

Large Band Gap Attenuation of CdS Nanoclusters after H₂S Exposure

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ABSTRACT: Large band gap attenuation of CdS nanoclusters in hybrid sol gel matrix comprised of 3-(trimethoxysilyl)propyl methacrylate (TMSPM), 15 wt. % zirconium, and various amounts of cadmium acetate was observed after H₂S exposure. Hybrid sol gel matrixes were prepared by hydrolysis and condensation reactions. The sol gels contained with various amount of cadmium acetate were spin coated to glass substrates and exposed to H₂S gas. The UV-visible absorption peaks were shifted toward blue with increasing the amount of CdS nanoclusters and were shifted to the red after thermal process. Significant amount of -OH absorption peaks were reduced after thermal process. Strong room temperature photoluminescence (PL) of CdS nanoclusters was observed after exposing to H₂S gas. The PL intensity increased for several minutes and slowly decreased thereafter. The luminescence peaks were continuously shifted toward blue as the time passed. Extraordinary Stokes shift (approximately 160 nm) was observed.

Key words: CdS nanoclusters, Large band gap shift, Sol gel matrix, Large Stokes shift

1. Introduction

Photoluminescence (PL) process and electron transfer process are competing mechanism. The rate of charge recombination or charge separation can be controlled by changing the relative energy gap of components, their surrounding environments, or their geometries¹⁻³⁾, which is not able to be controlled by the external field. Many researchers have tried to control the mechanism of the excited electrons generated by the absorption of photons. Cadmium sulfide (CdS) is a direct band gap semiconductor with the gap energy of 2.42 eV⁴⁾ and has been applied numerous solar cell researches and industry fields due to its excellent charge separation property when light irradiates to CdS⁵⁻⁶⁾. Room temperature luminescence of CdS nanoparticle was reported for the first time in 1996⁷⁾. The CdS quantum dot forms intermediate state between bulk crystal and molecular cluster, which attributes electron transfer process (conducting process) or light-emitting recombination process (PL process). The quantum dot systems can be applied for optical switches, optical amplifiers, laser diodes, and electroluminescence devices. The ideal system for understanding quantum dot

properties and application of high quality optical devices would be molecularly dispersed quantum system.

The sol gel process can be produced high purity glass and can be controlled the material composition⁴⁾. Silicate sol gel glasses can be obtained by hydrolyzing sol gel monomer precursors. The hydrolysis process replaces -OR groups to -OH groups and subsequent condensation process forms Si-O-Si bonds. Hybrid sol gel process has much attention in recent years due to easy process for waveguide fabrication⁵⁻⁷⁾. A 3-(trimethoxysilyl)propyl methacrylate (TMSPM) has three methoxy groups and one propylmethacrylate group for lithography process. Many researchers have used TMSPM due to easy lithography process to form desired pattern⁸⁻¹⁰⁾.

2. Experimental

2.1 Sol-gel preparation of TMSPM

Zirconium isopropoxide (70% solution in 1-propanol), TMSPM (98%), and vinyltrimethoxysilane (VTMS, 98%) were purchased from Sigma Aldrich and used as received. Methacrylic acid (99% with inhibited with 250 ppm MEHQ, Sigma Aldrich) was filtered through inhibitor remover column (Sigma Aldrich) before using. Deionized (>15 MΩ) water was used for this

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research. TMSPM and 0.02 molar aqueous nitric acid (1:1.5 molar ratio) were mixed and stirred for 1 h. Zirconium isoproloxide and methacrylic acid mixture (1:1 molar ratio) were added drop-by-drop to the prehydrolyzed sol, and additional water was added to the sol gel after 1 h. The Zr-doped and undoped sols were aged for 2 days at room temperature.

2.2 UV-visible absorption and FTIR transmission spectra

The sol was aged for 48 h before cadmium acetate addition. Various amounts of cadmium acetate were directly added to the sol with stirring for 10 min. The cadmium doped sol gel was spin coated to the quartz substrate to investigate UV-Visible spectra. The thin film was exposed to the H₂S gas for 10 min. Colorless films start to change week yellow color depending on the amounts of CdS nanoclusters and exposure time. UV-Visible spectra were recorded using a Thermo Scientific Genesys 10S UV-visible spectrometer before heating. The films were heat treated at 85°C for 5 min, and then UV-Visible spectra were obtained. The infrared spectra were recorded in the wavenumber range of 4000-400 cm⁻¹ with a Nicolet iS5 FTIR spectrometer with a KBr plate prior heating and after various durations of heating at 85°C for the 16631 ppm CdS sample.

