

Comparison of UV optical properties of ZnO nanoparticles dispersed in traditional organic and novel bio-molecular solvents

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Two types of ZnO nanoparticles were dispersed in a bio-molecular solvent and in ethanol. The mixtures were characterized by photoluminescence and absorbance measurements. Strong UV emission was observed near the band gap of ZnO at 380 nm. The parasitic green emission which normally appears in ZnO suspensions was weakened when ZnO was dispersed in the bio-molecular solvent. Suspensions were spin-cast on quartz, and then Al contacts were deposited by a standard lift-off

process via e-beam lithography. Point contact current-voltage characteristics of the samples were measured under equal intensity conditions using 340 nm UV LED and white LED sources. The ratio of the UV photo-generated current to dark current was as high as 10^5 . Finally, the photocurrent response spectrum was measured. The results show that ZnO nanoparticle is favourable for visible blind UV photodetectors.

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1 Introduction ZnO is a direct wide bandgap semiconductor material (documented values range from 3.2 eV to 3.4 eV), with attractive characteristics including large exciton binding energy (60 meV), high radiation hardness, and relatively low growth temperature [1-5]. These characteristics have prompted its use for transparent conducting electrodes, varistors, gas sensors, UV photodetector and light emitting diodes. ZnO nanoparticles have been created from bulk material by chemical means under room environment [6]. Nanoparticle-based devices take advantage of three dimensional quantum confinement effects, are easy to fabricate, can have a large active area, and are relatively low cost [7]. ZnO nano-materials often exhibit a strong, parasitic green photoluminescence caused by excess Zn^{2+} ions and oxygen deficiency [8-11]. These defects must be avoided to improve overall UV performance.

In this paper, performance comparison of ZnO nanoparticles dispersed in ethanol and a bio-molecular solvent is performed. Green quenching effects are achieved by dispersing ZnO in a bio-molecular solvent. The UV performance of ZnO is characterized by photoluminescence

and absorption. The nanoparticles are deposited on quartz substrates using basic spin-casting techniques. Finally, a standard lift-off process is used to fabricate a photoconductive UV detector by evaporating Al as ohmic electrodes on the ZnO nanoparticles coated surface.

2 Experiments ZnO bulk material was reduced in size by a top-down wet-chemistry synthesis process into nanoparticles which were uncoated (sample A) or coated (sample U) with polyvinyl-alcohol (PVA). Each of the two samples was respectively dispersed in a bio-molecular solvent, a material used to aid in self-assembly [12-14], and in ethanol to form 30 mg/ml suspension. The nanoparticle solutions were characterized by their excitation and emission spectra by a SLM8100 fluorometer. These solutions were then spin-cast on quartz plates and annealed in air at 150 °C for 5 minutes. Their absorbance characteristics were measured using a Shimadzu UV-Vis 2550 spectrophotometer. Two irregular 100 nm Al contacts were deposited by E-beam lithography through a foil mask. Point contacts current-voltage characteristics of samples were

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measured using a HP4155B semiconductor parameter analyzer under darkness, then using equi-intensity 340 nm UV LED and white LED sources. Finally, the photocurrent response spectrum was measured utilizing a Keithley 236 sourcemeater and using a Shimadzu UV-Vis 2550 spectrophotometer as the excitation source, scanning wavelengths from 200-900 nm. These measurements were performed at room temperature in air.

3 Results and discussions Figure 1 is a high resolution SEM image of sample U dispersed in ethanol and then spin-cast on quartz plates. It reveals that the nanoparticles' sizes are not uniform. The size ranges from 20 nm to 150 nm and an average value is approximate 100 nm. Sample A in ethanol spin-cast on quartz plates has similar results.

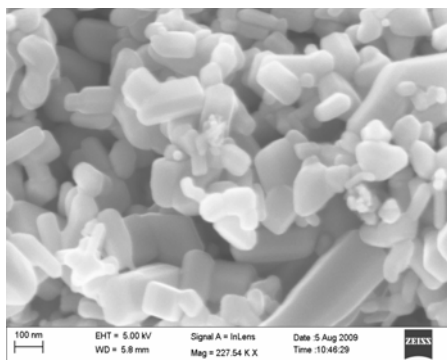


Figure 1 High resolution SEM results of ZnO U dispersed in ethanol and then spin-cast on quartz plates.

The photoluminescence measurements of sample A and sample U each dispersed in ethanol and a bio-molecular solvent are depicted in Fig. 2 and Fig. 3. For the excitation spectra, the emission detector is fixed at 510 nm while the excitation wavelength is scanned from 250 nm to 450 nm. Based on this measurement, the absorption wavelength that causes green parasitic emission can be determined. For the emission spectra, the excitation wavelength is fixed at 330 nm, while the detector is scanned from 360 nm to 550 nm. These results directly indicate any enhanced UV, reduced visible and diminished parasitic green emission due to the ZnO nanoparticle coatings.

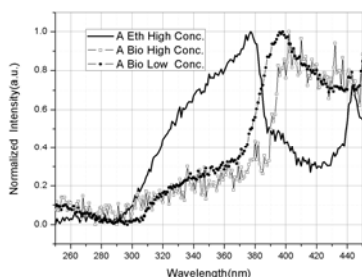


Figure 2 (a) Normalized excitation spectra of uncoated ZnO (Sample A) in solvents with $\lambda_{em} = 510$ nm.

