OPTICAL BEHAVIOUR OF ZnO/Au NANOJUNCTIONS

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ZnO/Au nanojunctions were prepared by electrochemical method at room temperature. Nanojunction formation is vivid from appearance of ZnO and Au features in x-ray diffraction pattern. Optical absorption spectra reveal excitonic as well as surface plasmon resonance (SPR) feature in case of nanojunctions. Bleaching of the excitonic feature associated with the blue shift, is a signature of charge transfer from Au to ZnO at the interface of nanojunction. An increase in intensity of band edge luminescence and quenching of green emission indicates the passivation of surface defects due to formation of nanojunctions.

1. INTRODUCTION

The semiconductor nanocrystals (NCs), especially II-VI groups, have attracted a great deal of attention due to their optical properties based on the quantum confinement effect [1-3]. Most of the research is carried out on nanocrystals to obtain modulated band gap emission or improved luminescence efficiency of nanometer-sized semiconductors [4-14].

Increase in surface to volume ratio is found to be beneficial in interface related ferromagnetism and for enhanced photovoltaic and photocatalytic activity of NCs. Substantial volume of work [15-19] is initiated on the nanojunctions to understand the charge and energy transfer. Improved functionalities and tunable physical and chemical properties have attracted much interest in the growth of oxide semiconductor-metal nanojunctions, such as TiO_2/Au and ZnO/Au. The position of characteristic surface plasmon resonance (SPR) band of metal nanocrystals depends on the quasi − free electron concentration. Also, coupling of oxide semiconductor and noble metal allows tailoring of SPR by electron transfer between metal and semiconductor. For macroscopic n-type materials in contact with metals a Schottky barrier normally forms at the junction between the two materials, which reduces the kinetics of electron injection from the semiconductor conduction band into the metal [20]. ZnO/Au, Ag, Pt, Cu nanojunctions were prepared [20] by wet chemical synthesis.

In the earlier work, the charge transfer from ZnO nanocrystals to Ag nanocrystals was observed [21] in coupled ZnO/Ag nanocrystals. Here, we explore the behavior of ZnO nanocrystals coupled with Au nanocrystals. Different size nanocrystals were synthesized using electrochemical method by varying the ratio of electrolytes, deposition time, or deposition current. In this paper, we report the optical behavior of ZnO/Au nanojunctions.

2. EXPERIMENTAL

ZnO/Au nanocrystals were synthesized by electrochemical route at room temperature [22]. The synthesis method used in this work is a modified version of the one, reported by Reetz, et al. [23]. An electrochemical bath consisted of a mixture of acetonitrile (CH_3CN) and tetrahydrofuran [THF, $(CH_2)_4O$] in the ratio 4:1, along with tetraoctylammonium bromide [TOAB, $C_{32}H_{68}BrN$] as a cationic surfactant and cetyltrimethylammonium bromide [CTAB, $(C_{16}H_{33})N(CH_3)_3Br$] as a co surfactant. The cell consists of three electrodes, viz. zinc (Zn), gold (Au), and platinum (Pt). Zn and Au act as an anode, while Pt acts as cathode. The constant current was passed through electrolyte under N_2 atmosphere for few hours to obtain ZnO, Au and ZnO/Au nanocrystals. The ZnO/Au nanocrystals were prepared by passing the current through Zn foil (30 mA/cm^2) for half hour and then through Au foil (1 mA/cm^2) for varying time. The nanocrystals were settled down at the bottom of the electrochemical cell. They were separated out by centrifugation and washed several times with acetonitrile.

The X-ray diffraction (XRD) of ZnO nanocrystals and ZnO/Au nanojunctions was carried out on a Bruker AXS D8 advance powder X-ray diffractometer, with Cu K_α ($\lambda = 1.5402$ Å) as the incident radiation. Room temperature optical absorption spectra were recorded using JascoV-670 UV visible spectrophotometer while photoluminescence (PL) study was carried out using Perkin Elmer LS 55 spectrophotometer.

3. RESULTS AND DISCUSSION

The structural analysis of ZnO/Au nanojunctions is carried out on the basis of XRD patterns as shown in Fig. 1. The formation of wurtzite ZnO and face-center cubic (FCC) gold is confirmed. No other crystalline impurities or noticeable shift was observed in the diffraction peaks.