2.3 Luminescence Spectra

Due to the PL intensities are very sensitivity for the sample's position and angle, all the sample positions and angles were fixed and tested several times for the reproducibility test. Various concentrations of the sol gel films were prepared with the same method as mentioned before. Emission spectra were recorded using a Hitachi 4500 Fluorescence spectrometer before heat treatment. The samples were heat treated at 85°C for 15 h, and PL spectra were recorded with excitation wavelength at 355 nm.

3. Results and discussion

3.1 UV-visible absorption spectra

The CdS semiconductor is a direct band gap material with a bulk band gap of 2.42 eV⁸⁾. Diverse band gap energies of CdS were reported with CdS nanostructures including 3.2 eV with thin CdS film (2-3 nm)⁹⁾, 2.54-2.65 eV with 8.5-12.5 nm CdS nanoparticles¹⁰⁾, and 2.58 eV with grain size of 10 nm¹¹⁾. Three different concentrations (16631, 27564, and 44178 ppm) of

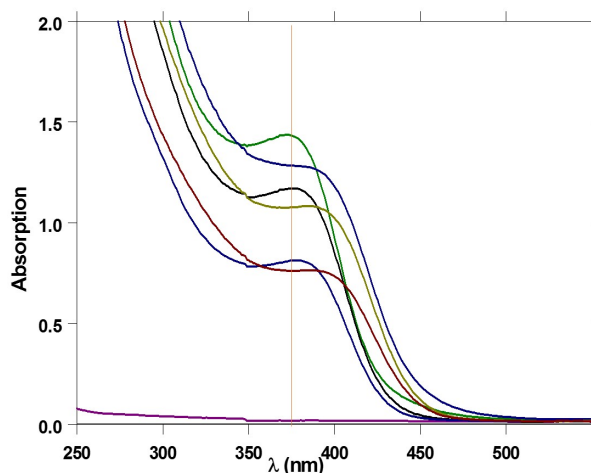


Fig. 1. UV-visible spectra of three different concentrations of CdS with before and after heating

cadmium were dispersed into the hybrid sol gel matrix. Fig. 1 shows the UV-visible absorption spectra before and after thermal process. The absorption intensity increased, and the absorption maximum peak shifted toward blue as the doping level increased, which could be due to the dangling bond or hydrogen bond formation by extra H₂S molecules for low concentration of Cd²⁺. The CdS nanoclusters having hydrogen bond or dangling bond may feel bigger nanoclusters than the nanoclusters without the extra bonds. The band gap energies for the 16631, 27564, and 44178 ppm CdS nanoclusters are 3.22, 3.25, and 3.31 eV, respectively. The band gaps of all three samples shifted toward red, which indicate the formation of interaction between nanoclusters with removal of extra dangling bonds during the heating process.

3.2 FTIR transmittance spectra

The near infrared absorption of -OH group is in the communication wavelength range and has been a major drawback for the transmission of telecommunication wavelength and for the quenching of the luminescence. The end group of the silica based sol-gel materials is composed with Si-OH, which is worthwhile to investigate the effect of -Si-OH group on the luminescence. Fig. 2(a) shows the FTIR transmittance spectra with various heating period in the range of 4000 - 500 cm⁻¹. Most of the transmittance spectra were not changed except Si-OH group absorption. The Si-OH group absorption decreased with increasing the heating time, which indicates the reduction of Si-OH group or H₂O in the film as shown in Fig. 2(b).