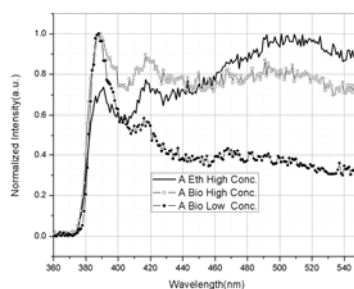


Figure 2 (b) Normalized emission spectra of uncoated ZnO (Sample A) in solvents excited at 330 nm

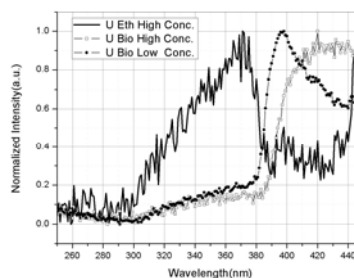


Figure 3 (a) Normalized excitation spectra of coated ZnO (Sample U) in solvents with $\lambda_{em} = 510$ nm.

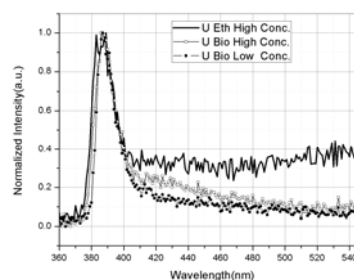


Figure 3 (b) Normalized emission spectra of coated ZnO (Sample U) in solvents excited at 330 nm.

The excitation spectra in Fig. 2(a) and Fig. 3(a) clearly show most of the green emission (510 nm) comes from the absorption inside the bandgap of ZnO when ethanol acts as solvent, while it results from defects outside the bandgap when ZnO is in the bio-molecular solvent. Using the bio-molecular solvent for better dispersion of the ZnO nanoparticles demonstrates a reduction in the parasitic ZnO green photoluminescence for UV-photo-excitation. This reduction effect is shown in the emission spectra of Fig. 2(b) and Fig. 3(b). Additionally, the spectra indicate lower concentrations exhibit less of the characteristic ZnO nanoparticle parasitic green photoluminescence, as expected. Comparing Fig. 2 with Fig. 3, the effect of the bio-molecular solvent is more apparent in sample A than in sample U. This may be due to the interaction between bio-molecular solvent, acting as surface passivation, and ex-

cess Zn^{2+} , normally considered a great contribution to green emission [8-11]. The UV/green emission contrast ratio in the sample U is better, possibly due to the PVA coating's effect on Zn^{2+} .

The absorption spectrum in Fig. 4 demonstrates an increase in UV absorption when using bio-molecular material (in comparison with ethanol) as the solvent. This is consistent with the photoluminescence results. The absorption spectra also indicates that under higher concentration the cut-off wavelength of sample A and sample U are 390 nm, while they are 380 nm under lower concentration. Based on the idea that UV band of ZnO undergoes a blue shift with decrease of the particles size [8, 9, 11], our blue shift may result from the bio-molecular solvent helping keep the size of particles and also prevent them from congregating when the concentration is low. It is also noticed that there are two peaks at around 350 nm and 375 nm when samples are in high concentration. This may be caused by the non-uniform size distribution of nanoparticles, since with different sizes ZnO has different absorption cut-off wavelengths. This non-uniform size distribution is also indicated in the high resolution SEM results.

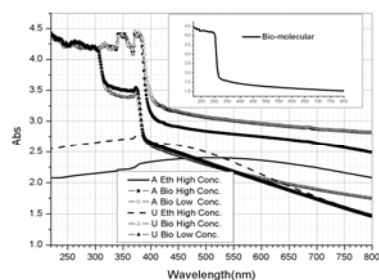


Figure 4 Absorption spectra of ZnO dropped on quartz plate (Inset is the absorption spectra of bio-molecular solvent)

There is no significant difference observed in the absorption spectra of sample A and sample U. That is the same as the results in the literature [9, 10], in which there are no significant differences in absorption spectra of ZnO even if they have different capping agents or doping.

Figures 5 and 6 are the I-V plots of sample A and sample U in ethanol under dark, and then with equi-intensity 340 nm UV LED and white LED illumination. Both the results show white LED generated currents are not significant.

The UV photo-generated current to dark current ratio (on/off ratio) in sample A is 4 when the bias is 20 V. This means the ratio of UV to white light generated current is also very small. Since sample A has a lot of defects, shown in the previous emission results, most of the photo-generated carriers are trapped by the defects during their transport to the terminals.

For sample U the I-V plot shows much improved UV detection performance. The dark current is on the order of pico-Amps. Under 340 nm UV LED illumination, the ratio

of photo-generated current to dark current (on/off ratio) is as high as 200,000 when the bias is 20 V. Still, there is a small white LED generated current caused by the defects of materials, which is also indicated in the photoluminescence and absorption results.

