passivation of the oxygen vacancies because the oxygen species that could passivate the oxygen vacancies can be contributed only from the electronegative oxygen of the aldehyde group. This is unlikely because the attraction is weak compared to the formation of the Si−O−Zn covalent bond. As the silane surface coverage increases, the retention of the bimodal response is anticipated. However, the relative intensities of UV and visible emission are expected to be influenced by the particle size distributions, as in Usui et al. Investigations are underway to narrow the nano-ZnO broad size distribution and understand how particle aggregation influences surface-modified nano-ZnO optical properties.

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Conclusions

We have described a novel surface-modification approach that results from the covalent attachment of an organosilane linker to nano-ZnO, which introduces an amine-reactive functionality for subsequent molecular (e.g., biomolecule) derivatization. This surface functionalization approach results in stable (minimum of 12 months), enhanced (2- to 3-fold increase), reproducible UV emission while maintaining the visible emission, which has been quenched in most other modification studies to date. Although the silane linker investigated here incorporates an amine-reactive aldehyde, other linkers are available to introduce alternative reactive groups. This could include multiplexing through the deposition of several organosilane linkers at one time to introduce multiple reactive groups and to provide supplementary attachment sites to bind a series of target biomolecules. Upon biomolecule covalent attachment, the nano-ZnO powders can be optically probed for further induced changes in peak intensities and/or peak shifts. Experiments in this area are currently underway.

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