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Plasmon mediated enhancement of visible light emission of Au-ZnO nanocomposites

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ABSTRACT

We report on the enhancement of the visible luminescence of Au-ZnO nanocomposites synthesized via a simple photoreduction method. The attachment of Au nanoparticles on the surface of ZnO nanostructures has been observed using transmission electron microscopy. Raman analysis reveals an increase in disorderness via lattice defect formation due to Au attachment and thus results in the appearance of silent modes of ZnO. The photoluminescence spectra of ZnO is found to be dominated by defect related visible emission, which is enhanced with the inclusion of Au nanoparticles. At room temperature, the green emission for nanocomposites has been found to be enhanced by seven times as compared to the pristine ZnO. Temperature dependent photoluminescence of Au-ZnO nanocomposites has been investigated to elucidate the origin of green luminescence and the enhancement of intensity. The gradual dominance of the green emission is originated from the surface plasmon oscillation of Au followed by the electron capture at the singly ionized oxygen vacancies of ZnO. The observed enhancement of visible light emission of ZnO using Au nanoparticles can establish the platform to fabricate efficient ZnO based visible light emitting devices and display systems.

1. Introduction

Localized surface plasmon resonance (LSPR) of metal nanoparticles offer unique pathway to enhance the Raman and photoluminescence intensity. The interaction of electromagnetic radiation on the metal-semiconductor interfaces at nanoscale is of great interest for many applications including photodetectors, light emitting diodes (LEDs) and surface enhanced Raman scattering (SERS) [1–3]. Zinc oxide (ZnO) is a wide band gap n-type semiconductor and hence it is attractive for optoelectronic device application in the ultra violet (UV) wavelength range [4,5]. It has a large exciton binding energy (60 meV), due to which it can give a strong UV emission at room temperature. Apart from the band edge emission in the UV region, it also exhibits an emission in the visible range, which is attributed to the intrinsic defects of ZnO [6]. The strong UV emission makes the system a potential candidate for UV light emitting diodes (LEDs) [7,8]. On the other hand, the visible emission occurs in green (GE) or yellow region makes it promising for visible light emitting diodes. The origin of GE has always been a point of curiosity and has been explored by several groups. The possible reasons for the GE are intrinsic point defects including zinc vacancy (V_{Zn}), oxygen vacancy (V_O), zinc interstitials (Zn_i) and oxygen antisites (O_{Zn}) of ZnO [9–11]. However, it is very difficult to expect a particular intrinsic defect for GE as it highly depends on the experimental conditions such as annealing temperature and environment.

Previously, several groups have investigated the enhancement in UV photoluminescence of ZnO using metal nanoparticles. Su et al. reported an enhanced UV emission by decorating Ag nanoparticles on the surface of ZnO nanorods [12]. Shao et al. achieved an enhanced near band edge emission of PVA-ZnO hybrids by incorporating SiO_2-Au core/shell nanoparticles [13]. However, the exploration and enhancement of the visible emission in ZnO can be beneficial for achieving white light emission. In this context, exploitation of metal nanoparticle induced localized surface plasmon resonance (LSPR) effect can be effective to obtain enhancement in the visible emission of ZnO. The enhancement of visible emission of ZnO using plasmonic nanoparticles has rarely been investigated.

In this paper, we report the influence of Au nanoparticles on the enhancement of green emission of Au-ZnO nanocomposites prepared by simple photoreduction method. Interactions between Au and ZnO nanostructures have been studied by X-ray photoelectron and Raman spectroscopy techniques. Further, the origin of green luminescence in the nanocomposites has been investigated by temperature dependent

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photoluminescence in the range from 10 K to 300 K.