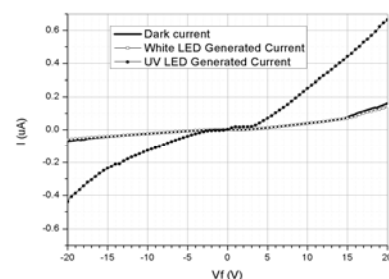


Figure 5 I-V plot of uncoated ZnO (Sample A) dispersed in ethanol and then spin-cast on quartz plate.

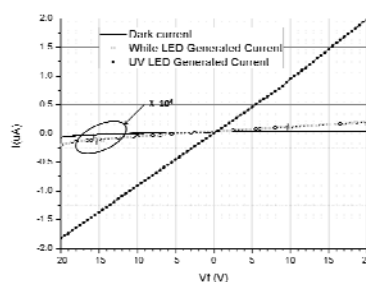


Figure 6 I-V plot of coated ZnO (Sample U) dispersed in ethanol and then spin-cast on quartz plate.

Based on the work function of Al (4.08 eV) and electron affinity of ZnO (4.5 eV), Al is supposed to form ohmic contacts with ZnO that usually performs as an n-type semiconductor. This can be verified by the I-V plot of sample U. While for sample A, the I-V plot shows the contacts appear to be Schottky type. It is reported that ZnO and gold formed ohmic contacts due to different surface impurities and defects of ZnO, even though ZnO and gold are supposed to form Schottky contacts [7]. Following that logic, we believe that ZnO and Al can also form two types of contacts based on different surface impurities and defects in ZnO. Since sample A and sample U have different surface defects, it is therefore reasonable that they form different types of contacts with Al.

The dark currents of sample A and sample U dispersed in bio-molecular solvent and spin-cast on quartz plates are higher than that of samples dispersed in ethanol solvent, while no more significant photo-generated current is observed. Since the rate of evaporation of the bio-molecular solvent is less than that of ethanol, the density of spin-cast ZnO nanoparticles with bio-molecular solvent is much less than with ethanol. The SEM results support this fact. However, our results demonstrated the UV optically-enhanced performance by using the bio-molecular solvent. We be-

lieve a significant enhancement of UV-generated current will be achieved if higher density ZnO nanoparticles can be applied effectively to the appropriate MSM substrate. Higher density may be achieved by the judicious selection of solvents and evaporation rate of the colloidal solution. We are continuing to work on this idea.

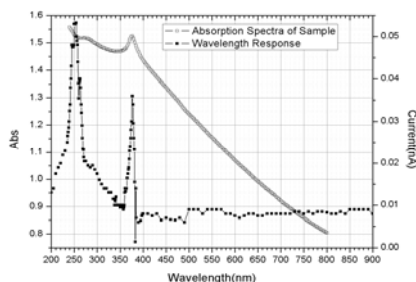


Figure 7 Photocurrent response spectrum and absorption of coated ZnO (Sample U) nanoparticles dispersed in ethanol and then spin-cast on a quartz plate.

Figure 7 shows that the photocurrent response spectrum reaches two very sharp peak values at 376 nm and 254 nm. The width of the peak is about 10 nm and 20 nm, respectively. The peak at 376 nm corresponds to the band-gap energy of ZnO. When the wavelength decreases, the absorption coefficient will increase and the penetration depth of UV light will be shallower, thus increasing the concentration of carriers near the surface of the film. As a result, the lifetime of the photo-generated carriers will decrease and lead to a drop in the current [1]. When the incident wavelength is greater than the cut-off wavelength of ZnO, the light passes through the ZnO active layer and there is no current generated. That forms a peak around the band gap of material. Since nanoparticles have much larger surface area than bulk material, this peak mostly appears in samples based on nanoparticles. Compared with the peak in [1], our peak is 60 nm smaller than their peak. That implies the surface defects in our samples are more serious. The peak at 254 nm (4.878 eV) is a new peak and did not show up in any other papers. That maybe corresponds to the ground state energies of ZnO exciton. Our value is close to the calculated result of 4.645 eV (at film thickness 1nm) based on effective mass approximation and the correction due to film thickness as well as the quantum tunnelling of the exciton wave function through the film in paper [15]. Paper [16] also observed a strong absorption around 5.6355 eV (220 nm) which is close to the calculated result 5.477 eV without correction in paper [15]. The results show that the absorption peak in wavelength shorter than the band gap of ZnO corresponds to a more complete description of the structural properties of ZnO nanoparticles. Further study is needed to verify this explanation.

4 Conclusions The excitation and emission spectra show ZnO samples in this paper have good UV emission

quality. The enhanced UV optical properties and reduced parasitic green photoluminescence of ZnO nanoparticles dispersed in bio-molecular solvent are observed. Photoconductive detector based on ZnO nanoparticles shows the ratio of 340 nm UV LED photo-generated current to dark current is as high as 200,000 when the bias is 20 V, and the dark current typically in the pico-Amp range. The photocurrent response spectrum of this photodetector reaches two very sharp peak values at 376 nm and 254 nm, which is very different from the photocurrent response spectrum of bulk ZnO material. These results indicate that ZnO nanoparticles could be applied in low cost, high sensitive and visible blind UV photodetectors with sharp response spectral peaks.

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