The intensity of Au peaks slightly increases with increasing deposition time of Au. Simultaneously, the intensity of ZnO peaks goes on decreasing. The broad peaks of ZnO with increasing deposition time of Au confirmed the decrease in size of ZnO nanocrystals. The reason is that, Au helps to prevent the agglomeration of ZnO nanocrystals. The average diameter of ZnO nanocrystals estimated by Scherrer formula [24] is observed to vary from ~ 5.6 ($\pm$ 1.1) nm (ZnO) to 3.6 ($\pm$ 1.2) nm (ZnO/Au).

The room temperature optical absorption spectra of ZnO and ZnO/Au nanojunctions are depicted in Fig 2. The excitonic peak of ZnO nanocrystals is observed at 334 nm. A blue shift of 17 nm in absorption edge is observed for ZnO/Au nanojunctions (317 nm) compared to ZnO nanocrystals (334 nm). Decrease in size of the ZnO nanocrystals may be responsible for the blue shift. SPR is clearly observed in the optical absorption of ZnO/Au nanojunctions. The intensity of Au SPR peak increases and it red shifts with increasing Au deposition time (as shown in inset of Fig. 2). The position of plasmon absorption is related [25] to electron density of metal. Thus, the increase in intensity and red shift of the SPR of ZnO/Au nanojunctions indicates the decrease of electron density of Au due to transfer of electron from Au to ZnO. Electron affinity of ZnO is 4.5 eV [26] while the work function of Au is 5.1 eV and that of Ag is 4.73 eV [27].
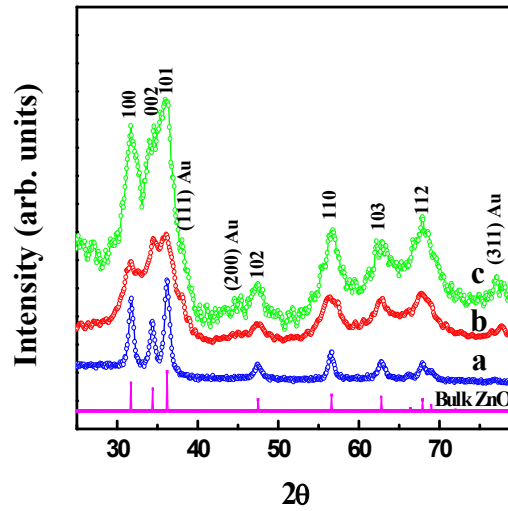
Fig. 1 – *X-ray diffraction pattern of ZnO nanocrystals (a) ZnO/Au nanojunctions with Au 20 min (b) and ZnO/Au nanojunctions with Au 40 min (c) deposition time*
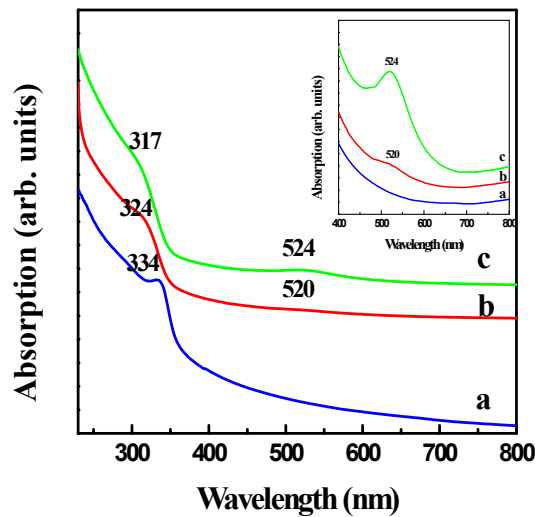

Fig. 2 – *Room temperature absorption spectra of ZnO nanocrystals (a) ZnO/Au nanojunctions with Au 20 min (b) and ZnO/Au nanojunctions with Au 40 min (c) deposition time*

Consequently, electrons will transfer from Au to ZnO until two systems reach a dynamic equilibration. In case of ZnO/Ag [21], the appearance of sharp ZnO excitonic feature indicated the charge transfer from ZnO LUMO orbital to Ag nanocrystals. But in case of ZnO/Au NCs, due to transfer of electrons from Au to ZnO, the electrons accumulate within the LUMO levels of ZnO nanocrystals and hence cause the bleaching of the excitonic feature [29]. Furthermore, the local electrical field must have been formed [28] at the interface between ZnO and Au NCs due to transfer of electrons from Au to ZnO.

