Attachment of Quantum Dots and Gold Nanoparticles on ZnO Nanorods

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ABSTRACT

ZnO nanorods were fabricated on various substrates with precursor solution of zinc nitrate hexahydrate ((ZnNO₃)₂·6H₂O) and hexamethylenetramine (C₆H₁₂N₄) (1:1 molar ratio) at 95°C for 9 hours. In order to optimize the light absorption characteristics of ZnO nanorods, CdSe/ZnS core-shell quantum dots (QDs) of various diameters were attached to the surface of ZnO nanostructures grown on ITO and gold-coated silicon substrates. Density of quantum dots was varied by controlling the number drops on the surface of the ZnO nanorods. For a 0.1 M concentration of QDs of 10 nm diameter, the photoluminescence (PL) intensity increased as the density of the quantum dots on ZnO nanostructures was increased. For quantum dots at 1 M concentration, the PL intensity at 385 nm increased at the beginning and then decreased at higher density. We will discuss the observed changes in PL intensity with QD concentration with ZnO-QD band structure and recombination-diffusion processes.

Keywords: nanorods, ZnO, nanotubes, quantum dots, gold nanoparticles

1 INTRODUCTION

Zinc Oxide as a wide band gap semiconductor holds great deal of appeal in current semiconductor research. Due to its direct wide band gap (3.7 eV), ZnO is an excellent semiconductor material for optoelectronics applications. ZnO nanorods grown by hydrothermal techniques are of great interest for potential applications in photovoltaic and optoelectronic devices. Wet chemical methods hold great promise for fabricating highly oriented ZnO nanorods at low temperature. In this study we investigate the optimization of the optical absorption properties by a low temperature, chemical bath deposition technique. Fabrication of ZnO nanotube and nanorod arrays with gold nanoparticles and quantum dots is crucial for improving the physical properties of nanomaterials and for developing new generation of nanostructured devices such as solar cells. Quantum dots (QDs) made of CdS, CdSe, InP, or InAs are intensely studied for photovoltaic applications. QDs provide the ability to match the solar spectrum by changing particle size. In addition, QDs also improve the efficiency of the device by generating multiple electron-hole pairs per photon [1]. Gold nanoparticles are also efficient in passivating the nanostructures, defect surfaces and enhancing the optical absorption of ZnO.

2 EXPERIMENTAL TECHNIQUES

Synthesis of ZnO nanorods by chemical bath deposition method has been previously published and will not be repeated here [2, 3]. Nanorods grown on various substrates were examined by X-Ray Diffraction (XRD) to identify the crystallinity and phase purity of the nanorods. The morphology and microstructure of as-prepared ZnO nanorods were observed by scanning electron microscopy (SEM). A room temperature photoluminescence (PL) measurement with the excitation source of 325 nm was employed to characterize the optical properties of the as-grown ZnO nanorods arrays. PL measurements were made on a Jasco FB 6500 spectrofluorometer excited by a wavelength of 325 nm where the measurement emission wavelength ranged from 350 nm to 650 nm.

2.1 Attachment of Gold Nanoparticles

GNPs in this study were kept in sodium citrate solution. For attachment to ZnO nanorods, GNPs had to be separated from sodium citrate which prevented the nanoparticles from sticking together. A centrifuge process was applied to get rid of the sodium citrate as follows: (1) 500 ml of dark red gold nanoparticles solution was transferred to the centrifuge machine which was set at a speed of 13,000 rpm for 2 minutes. (2) The supernatant after the first centrifugation was saved in the container for the second centrifugation at 14,000 rpm for 5 minutes. The pellets, which were big particles and aggregates, were discarded. (3) The supernatant of the second centrifugation was discarded, and the pellet was kept and dissolved in 500 µL of high purity water, then centrifuged at 14,000 rpm for 10 minutes. (4) Again, the pellet of the third centrifugation was kept and re-dissolved in 100 µL of high purity water. After third centrifugations, the gold nanoparticles appeared to be red purple when observed by the naked eye. A 10 µL needle syringe was prepared to measure the volume of the gold
nanoparticles. A spot in the ZnO nanorod substrate was chosen to attach the gold nanoparticles. 5 µL of gold nanoparticles were transferred to the selected spot, and then the sample was dried dry in a desiccator before a PL measurement was taken. After the PL spectrum measurement, a new drop of gold nanoparticles (5 µL) was added to the same spot, which resulted in doubling of the concentration of gold nanoparticles. The procedure was repeated and the dried sample was examined by a PL measurement after changing the concentration.

