Electric field induced reversible control of visible photoluminescence from ZnO nanoparticles

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Reversible control of the photoluminescence of ZnO occurring in the visible range, has been achieved by application of a few volts (<5 V) to a device consisting of nanostructured ZnO film sandwiched between indium tin oxide electrode and polyethylene oxide-lithium perchlorate, a solid polymer electrolyte. The photoluminescence intensity shows nearly 100% modulation with a response time less than 30 s, when the bias is applied at the electrolyte electrode. A model is proposed for the observed effect that is based on defect states of ZnO and the band bending at the ZnO-electrolyte interface that can be changed by the applied bias.

ZnO, a wide band gap (3.3 eV) semiconductor with wurtzite structure ($P6_{3}mc$) is a well-known material for applications in the ultraviolet (UV) region of the electromagnetic spectrum. Over the past decade, tremendous progress in research has been achieved for the use of ZnO as an opto-electronic material.\textsuperscript{1} In particular, nanostructured ZnO that can be fabricated at temperatures below 100 °C, can be used for innovative applications. The room temperature photoluminescence (PL) of ZnO nanoparticles (NPs) of size below 20 nm typically exhibits near band edge (NBE) emission in the UV region and a broad emission band in the visible region of the spectrum.\textsuperscript{2} Fine control of this defect related visible PL is challenging because of its dependence on many environmental parameters. Factors like size and shape of the material, polar nature of the surrounding medium and type of defects involved in the emission processes were identified and the positively charged oxygen vacancies were commonly attributed as likely origin of this emission.\textsuperscript{3,4} It will be an interesting proposition if a full reversible control of this visible emission is achieved by application of a voltage bias. This will not only be of scientific interest but can also have an application potential.

NBE emission of a semiconductor, that has an excitonic origin, can be controlled by application of electric field at the semiconductor-metal (S-M) and semiconductor-electrolyte (S-E) junction. For example, reversible change in excitonic PL from epitaxial GaN (Ref. 5) was seen by application of electric field at the S-M junction. In a recent report, reduction in the visible emission and enhancement of the UV emission has been observed in a ZnO based metal-insulator-semiconductor structure on application of a bias.\textsuperscript{5} Reduction in PL from n-GaAs electrode immersed in aqueous ditelluride electrolyte by application of external voltage has also been reported.\textsuperscript{6} Recently it has been demonstrated by us that ZnO NPs suspended in an electrolytic solution show reduced visible emission.\textsuperscript{7} In this letter we describe reversible control (reduction as well as enhancement) of the visible PL from ZnO NPs by application of small voltage (<5 V) at S-E junction. The observed enhancement as well as reduction is substantial.

A device consisting of indium tin oxide (ITO)/ZnO NPs/polymeric electrolyte (Fig. 1) has been constructed to demonstrate the effect field controlled visible PL. The film of ZnO NPs of size ~10 nm [see inset of Fig. 2(a)], synthesized by solution route\textsuperscript{8} is obtained by adding NP-ethanol dispersion on ITO coated glass substrate at room temperature. To ensure the presence of a ZnO layer all over the surface, a thick film is deposited. The average thickness was found to be ~200–300 nm. When the ZnO film dries off, a gel of polyethylene oxide (PEO) having molecular weight 100000 and lithium perchlorate (LiClO$_4$) is deposited on the ZnO layer. After the gel becomes solid, it holds securely the electrical connections (Cu wires) as shown in Fig. 1. The PL spectra were measured by a spectrofluorimeter (Jobin Yvon Fluromax 3). The bias voltages were supplied by a Stanford Research System DS345 synthesized function generator.

The device has been illuminated by UV light of energy higher than the band gap of ZnO. However, the upper energy is limited by the transmittance of ITO. We excite the device through ITO glass face and the emitted signal is collected in the reflection mode. In this arrangement, the thick ZnO film acts as an absorbing layer before the illumination reaches the electrolyte at the interface. This eliminates the PL from the polymer that occurs at around 425 nm. ZnO NPs sandwiched in the device show maximum NBE PL near 390 nm and visible PL around 500–550 nm when illuminated in the win-

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{device.png}
\caption{(Color online) Illustration of the device fabricated. The biasing arrangement demonstrated here (negative bias to electrolyte) leads to enhancement of intensity and vice versa.}
\end{figure}