Fig. 3 exhibits the room temperature PL spectra of ZnO nanocrystals and ZnO/Au nanojunctions excited at 325 nm.
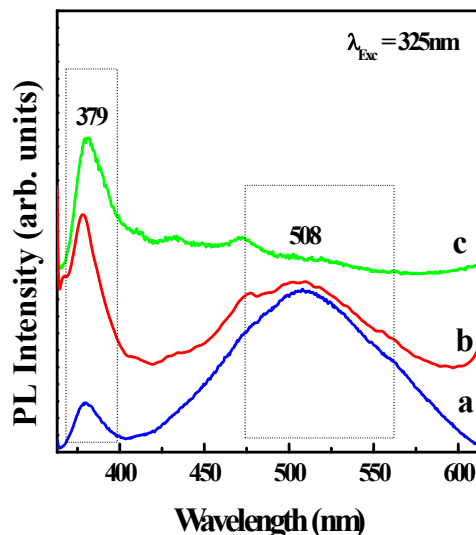

Fig. 3 – Room temperature photoluminescence spectra of ZnO nanocrystals (a), ZnO/Au nanojunctions with Au 20 min (b) and ZnO/Au nanojunctions with Au 40 min (c) deposition time.

The band edge luminescence of ZnO is observable at 379 nm while green emission is observable at 508 nm. As shown in Fig. 3, ZnO/Au nanojunctions prepared at different deposition time exhibit stronger UV emission and weaker visible emission than that of ZnO. There are two viewpoints on the electron transfer between ZnO and Au, which are responsible for quenching of green emission and the enhancement of band edge luminescence of ZnO nanocrystals. Wood et al. [20] and Subramanian et al. [29] have observed that the electrons can transfer from metal (Ag, Au, Cu and Pt) to semiconductor (ZnO) under UV light excitation in order to equilibrate Fermi-level. The Fermi level of gold (E_F = 0.5 V vs NHE) is more positive than the conduction band energy of ZnO (E_{CB} = – 0.6 V vs NHE). There by electrons transfer from Au to ZnO. Electron accumulation (or hole depletion) within semiconductor makes the subsequent electron-hole charge separation very inefficient due to rapid reaction of the nascent holes with the resident excess electrons in *n*-type semiconductor [20, 29, 30]. That is transfer of electrons from Au to ZnO can lead to accumulation of electrons near the conduction band, which increases the recombination of electrons in conduction band to holes in valance band of ZnO. The radiative transitions subsequently dominate the intensity of band edge emission in the present case. Another mechanism is the decrease in number of singly ionized oxygen vacancies (V_0^+) [29, 30] by capturing electrons when more electrons are transferred from Au to ZnO, further causing quenching in visible emission.

Also, the absorption of visible light by Au will be responsible for exciton-surface plasmon coupling, which helps to transfer electrons from Au to ZnO, resulting enhancement in UV emission intensity [30].

Photoluminescence excitation **(PLE)** spectra of ZnO nanocrystals and ZnO/Au nanojunctions are recorded at constant emission wavelength **(530 nm)** as shown in Fig. 4. Subtle blue shift in the PLE spectra is observed and is similar to the optical absorption behavior.
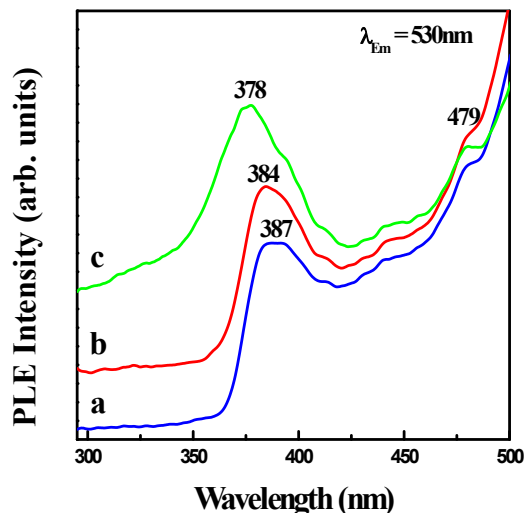

Fig. 4 − *Room temperature photoluminescence excitation spectra of ZnO nanocrystals (a), ZnO/Au nanojunctions with Au 20 min (b) and ZnO/Au nanojunctions with Au 40 min (c) deposition time*

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