2.2 Attachment of Quantum Dots

The quantum dots in our attachment experiment were purchased from Evident Tech. Company, with CdSe/ZnS as the material system, appearing red in color. The initial concentration of QDs was 1 µM in aqueous solution assuming that no citric salt was present. Therefore, there is no need to centrifuge it through multiple cycles. In order to obtain 0.1 µM QDs, 50 µL of the quantum dots was dissolved in 450 µL of high purity water. The attachment procedure was the same as that for gold nanoparticles.

3 RESULTS

Figure 1 shows a typical SEM image of the as-grown arrays of ZnO with high density of GNPs concentrations on ITO substrates. The ZnO nanorod/GNPs composites appear as small white dots decorating the nanowall background. Figure 2 shows SEM images of ZnO nanorods before and after attaching quantum dots. The ZnO surfaces in Figure 2 (a) were flat and even without any lumps or rough areas, compared with nanorods after attaching quantum dots. (Figure 2(b)).

3.1 PL Analysis of Gold Nanoparticles and Quantum Dots

Figure 3 shows the PL data for ZnO nanorods after attaching gold nanoparticles at different concentrations. Three sets (1), (2), and (3) of ZnO nanorod samples were examined. In order to make the PL intensity data comparable, one should make sure that the coated area was placed in the same position by using the visible excitation wavelength to detect the coated area before adjusting to the 325 nm wavelength.

The concentration of gold nanoparticles was calculated based on Equation 1 with absorption at a wavelength of 450 nm [4]. Absorption profile of gold nanoparticles was measured using the HP UV-Visible absorption spectrometer.

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N = \frac{A_{450} \times 10^{14}}{d^2 - 0.295 + 1.36 \exp\left(-\frac{(d - 96.8)^2}{78.2}\right)}
\]

Where \(N\) is the number density of gold nanoparticles in nps/ml, \(A_{450}\) is the absorption at 450nm, \(d\) is the average diameter of the gold nanoparticles.

From Figure 3 two emission bands were found in the PL spectrum: one is an UV emission band due to excitonic recombination, and the other one is the visible emission band which is attributed to point defects such as oxygen vacancies or impurities.

The radiative UV emission at 385 nm is quenched as a result of fewer excited electrons returning from the conduction band to the valence band. This trend is reflected in the decrease of PL intensity with higher gold nanoparticle concentration (Figure 3). We have performed the experiments on three samples to make sure that there is a well defined decrease in PL intensity with increasing gold nanoparticle concentrations. Various sample sets have
slightly different shape trends due to distinction of ZnO nanorods tested samples. All of them showed a decrease in PL intensity with increasing GNP concentration.

Figure 3: PL intensity of ZnO nanorods with various concentration of GNP.

Three sets of ZnO nanorods samples were prepared for the PL data of quantum dots (QDs) with 605 nm wavelength. Figure 4 shows the room temperature PL spectra of quantum dots-coated ZnO nanorods. Measurement procedures for PL in QDs are the same as for the gold nanoparticles. The trends in PL intensity with increasing concentrations of gold nano particles and quantum dots are shown in Figures 5 and 6. For studying the PL intensity changes with concentrations, we used 0.1 and 1 molar concentrations. The average diameter of quantum dots were about 10 nm. Density of quantum dots was varied by controlling the number drops on the surface of the ZnO nanorods. As shown in Figure 5, for the 0.1 M concentration of QDs of 10 nm diameter, the photoluminescence intensity increased as the density of the quantum dots on ZnO nanostructures was increased.

Figure 5: PL intensity (UV peak) change with various concentration of 605 nm QDs (at 0.1 micro molar concentration).

