Printed in the Republic of Korea
ANALYTICAL SCIENCE
& TECHNOLOGY
Vol. 20, No. 5, 413-418, 2007

Preparation and characterization of CdS nanoparticle on the surface of silica nanoparticles

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(Received July 31, 2007; Accepted October 1, 2007)

실리카 나노입자 표면에 CdS 나노입자의 제조 및 평가

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(2007. 7. 31. 접수. 2007. 10. 1. 승인)

요 약: 방사선 방법에 의해 실리카 나노입자에 CdS 나노입자를 코팅하였다. TEM분석결과, SiO_2 나노입자 표면에 CdS의 입자의 크기는 대략 20 nm임을 확인 하였다. 또한, XRD 분석결과 결정체 화합물임을 확인하였다. PL 분석결과 PVP-CdS 나노입자와 SiO_2@CdS 복합체의 경우, 방출특성이 상당히 다르다는 것이 확인되었다. PVP-CdS의 경우, 방출스펙트럼이 550 nm-600 nm 에서 나타나고, SiO_2@CdS의 방출스펙트럼의 경우 단파장 이동함을 확인하였다. 또한 새로운 피이크 (450 nm) 나타남을 확인하였는데, 이는 CdS 의 유발양자 제한 효과에 의한 것으로 사료된다.

Abstract: Poly(vinylpyrrolidone) stabilized cadmium sulfide (CdS) nanoparticles were loaded onto the surface of silica (SiO_2) nanoparticles by using γ-irradiation. TEM micrograph reveals the presence of ~20 nm sized CdS nanoparticles on the surface of SiO_2 nanoparticles. XRD patterns confirm the crystalline. PL spectra of the simple PVP-stabilized CdS nanoparticle and SiO_2@CdS composite confirm the differences in the emission characteristics between them. Two prominent emission peaks were noted around 550 nm and 600 nm for PVP-stabilized CdS nanoparticles). The emission peaks noted for the PVP-stabilized CdS nanoparticles were found to be blue shifted for SiO_2@CdS composites. Besides, an additional emission peak around 450 nm was noticed for the SiO_2@CdS composite. The presence of CdS nanoparticles influence the emission characteristics and induce quantum confinement effect.

Key words: CdS nanoparticle, γ-Irradiation, Silica nanoparticle, SiO_2@CdS, Emission spectra

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1. Introduction

Recently, nanometer size CdS materials have attracted much attention because of their wide application as optical memories, and as fast response photo-luminescent and electro-luminescent devices.[1-4] The nanometer size materials have a large percentage of surface atoms and they are very active under ambient conditions. In order to avoid the degradation of the active sites, they are usually protected by using polymer or surfactants or embedded over host to generate nanocomposites. Stabilization of CdS nanoparticles with poly(cysteine acrylamide) has been reported.[5]

Incorporation of semiconductor nanoparticles into polymer, glass, or ceramic matrix materials induces interesting optical properties including absorption, luminescence and nonlinearity and results applications.[6-9] The small particle size enhances optical responses (quantum-confinement effect) of the nanoparticles and the matrix material stabilizes the particle size, limit the particle growth and confine the carriers. The high activity of the surface atoms with the formation of surface states causes lower luminescence efficiency for the nano-scale semiconductors. Encapsulation is needed to improve the surface properties of these particles.

Gamma-irradiation was extensively used to generate novel nano-scale materials with unusual properties, owing to the advantageous aspects in the preparation of materials, such preparation at room temperature and in ambient pressure without having any additional impurities arising from the chemicals used for the reduction of metal ions.[10-12]

Y. Xie *et al.*[13] reported the preparation of γ-irradiation induced spherical assemblies of 10 × 50 nm CdS nano-fibers in poly(vinyl acetate) with an average diameter of 120 nm. During irradiation, reaction between cadmium chloride and carbon disulfide and the polymerization of vinyl acetate occurred simultaneously in the one-spot heterogeneous synthesis leading to the formation of spherical assemblies of semiconductor in the polymer host. The resulting CdS nano-fibers possessed good crystallinity. Preparation was done at ambient temperature and pressure.

Previously, photoluminescent CdS/poly(acrylonitrile) (PAN) nanocomposites were prepared by γ-irradiation induced emulsion polymerization.[14] Though PAN possessed adequate thermal characteristics, the insulating nature of PAN restricted the use of CdS/PAN nanocomposites as electroluminescence materials. In the process of circumventing the problem associated with CdS/PAN nanocomposite, the conducting poly(vinylcarbazole) was used to make the nanocomposites with CdS, Ag, Pd_{50}-Ag_{50}, and Pt_{50}-Ru_{50} nanoparticles using γ-irradiation in THF-water mixture solution.[15] However, CdS nanoparticles could not be inserted into PVK matrix due to the hydrophobic nature of PVK matrix.

