

Photoluminescence of Electrodeposited ZnO Hybrid Thin Films

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Abstract: Photoluminescence (PL) properties have been studied for electrodeposited porous ZnO thin films hybridized with luminescent rare earth metal complexes and organic molecules. Nanoporous ZnO films were cathodically electrodeposited from the bath containing eosin Y (EY). Various bridging ligands (BLs) having carboxylic acid group as anchor was loaded to ZnO. These BLs have the moiety to coordinate to metal ions and thus can form complexes on ZnO surface by uptaking metal ions such as Eu^{3+} , Tb^{3+} and Al^{3+} . Fluorescent organic molecules having carboxylic acid group has been chosen and are also attached from their solutions. Some of the hybrid thin films with metal complexes exhibited PL, while none of organic molecules showed PL. Especially efficient were the films with Eu^{3+} complexes. Its PL intensity was further increased by capping Eu^{3+} with β -diketones. The quantum efficiency for its PL was determined as 21 % when only the ligand to metal energy transfer is taken into account.

Key words: Electrodeposition, ZnO, luminescence, lanthanide, thin films

1. Introduction

Semiconductor nanostructures have attracted much attention in recent years. In comparison with the bulk materials, they are to have unique properties such as the quantum size effect [1]. Among compound semiconductors, metal oxides and nitrides are especially interesting for their electronic and optoelectronic properties, finding various applications such as dye-sensitized solar cells, gas sensors, catalysts and phosphors [2-7].

Zinc oxide (ZnO) has a large exciton binding energy (60 meV) and a wide band gap (3.4 eV), making its exciton stable at room temperature. Because of such properties, ZnO nanocrystals are suitable host materials for doping with luminescent centers such as rare earth metals [8-10]. It is well known that rare earth complexes exhibit extremely sharp visible light emission compared with fluorescent dyes and polymers [11-13]. 4f orbitals are effectively shielded from the influence of the surrounding by overlaying the 5s and 5p orbitals. Furthermore, the lanthanide ions can be excited via an intramolecular energy transfer from the triplet excited state of the ligands. The internal quantum efficiency of the rare earth complexes as emitter layers can theoretically be as high as 100%. In organic light emitting diodes (OLEDs), such metal complexes are doped into organic semiconductors [11,12]. However the organic layers usually have low carrier mobility and are unstable against oxygen and moist. Hybridization of organic molecular light emitters with inorganic semiconductors with high carrier mobility and chemical stability is therefore a promising strategy. Such compounds exhibit increased thermal and emission stability in time [14].

Recently, we have shown that organic dye molecules can be hybridized with ZnO during its cathodic

electrodeposition by simply adding water soluble dye into the deposition bath. Self assembly of ZnO/dye hybrid nanostructure evolves because of adsorption of dye molecules to the growing surface of ZnO [15-19]. These hybrid thin films perform as efficient photoelectrodes for dye-sensitized solar cells (DSSCs). The same approach of materials synthesis has successfully been applied to preparation of hybrid thin films of ZnO and rare earth metal complexes, which exhibit photoluminescence (PL) in different colors, since a large amount of complexes can be attached owing to the high surface area [13].

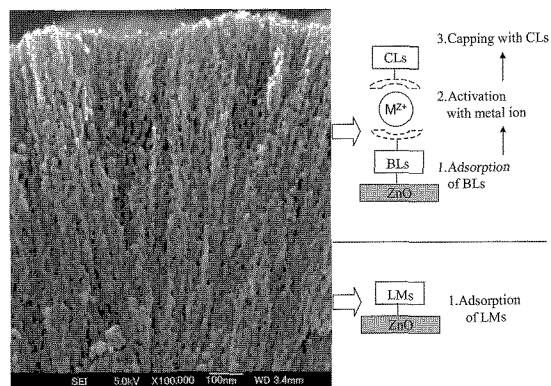


Fig.1 Cross sectional view of electrodeposited porous ZnO film and procedure to synthesize luminescent hybrid thin films.