2. Experimental

The Au-ZnO nanocomposites were prepared by photosynthesis method, as reported previously [14]. Briefly, ZnO nanostructures were prepared by a simple wet chemical process using $Zn(NO_3)_2{\cdot}6H_2O$ and NaOH at 200 °C. A six gram of $Zn(NO_3)_2{\cdot}6H_2O$ was dissolved in 500 ml deionized (DI) water in an ultrasonic bath at room temperature. Then, a 1.5 g of NaOH aqueous solution was added drop wise to the Zn $(NO_3)_2{\cdot}6H_2O$ solution at room temperature under vigorous stirring and heated at 200 °C for 12 h. The extracted ZnO nanostructures from the combined solution were cleaned with DI water for several times and dried under air at 100 °C. On the other hand, Au-ZnO nanocomposites were synthesized using ZnO nanostructures with different $HAuCl_4$ concentrations (4, 6 and 8 ml) under UV illumination (365 nm) for 10 h followed by annealing at 600 °C for 1hr in oxygen environment. A 100 mg of ZnO nanostructures and $HAuCl_4$ aqueous solution (2.5×10^{-3} M) were dispersed in 100 ml DI water by strong sonication for 25 min. The solutions are in acidic nature with a pH value of 5.0, 4.5 and 4.0 for 4, 6 and 8 ml of $HAuCl_4$ concentrations, respectively. Then, these solutions were kept under UV-light irradiation for 10 h. The obtained Au-ZnO samples were cleaned several times with DI water and dried under air at 100 °C. Subsequently, the plasmonic Au-ZnO material was annealed at 600 °C in oxygen atmosphere for 1 h, indicating the formation of Au-ZnO nanocomposites. To study the structural and optical properties of these samples, we have deposited a thick layer of ~ 1 μm of Au-ZnO nanocomposite films on Si substrates.

The morphological and structural properties have been studied by TEM (JEOL, JEM – 2100) and XRD (Philips, X-Pert MRD). The chemical states of Au and ZnO were studied using X-ray photoelectron spectroscopy (XPS) (ULVAC – PHI, INC, Japan) with a microfocused (100 mm, 25 W, 15 kV) monochromatic Al-Kα beam. To study the strain and intermixing of Au nanoparticles with ZnO, Raman spectroscopic measurement was performed for all the nanocomposite samples using a pump excitation wavelength of 514.5 nm. Photoluminescence measurements were carried out in the temperature range from 10 to 300 K using a He-Cd laser operated at a wavelength of 325 nm with an output power of 1.3 W/cm^2. The emission signals were analyzed using a TRIAX-320 monochromator fitted with a Hamamatsu photomultiplier detector.

3. Results and discussion

We have prepared Au-ZnO nanocomposites by photosynthesis method with increasing $HAuCl_4$ concentration of 4, 6 and 8 ml, and the samples hereafter designated as AZ4, AZ6 and AZ8, respectively. Fig. 1a–d illustrate the transmission electron microscopy (TEM) images of ZnO, AZ4, AZ6 and AZ8. As seen in figure, pure ZnO has the sheet-like nanostructures, which are observed in the Fig. 1e. The Au-ZnO nanocomposites exhibit well decorated Au nanoparticles on the surface of ZnO nanostructures, which are clearly shown in the Fig. 1f–h. The size distributions of Au nanoparticles extracted from several TEM images (not shown here) are found to be broad in nature, as shown in the inset of Fig. 1b–d. It is to be noted from the several TEM images (not shown here) that the density of Au nanoparticles varies with increasing Au concentration. X-ray diffraction (XRD) patterns of Au-ZnO nanocomposites along with the pure ZnO are shown in Fig. 2. All the samples show the diffraction peaks corresponding to the wurtzite hexagonal structure of ZnO. For Au-ZnO nanocomposites, in addition to the diffraction peaks of ZnO, extra peaks are observed at $2\theta = 38.19^\circ$ and 64.65°, which are correspond to the (111) and (220) diffraction of face centred cubic phase of Au, respectively. The XRD pattern does not show any change in peak position and FWHM for nanocomposite samples with the inclusion of Au nanoparticles on the surface of ZnO as compared to pure one.