Figure 6: PL intensity change (UV and VL peak) with various concentration of 605 nm QDs (at 1 micro molar concentration).

It is well known that the size and shape of quantum dots decide their electronic properties. Generally, smaller quantum dots emit higher frequencies of light after excitation at UV frequencies due to their larger band gaps. Therefore, the wavelength of the emitted fluorescent light is inversely proportional to the size of the quantum dot, i.e. as the quantum dots shrink in size, the emitted light become shorter in wavelength moving toward blue. In this study, quantum dots with three types of emission wavelength peaks at 490nm, 514nm, and 605nm were investigated. We investigated the change in PL intensity for these quantum dots. All procedures used in this study were kept the same as our previous attachment method, except that 1 µM ZnS capped CdSe quantum dots (higher concentration) were
used to attach on the surface of ZnO nanorods. The change in PL intensity for 605 nm at low molar concentration is shown in Figure 5. At 1 µM concentration, the PL intensity corresponding to the UV emission at 385 nm increases and then decreases as shown in Figure 6. Similar trend was also observed in 409 nm and 514 nm QDs. In comparison, the PL intensity decreases as the gold nanoparticle concentration is increased (Figure 3 and 7).

Figure 7: PL intensity (UV peak) change with various concentration of GNPs

4 DISCUSSION

As shown in Figure 7, UV intensities decrease with increasing GNP concentrations. This may be due to the neutralization of photo generated charges by gold nanoparticles. Meanwhile, the surfaces of the ZnO nanorods are significantly changed by absorption of gold nanoparticles which can annihilate the oxygen vacancies or surface states. The radiative UV emission is quenched as a result of fewer excited electrons returning from the conduction band to the valence band.

The UV peaks were observed to increase with concentration of quantum dots as shown in Figure 5, which may be caused by CdSe QDs producing multiple electron-hole pairs per photon. Since the conduction band (CB) of ZnO is lower than that of CdSe, it is possible for photo generated electrons in CdSe to migrate from CdSe QDs to the ZnO nanorods, which means more electrons in the conduction band will go back to the valence band (VB) through an emission process. Consequently, the UV PL intensity at 385 nm of ZnO is effectively enhanced. However at high concentration of QDs as shown in Figure 6, the trend is different. At high concentrations of QDs, it is possible for photo generated electrons in CdSe to migrate from CdSe QDs to the ZnO nanorods, which means all electrons in the conduction band will not be able go back to the valence band via radiative channel. The decrease in PL intensity at higher QD concentration may be explained by considering electron-hole recombination and diffusion of electrons. At the beginning of the emission-recombination process, the excess of electron created from CdS QDs may migrate into the conduction band, leading to the process of excess electron-hole recombination, resulting in the increase in PL intensity. In addition to recombination, as more and more CdS QDs were added on the ZnO nanorods, the excess electrons and holes would tend to diffuse from the region of high concentration to the region of low concentration, preventing all electrons generated to decay via radiative recombination. This process could explain why the emission intensity at 385 nm (UV peak) decreased as the concentration of QDs was increased. On the other hand, the VL emission increased with the increase in concentration of QDs, because the VL emission reflects the emission wavelength of QDs and its intensity is proportional to the concentration of QDs. At higher concentration of QDs, the PL intensity peak at VL increases.

5 SUMMARY

In this study we attached gold nanoparticles (GNP) and CdSe/ZnS core-shell quantum dots (QDs) of various diameters on the surface of ZnO nanorods. The PL intensity at 385 nm decreased with increasing GNP concentrations. This may be due to the neutralization of photo generated charges by gold nanoparticles. Density of quantum dots was varied by controlling the number drops on the surface of the ZnO nanorods. For 0.1 M concentration of QDs of 10 nm diameter, the photoluminescence (PL) intensity increased as the density of the quantum dots on ZnO nanostructures was increased. For quantum dots at 1 M concentration, the PL intensity at 385 nm increased at the beginning and then decreased at higher concentration. The decrease in PL intensity at 385 at higher QD concentration may be explained by considering electron-hole recombination and diffusion.

REFERENCES