The synthetic strategy of the luminescent hybrid thin film is schematically presented in Fig. 1. Porous crystalline ZnO is prepared by hybridization with eosinY (EY) and subsequent extraction of EY. It is soaked in solution of bridging ligands (BLs) having carboxylic acid group as anchor to ZnO and another

moiety to coordinate to metal ions. The ZnO film modified with BLs is then soaked in the solution of central metal ions (CMs) to form complexes. The surface grafting is finally completed by capping ligands (CLs) which stabilize the complex. Alternatively, luminescent organic molecules (LMs) with anchoring group can also be attached directly to the porous ZnO. Suitable hole conductor may finally be deposited on such layer to construct a hybrid EL devices and that is the final goal of our study.

The aim of this study is to attempt to increase the variation of luminescent hybrid by combination of various, BLs, CMs and CLs. For those with good PL properties, their PL as well as the PL excitation (PLE) spectra were measured to discuss the PL mechanism. Absolute quantum yields of PL were also determined.

2. Experimental

2.1 Electrodeposition of porous ZnO thin films

Fluorine doped SnO₂ (FTO) coated glass (10 Ω/□ Asahi glass) sheets were cleaned ultrasonically in acetone, 2-propanol, soap solution, and water. They were activated in 45 % HNO₃ for 2 min and finally rinsed with distilled water prior to the deposition.

An aqueous solution was prepared as deposition bath to contain 5 mM ZnCl₂ (Merck) and 0.1 M KCl (Merck). Disodium salt of EY (Kanto) was added into the deposition bath at 45 μM for preparing ZnO/EY hybrid film. A three-electrode single compartment cell was used. FTO glass was used as a working electrode by applying it to a Radiometer Analytical (EDI101 and CTV101) rotating electrode system. The rotation rate was set to 500 rpm. A Zn wire (99.9%) was used as a counter electrode. The potential was referred to an Ag/AgCl. The cell was placed in a thermostat bath maintained at 70°C. Oxygen gas was bubbled at 100 ml min⁻¹ for 30 min prior to the actual electrolysis and the same gas flow was maintained during the deposition. The electrolysis was carried out for 20 min potentiostatically at -0.95 V (vs. Ag/AgCl). A Hokuto Denko HSV-100 was used for the potential control and the current monitoring. The obtained ZnO/EY hybrid film was converted to a porous ZnO by soaking it into a dilute KOH solution at pH 10.5 to extract EY.

2.2 Grafting of luminescent complexes and molecules

As shown in Fig. 1, the porous ZnO surface was modified by subsequently soaking the film into ethanolic solutions containing BLs, CMs and CLs at a few hundreds of μM, then refluxing the solutions for 1 h. Various BLs were tested but results with 2,2'-bipyridine dicarboxylic acid (dcbpy) and 8-hydroxyquinoline 5-sulfonic acid (hqs) (Fig. 2) are only reported here. The CMs such as Eu³⁺, Tb³⁺ and Al³⁺ were used as chlorides. The CLs (CL1-4) were β-diketones as shown in Fig. 2. ZnO surface was also furnished with LMs such as eosinY (LM1), 1-pyrene carboxylic acid (LM2) and Salicylic acid sodium salt (LM3) by refluxing the film in their 0.2 mM ethanolic solutions.

2.3 Photoluminescence measurements

The PL and PLE spectra of the solid samples were measured on a Hitachi F-4500 spectrofluorimeter at room temperature by placing the film at 45° angle

with respect to the excitation and the monitoring beams. The PL, PLE and absorption spectra were also measured for solutions of the metal complexes prepared by mixing BLs, CMs and CLs at stoichiometric ratio for known form of the complexes. Absolute PL quantum yield was measured on a Hamamatsu Photonics C9920-02 system equipped with an integration sphere to place the film sample and counting the number of photons detected by a diode array photometer.