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INBE are the intensities of visible and PL of ZnO NPs taken in suspension.3,8 However, the relative intensity of the surface related broad visible PL is reduced due to the surface passivation of ZnO NPs by the colloidal ZnO NPs can be changed at the ZnO-electrolyte interface by application of a bias. When ZnO is immersed in the electrolyte solution of ZnO NPs, the interface will be governed by the alignment of the redox potential. Eredox and Fermi level EF of the electrolyte Eelectrode. To quantify the response time, the PL intensity is measured in response to a square wave pulse of amplitude ±4.5 V at frequencies 0.001 Hz [Fig. 3(a)]. In addition, an amplitude modulated (varying from 0–4.5 V) square wave of frequency 0.01 Hz has been applied to demonstrate precise control over the intensity by voltage [Fig. 3(b)]. The observed phenomena, presented in this letter, can be explained using similar arguments involving band bending. The band bending and hence the population of the positively charged oxygen vacancies near the surface of the NPs are located predominantly near the surface of the NPs.8 Emission band appearing around 550 nm (which we call P2) has been suggested to originate from doubly charged oxygen vacancy (V_{\text{O}^2}^{\text{++}}), which is predominant in ZnO nanospheres. Whereas singly charged oxygen vacancy (V_{\text{O}}^{\text{+}}) is responsible for the emission band around 500 nm (which we call P1).3,4 It has been shown that emission intensity (comprising the intensities of the two lines) depends on the ionic environment and the zeta potential of the NPs.8 Emission intensity reduces when the zeta potential of the NPs decreases with larger change in the P2 line. The effect was explained in terms of band bending near the surface of the NP that depends on the population of the emitting species like charged oxygen vacancies and the width of the depletion layer. Earlier reports, including the investigations done by our group establish that the emission intensity from PEO-LiClO4, the interface will be governed by the alignment of the redox potential (E_{\text{redox}}) of the electrolyte with the electrochemical potential (Fermi level EF) of the NPs.
semiconductor.\textsuperscript{11} When they are different, this will lead to carrier transfer across the interface, which causes band bending. In the present case, when the n-type ZnO NPs are made to touch the electrolyte, there will be transfer of electrons from the ZnO to the electrolyte. Depletion of the majority carrier will create a depletion region in ZnO and the band bending occurs. The schematic of the band positions for the n-ZnO and the electrolyte in equilibrium (without bias) is shown in Fig. 4(a).

When a positive voltage is applied to the electrolyte, the electrolyte side of the ZnO-electrolyte interface accumulates the Li\(^+\) ions, which induces more negative charge in the surface region of ZnO NPs [Fig. 4(b)].\textsuperscript{11} The accumulation of the negative charge fills up the positively charged oxygen vacancies. This reduces the visible PL. The presence of more majority carrier reduces the band bending and can even lead to creation of accumulation layer. The presence of majority carriers in the accumulation layer also shows up as a substantial enhancement of the junction current. A reverse situation arises when negative bias is applied to the electrolyte\textsuperscript{11} as depicted in Fig. 4(c). It induces more positive charge on the ZnO surface. This increases the number of ionized oxygen vacancies and leads to enhancement of the PL. In this situation the depletion width ($W_D$) increases due to depletion of the majority carriers and the upward band bending becomes more severe. The presence of the depletion layer leads to reduction in the junction current by at least one order compared to that in the accumulation case.

Use of the polymer electrolyte is essential to achieve the reversible control over the visible PL. To test this hypothesis, we make a metal-semiconductor device consisting of ZnO NPs and a top Al layer. This exhibits small enhancement in NBE emission and a small reduction in visible PL at a much higher positive voltage ($\sim 12$ V) applied to the Al (data not shown). No enhancement in visible PL is seen. It is likely that the polymer electrode produces electric double layer at the interface and allows reversible control of band bending at lower voltages.

To summarize, a reversible control of the visible PL is demonstrated in films made from ZnO NPs, by the application of an electric field in a simple device geometry that uses polymer electrolyte as an electrode. Depending on the sign of the voltage bias, the emission intensity can be enhanced or reduced. It is proposed that the application of voltage bias controls alignment of the $E_F$ and $E_{\text{redox}}$. This affects the band bending at the interface and filling of the $V_o^-$ and $V_{o^+}$ states that control the emission intensity. The voltage control (by a small bias $<5$ V) that can enhance as well quench the visible emission has an application potential that is being explored.

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