In this study, poly(vinylpyrollidone) (PVP) stabilized CdS nanopartciles were loaded on the surface of silica gel (SiO_2) by using γ-irradiation. The presence of CdS nanopartciles over the surface of SiO_2 were confirmed by transmittance electron microscopy (TEM) and the size distribution of CdS nanoparticles were analyzed. The photoluminescent behavior of the PVP stablized CdS nanoparticles anchored onto SiO_2 (SiO_2@CdS) surface was followed and discussed.

2. Experimental

2.1. Materials

Tetraethyl orthosilicate (TEOS) was analytical reagent grade and supplied by Aldrich-Sigma Co.. PVP (MW. av. 10,000) was obtained from Tokyo Kasei (Japan). Cadmium sulfate ($3CdSO_4 \cdot 8H_2O$) was obtained from Junsei Chemical Co., Ltd. (Japan). Sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) was purchased from Shinyo Pure Chemical Co., Ltd. (Japan). Other chemicals of reagent grade were also used without further purification.

2.2. Preparation of SiO_2 nanoparticle by sol-gel method.

Synthesis of SiO_2 nanoparticles was performed with the following molar composition: 0.3 TEOS/1.0

NH_3/4.4 H_2O/17.0 EtOH. A typical procedure is outlined here. NH_4OH (40 mL, 28%) solution was added to a mixture of deionzed water (80 mL) and ethanol (1000 mL), and then stirred with 200 rpm till obtaining a clear solution. To this clear solution 60.0 mL of TEOS was added with stirring and a pH of 9.5 was maintained. White precipitate was formed after 6 hrs and the mixture was centrifuged with 1600 rpm, filtered and washed thoroughly with deionized water and followed by EtOH. The white solid was dried at room temperature and tested for the morphology by Energy Filtered Transmission Electron Microscopy (EF-TEM).

2.3. Radiolytic preparation of PVP-stabilized CdS and CdS-SiO_2 nanoparticles

PVP-stabilized CdS nanoparticles were prepared as follows. A solution containing sodium thiosulfate (0.05M) (sulfur source) and cadmium sulfate (0.05M) was prepared in water in the presence of PVP (colloidal stabilizer). The solution was irradiated by the Co-60 γ-ray source. The yellow colored precipitate was collected by centrifuge, filtered and washed with dilute acetic acid, absolute alcohol, and distilled water in sequence to obtain pure CdS nanoparticles. The yellow precipitate was dried in vacuum at 50°C for 7 hrs.

CdS@SiO_2 composite was prepared as follows. A mixture having $CdSO_4$ (3.85 g, 5.0 mmol), $Na_2S_2O_3$ (1.24 g, 5.0 mmol), 2-propanlol (10 mL) (as hydroxyl radical scavenger), ethanol (70 mL) (as morphology controller), SiO_2 colloids (200 mL) with SiO_2 of 3.0 g was prepared and stirred. The solution was then purged with nitrogen gas to remove the dissolved oxygen. The solution was then irradiated by γ-ray of 60-Co source for a total irradiation dose of 30 kGy.

2.4. Characterization

TEM photographs of PVP-stabilized CdS nanoparticles and CdS@SiO_2 were obtained using Field Emission Transmission Electron Microscope (FE-TEM, JEM-2100F, JEOL. Co. Ltd., Japan) and Energy Filtering Transmission Electron Microscope (EF-TEM, EM 912 Omega, Carl Zeiss, Germany) installed at Korea Basic Science Institute, Daejon. The photoluminescence (PL) spectra were recorded using a Shimazu model RF-5301PC spectroflurometer at an excitation wavelength of 270 nm.

3. Results and discussion

TEM image (*Fig.* 1a) and XRD pattern (*Fig.* 1b) of the PVP-stabilized CdS nanoparticle prepared by γ-irradiation are presented. TEM photograph (*Fig.* 1a) reveals the aggregated morphology.

The reason for the aggregation may be the extremely smaller size and higher surface energy of the nanoparticles formed during the irradiation.