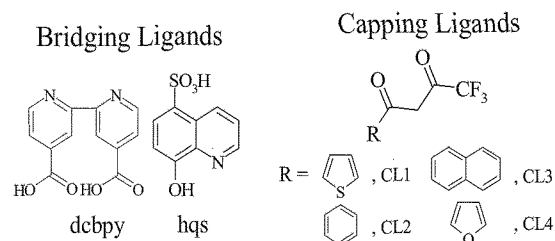


Fig.2 Molecular structures of BLs and CLs

3. Results and Discussions

About 50 film samples were prepared by combination of various BLs, CMs and CLs. Many of them were successfully attached to the ZnO surface and exhibited PL properties with different intensities, although formation of complexes were not achieved when CMs such as Pr³⁺, Sm³⁺, Dy³⁺, Ho³⁺, Tm³⁺ and Ir³⁺ were chosen. Among the samples, those with Eu³⁺ and Tb³⁺ attached through dcbpy as BL and Al³⁺ complex with hqs exhibited relatively intense PLs in visible region as shown in Fig. 3. The ZnO/dcbpy-Eu³⁺ film emits red light with several sharp peaks, characteristic of intra-4f transitions of Eu³⁺ attributed to ⁵D₀ → ⁷F₁, ⁵D₀ → ⁷F₂, ⁵D₀ → ⁷F₃ and ⁵D₀ → ⁷F₄ at 590, 612, 650 and 700 nm, respectively. The ZnO/dcbpy-Tb³⁺ film exhibits green emissions due to intra-4f transitions of Tb³⁺ assigned to ⁵D₄ → ⁷F_j (j = 6, 5, 4, 3) at 490, 543, 587 and 622 nm, respectively. In contrast to these lanthanoid complexes, the ZnO/hqs-Al³⁺ film exhibits a broad emission centered at 515 nm, similarly to the well known Al³⁺ 8-hydroxyquinoline complex (Alq₃) [20-22]. The broad character of PL arises from that the electronic transition of Alq₃ is localized in the quinolate ligands, in contrast to the rare earth metal complexes.

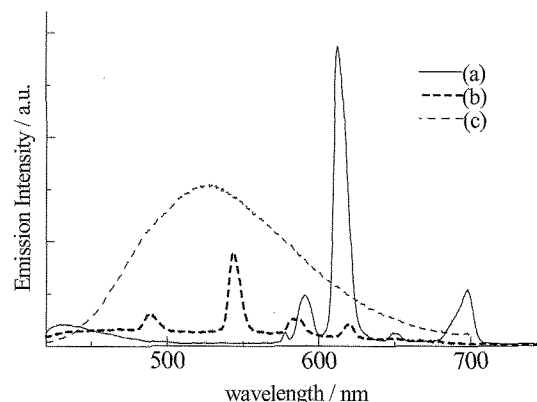


Fig.3 PL spectra of ZnO films hybridized with luminescent complexes excited at 315 nm. (a) ZnO/dcbpy-Eu³⁺, (b) ZnO/dcbpy-Tb³⁺ and (c) ZnO/hqs-Al³⁺.

All of LMs could also be attached to ZnO owing to the presence of carboxylic acid anchoring group, as confirmed by UV-Vis absorption spectroscopy. These LMs in solutions emit intense PLs in the visible, but they were completely quenched when hybridized with ZnO. Fast and efficient electron injection from photoexcited state of fluorescent dye molecules to the conduction band of ZnO is a key process in DSSCs [23]. It is likely that such electron transfer occurs for the LMs tested here, because the lowest unoccupied molecular orbitals (LUMOs) of LMs are located way above the conduction band (CB) of ZnO. From such thermodynamic arguments, however, the LUMOs of BLs are also above the CB of ZnO. It is understood that intramolecular energy transfer from BLs to CMs prevails to the quenching of excited state of BLs. The visible PL is therefore specific for the hybrid films with such metal complexes.

The PL intensity the hybrid film with Eu^{3+} complexes was further increased by capping the complex with CLs. The CLs are expected to coordinate to Eu^{3+} to stabilize the complex. On the other hand, no such enhancement was observed when Tb^{3+} samples were treated with CLs.