Fig. 3 shows the X-ray photoelectron spectroscopy (XPS) spectra of core level regions of (a) Zn 2p, (b) Zn 3p and Au 4f electrons and (c) O 1s. As seen in Fig. 3a, the binding energies (BE) of Zn $2p_{1/2}$ and $2p_{3/2}$ are located at 1044 and 1021 eV for all the samples, indicating the existence of Zn^{2+} chemical state [14]. The core level BE of Zn-3p and Au 4f electrons is shown in Fig. 3b. A distinct peak at 88 eV corresponds to the Zn $3p_{3/2}$, while the shoulder at 91.1 eV indicates $3p_{1/2}$ state of Zn. Moreover, a small peak at ~ 83.1 eV for AZ4 corresponds to the Au $4f_{7/2}$, whereas the Au $4f_{5/2}$ state cannot be distinguished properly owing to the overlap with Zn 3p peaks. As seen in figure, the BE peak position of Zn-3p electrons further indicates no change in the chemical state of Zn with increasing Au concentration. The peak position of Au-4f electrons for samples is listed in Table 1. Interestingly, compared with the pure Au [15], the BE of Au-4f is found to be slightly shifted towards lower BE side. The observed shift is a result of the strong interaction between Au NPs and ZnO without any chemical bonding. As reported earlier [14], electrons can transfer from ZnO to Au, leading to the formation of negatively charged Au nanoparticles on the surface of ZnO. This strong interaction can lead to tunable electrical and optical properties of ZnO due to the attachment of Au nanoparticles for efficient optoelectronic applications. Fig. 3c shows the core level XPS spectra of O 1s for pure ZnO and AZ8. The BE of O 1s is de-convoluted into two peaks 530 (O1) and 531.2 eV (O2). The dominant peak at 530 eV is due to the lattice oxygen of wurtzite ZnO and the higher BE peak is originated from the oxygen related defect region or from the adsorbed hydroxyl/oxygen species [14,16]. It is also observed that the ratio of the two peak areas (O1/O2) is found to be ~ 1.02 for bare ZnO and it is increased to be ~ 1.7 and ~ 1.2 for AZ6 and AZ8, respectively. The increased value of O1/O2 peak ratio nullifies the idea of increase in oxygen vacancy defect concentration after photoreduction process. The increased value of the ratio indicates the lowering of contribution of O2 due to the strong interaction between Au and ZnO, which modifies the surface charge distribution through electron transfer.

Fig. 4 illustrates the UV–vis absorption spectra of ZnO and Au-ZnO nanocomposites. The spectra of nanocomposite sample clearly display an absorption in the UV region attributed to the band edge absorption of ZnO and that in the visible region correspond to the localized surface plasmon absorption of Au nanoparticles. It is also observed that the plasmon band is found to be broad, indicating wide particle size distribution within the nanocomposites. These results further corroborate with the measured statistical size distribution from the TEM measurements, as shown in the inset of Fig. 1.

Fig. 5 represents the Raman spectra of the bare ZnO and Au nanoparticles loaded ZnO samples under an excitation of 514 nm of Ar laser. It is well established that at the Γ-point of the Brillouin zone for ideal ZnO, there exists following sets of phonon modes [17]:

$$\Gamma = 2A_1 + 2B_1 + 2E_1 + 2E_2 \quad (1)$$

A_1 and E_1 are polar in nature and split into two components transverse optical (TO) and longitudinal optical (LO) modes. The E_2 mode consists of low (E_2 low) and high (E_2 high) frequency phonons associated with the Zn and O atomic vibration in ZnO. On the other hand, B_1 modes (both low and high) are considered as silent modes in ZnO. In the present investigation, the E_2 (low) mode at ~ 95 cm^{-1} is found to be dominant in all spectra. For the pristine ZnO nanostructures, E_2 (high) is found at ~ 436 cm^{-1}, which is close to bulk ZnO (~ 437 cm^{-1}) [17]. The E_2 (high) mode for Au incorporated samples is found to exhibit a shift to lower frequency side (~ 429 cm^{-1} for AZ8). Such shift in E_2 (high) mode is correlated to the variation in lattice strain [18]. Although, XRD analysis does not indicate any strain in the crystal structure of ZnO but the attachment of Au on ZnO surface can introduce a local strain on the lattice of host ZnO near the interface. Since the Au attachment is only on the surface so that the lattice strain is formed near the surface and it is localized at the interface. But due to the fact that ZnO nanostructures are comparatively larger than the Au nanoparticles, the localized strain at the interface is unable to