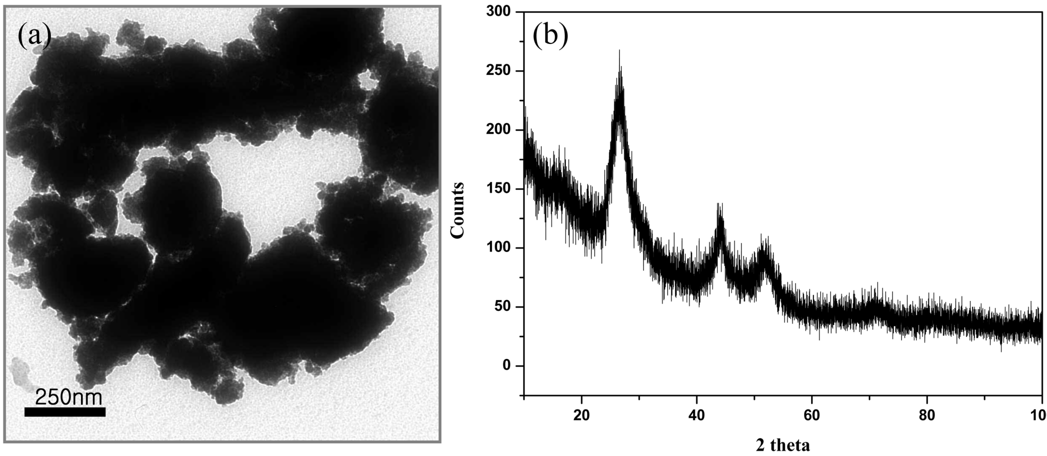

Fig. 1. TEM image (a) and XRD spectrum (b) of PVP-stabilized CdS nanoparticles.

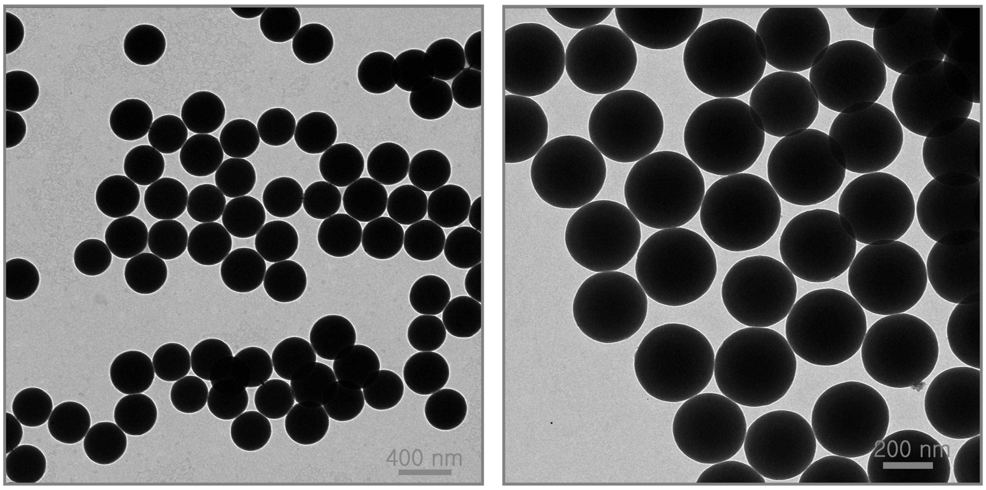

Fig. 2. TEM images of silica gel prepared by sol-gel method.

Precise determination of the size and size distribution of the CdS nanoparticles through TEM image was not possible due to the agglomeration. XRD pattern (*Fig.* 1b) of the PVP stabilized CdS nanoparticles prepared by γ-irradiation informs crystalline behavior. The three peaks with 2θ values of 27°, 44°, and 52° correspond to the (1 1 1), (2 2 0) and (3 1 1) crystalline planes, respectively, of CdS.[16] The peaks in the XRD pattern represent phases of CdS with cubic zinc blende structure. There are no other crystallites found in the examination. The average size of the CdS nanoparticles was estimated by the Debye Scherrer formula to be about 2.7 nm.[17]

Fig. 2 shows EF-TEM images of SiO_2 nanoparticles prepared by sol-gel method. Monodispersed silica gel particles with a particle size of 350 nm were formed by sol-gel method using water-ethanol mixture at pH = 9.5. Previously, we have reported the preparation of spherical porous silica with hexagonal channel (MCM-41) in water-methanol and water-ethanol mixture.[14] We have attempted to form Pd, Ag, and Pt_{50}-Ru_{50} nanoparticles in the pores of MCM-41 using radiation induced nanoparticles formation. Our results indicated that nanoparticles were not inserted into the pores of MCM-41 rather existed on the surface of MCM-41.[14]

TEM images of the CdS-loaded SiO_2 nanoparticles prepared by γ-irradiation clearly indicated that CdS nanoparticles with an average size of ~ 20 nm were