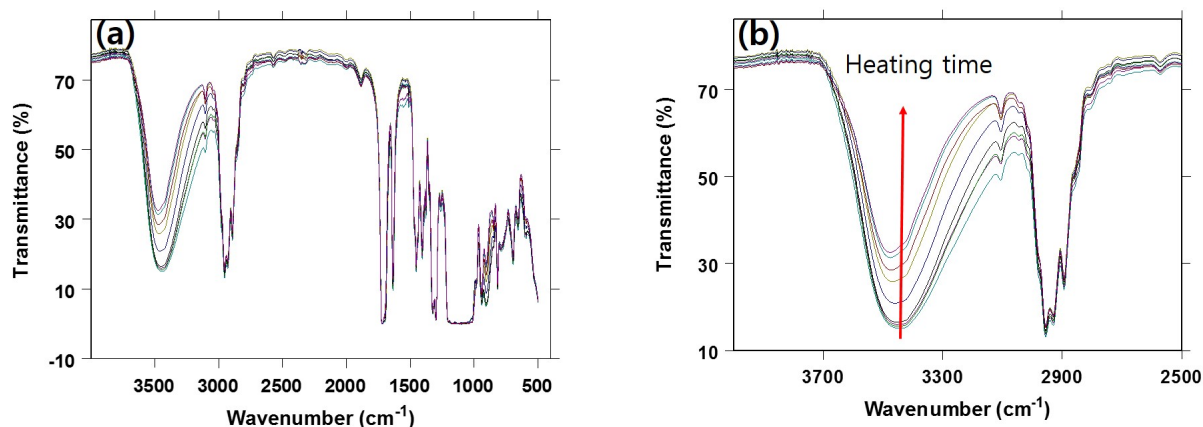


Fig. 2. Heating time dependent FTIR spectra in the range of (a) 4000-500 cm^{-1} and (b) 4000-2500 cm^{-1}

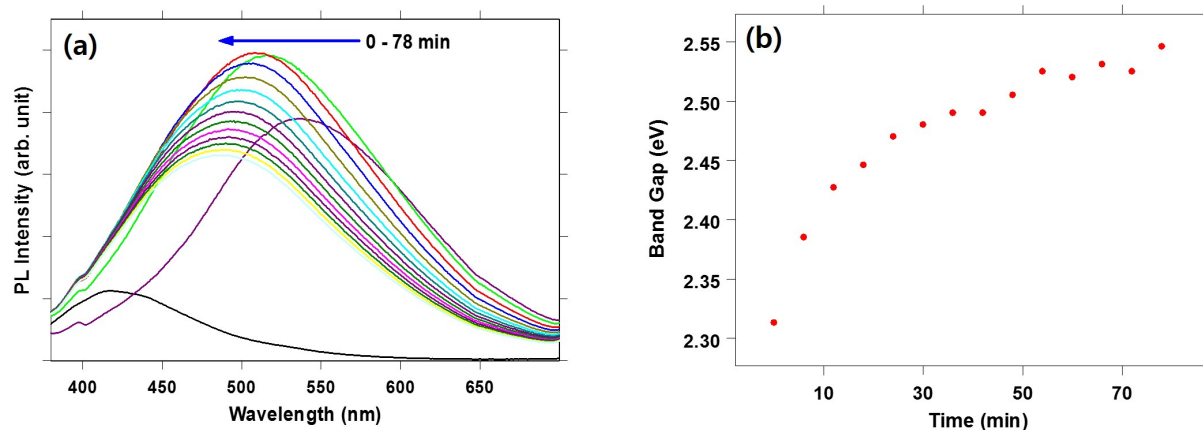


Fig. 3. (a) PL spectra after H_2S exposure and (b) time dependent band gap change after H_2S exposure

3.3 Luminescence Spectra after H_2S exposure

Fig. 3(a) shows time dependent emission spectra before and after H_2S exposure. Before H_2S exposure, there is small fluorescence peak at 416 nm (2.98 eV), which is due to the silica related luminescence¹²⁾. The H_2S exposed sample was placed to a fluorescent spectrometer and obtained time dependent luminescent spectra. Strong luminescence appeared after H_2S exposure with emission peak at 2.31 eV, and the emission peak shifted toward blue with the time passing as shown in Fig. 3(b). The band gap shifted from 2.31 to 2.55 eV during 78 min. Time dependent band gap shift can be due to the hydrogen bond and dangling bond formation around the CdS nanoclusters in the initial stage, which feels larger quantum state. The extra bonds (dangling bonds and hydrogen bonds) disappears during the H_2S evaporation with the time.

4. Conclusions

TMSPM waveguide sol gel doped with 15 wt.% of zirconium

was synthesized. The CdS quantum dots were incorporated in the sol gel matrix by addition of Cd^{2+} and exposure of H_2S gas. The viscosity of TMSPM sol gel increased in the initial hydrolysis process and slowly increased after initial hydrolysis process. The UV-visible absorption peak shifted toward blue with increasing the CdS concentration. The luminescence intensity increased and the band gap also increased with the time after H_2S exposure.

Acknowledgements

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