Effect of Acrylic Acid Passivation on the Photoluminescence and Photoacoustic Characteristics of Mn-Doped ZnS Nanoparticles

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It was in 1994 that Bhargava et al.[1] reported a high quantum efficiency (~18%) Mn-doped ZnS nanoparticle (ZnS:Mn), suggesting that ZnS:Mn might form a new class of luminescent material. Here, we present our results on photoluminescence (PL) and photoacoustic (PA) characterization involving UV irradiation. The effect on the PL and PA intensities during prolonged UV irradiation and varying modulation frequencies are looked into. These investigations can perhaps give a greater insight on the interactions occurring in the samples, giving information on the radiative processes and the nonradiative processes occurring during irradiation. The luminescent decay time constants before and after exposure is also looked into.

Two types of nanocrystalline ZnS:Mn, with and without acrylic acid (AA), were synthesized using an inorganic synthesis method [2] resulting in a calculated 2 nm particle diameter size (from XRD pattern). The optical absorption spectra were obtained using a PA technique [3,4] showing peaks at around 3.8 eV, attributed to the lowest transition energy due to quantum confinement effects [5]. PL spectra exhibited peaks at around 2.1 eV with a 340 nm excitation wavelength. Addition of AA increased the photoluminescence obtained.

Figure 1 shows the UV irradiation time dependence of the PA intensity for the sample with AA. The PA intensity exhibited a decrease with time, indicating a decrease in the nonradiative processes. A corresponding increase in the radiative process was indicated in the increase of PL intensity (for both samples) upon exposure in Figure 2. The increase in the PL intensity of the samples containing AA maybe attributed to polymerization of the AA, leading to a better surface coverage and greater lessening of the surface defects. On the other hand, the PL intensity increase for the sample without AA can be caused by either photo-oxidation or photocorrosion. Both the PA and PL intensities were also observed upon variation of the modulation frequency (Figs. 1 and 2). It was found that the measured intensities for both the PA and PL signals decreased with the increase of modulation frequency, for both samples. This dependence on the modulation frequency could indicate the possibility of a correlation between surface reaction and relaxation processes of photoexcited electron.

Preliminary studies on the effect of UV irradiation on the photoluminescence time decay were also done. For ZnS:Mn without AA, a slower time decay constant was observed after 24 h of UV exposure (Fig. 3). On the other hand for the sample with AA (Fig. 4), it was found that there was no appreciable change in the time decay constant. This could indicates that the luminescent decay mechanism for the two sample are different.

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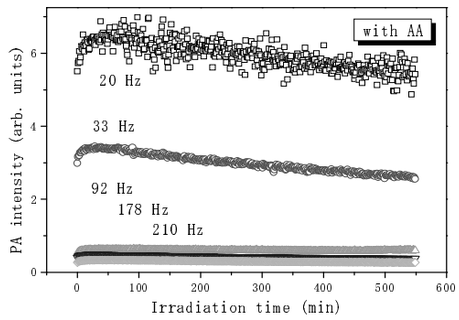

Figure 1: Irradiation and modulation frequency dependences of PA intensities for Mn-doped ZnS nanoparticles with AA. (340 nm)

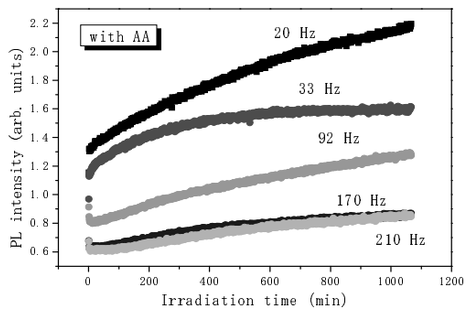

Figure 2: Irradiation and modulation frequency dependences of PL intensities for Mn-doped ZnS nanoparticles with AA. (340 nm)

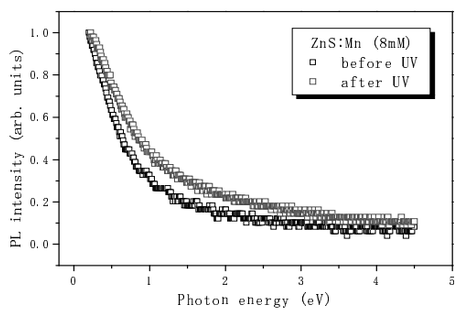

Figure 3: PL time decay measurements for Mn-doped ZnS nanoparticles before and after UV exposure. (PL observed at 595 nm)

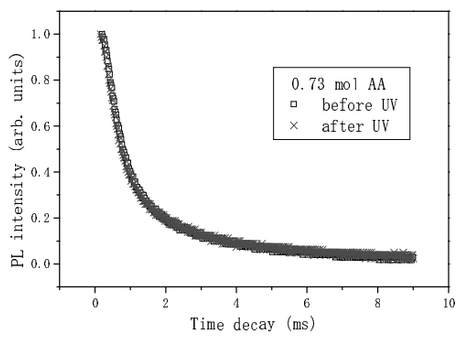

Figure 4: PL time decay measurements for Mn-doped ZnS nanoparticles with AA, before and after UV exposure. (PL observed at 595 nm)