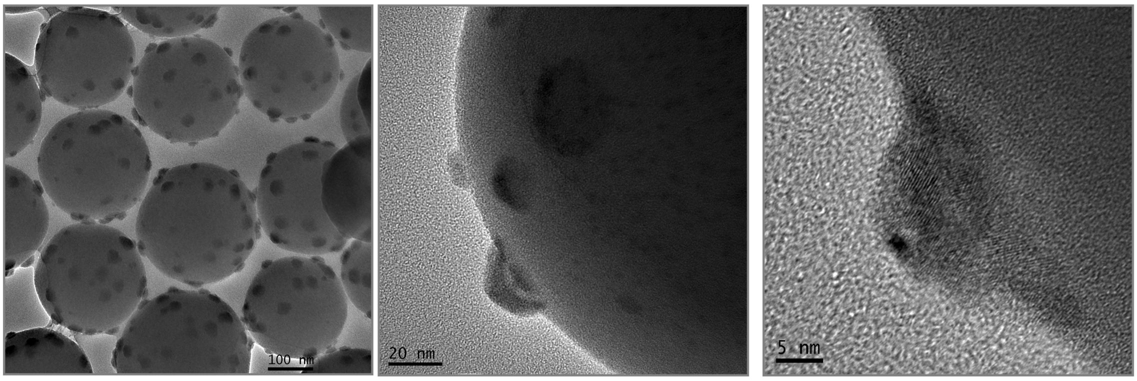

Fig. 3. TEM images of the CdS-loaded silica nanoparticles prepared by γ-irradiation.

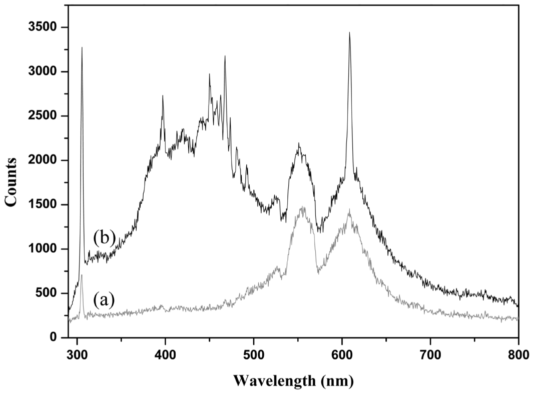

Fig. 4. PL spectra of the PVP-stabilized CdS nanoparticle (a) and CdS@SiO_2 composite(b).

found on the surface of SiO_2 nanoparticles. In comparison to the PVP protected CdS nanoparticles prepared in the absence of SiO_2 nanoparticles, the CdS nanoparticles formed on the surface of SiO_2 nanoparticles were uniform and larger sized. This may be ascribed to the surface effect of SiO_2 nanoparticles. Further, CdS nanoparticles were generated preferentially on the surface of SiO_2 nanoparticles during γ-irradiation. Otherwise, the reduction of cadmium ions by the hydrated electron generated by γ-radiation was more facile on the surface of more hydrophilic SiO_2 than the hydrophobic pores in silica.

PL spectra (*Fig.* 4) of the simple PVP-stabilized CdS nanoparticle (*Fig.* 4a) and SiO_2@CdS composite (*Fig.* 4b) prepared by γ-irradiation reveal the differences in the emission characteristics between them.

Two prominent emission peaks were noted around 550 nm and 600 nm for PVP-stabilized CdS nanoparticles (*Fig.* 4a). The emission peaks noted for the PVP-stabilized CdS nanoparticles were found to be blue shifted for SiO_2@CdS composites (*Fig.* 4b). Besides, an additional emission peak around 450 nm was noticed (*Fig.* 4b) for the SiO_2@CdS composite. The emission peak around 600 nm was assigned to the luminescence of the surface trap, i.e., coming from the recombination of the electrons trapped inside a sulfur vacancy with the holes in the valence band of CdS nanoparticles.[18-20] A possible explanation for the occurrence of emission peak is that it originates from the nano-sized CdS particles, whose electrons are excited to a higher energy state. Then, the electrons come down to an intermediate energy level through a non-radiation route and combine with the holes in the valence band to produce PL. The intermediate energy state corresponding to 550 nm emission may result from the surface states or the dangling bonds of the porous silica matrix.[21] The emission band around 450 nm was related to the band edge emission coming from the direct recombination of the conduction band electrons and the valence band holes. The difference in the emission characteristics and a blue-shift in emission characteristic may be ascribed due to the quantum confinement.

4. Conclusions

CdS nanoparticles could be doped/loaded onto the surface of SiO_2 nanoparticles by using γ-irradiation. While XRD patterns of SiO_2@CdS indicate the crystalline signature of CdS, HR-TEM adds evidence for the presence of CdS nanoparticles of sizes averaging ~20 nm on the surface of SiO_2. The presence of CdS nanoparticles influences the emission characteristics and induces quantum confinement effect. The PVP stabilized CdS nanoparticles loaded on the surface of SiO_2 may find applications in optoelectronics.

Acknowledgement

This work was supported by the Science Foundation of Hannam University (2007).

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