The PLE spectra of the film samples are compared to the absorption spectra of BL and CL in Fig. 4. The PLE of ZnO shows several features below ca. 250 nm originating from transitions in ZnO. These features are also recognized in the hybrid film samples with the higher intensities, suggesting energy transfer from ZnO to the complex. However, the PL of ZnO/dcbpy- Eu^{3+} system seems to reflect mainly the broad peak at around 310 nm. The shape of this peak resembles with that of the absorption of dcbpy appearing at somewhat shorter wavelength of 297 nm. It is reasonably understood that the PL originates by photoexcitation of the ZnO-bound dcbpy and energy transfer to Eu^{3+} . Similar features were observed in the PLE spectrum of ZnO/dcbpy- Tb^{3+} indicating energy transfer from dcbpy to Tb^{3+} as the mechanism of PL.

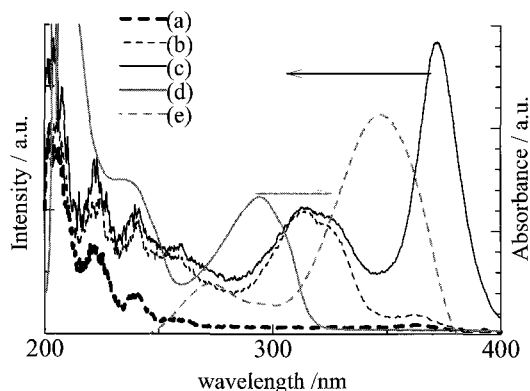


Fig.4 Comparison of PLE and absorption spectra; PLE of (a) ZnO, (b) ZnO/dcbpy- Eu^{3+} and (c) ZnO/dcbpy- Eu^{3+} -CL1 with monitoring emission wavelength of 612 nm. Absorption spectra of ethanolic solutions of (d) dcbpy (d) and (e) CL1.

For the ZnO /dcbpy- Eu^{3+} -CL1 sample, a sharp peak appears at 372 nm. The absorption spectrum of CL1 shows a peak at 347 nm, although much broader in shape. When the ZnO/dcbpy- Eu^{3+} sample was treated with CL2, 3 and 4, similar peaks appeared in their PLE

spectra at 366, 374, and 368 nm, respectively. All of these peaks are red-shifted by ca. 30 nm from those of the absorption of respective CL molecules in solution. These new peaks therefore seem to arise from the CLs coordinating to the Eu complexes bound to ZnO. It has been elucidated that the PL of the Eu complex bound to ZnO mainly occurs via energy transfer from BL and CL, although contribution of energy transfer from ZnO cannot be completely ruled out.

The PLE spectrum of ZnO/hqs- Al^{3+} sample shows totally different features from those with the lanthanoid complexes. The PLE spectrum of the film sample is compared with the absorption spectra of the solutions of hqs and $\text{Al}(\text{hqs})_3$ complex in Fig. 5. The hqs molecule possesses a sharp absorption peak at 240 nm and a broad one at 310 nm. When it is complexed with Al^{3+} , they are red-shifted to 255 nm and 360 nm, respectively. These characters are similar to those of Alq_3 complex in DMF solution [20-22]. The PLE spectrum of the film sample monitored for PL at 515 nm shows two peaks related to photoexcitation of the surface complex. The relatively sharp peak is further shifted to 365 nm, while the broad one remains at the same position. It should be noted that the proportion of these two peaks totally differ from that of the molecular absorption. It is also noticed that the intensity of the PLE spectrum around 280 nm, where a valley is created for the absorption of the complex, remains rather high. These features suggest contribution of ZnO to the PL by energy transfer to the complex.

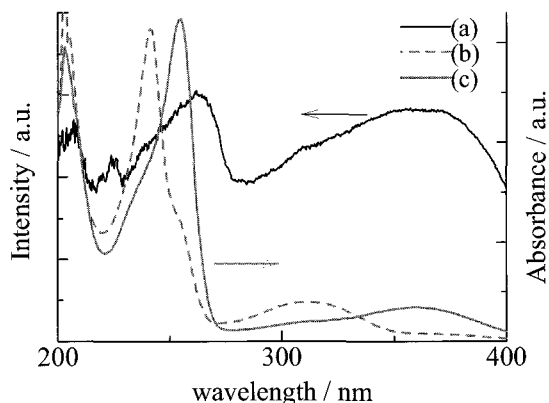


Fig.5 Comparison of (a) PLE spectrum of ZnO/hqs- Al^{3+} hybrid thin film with absorption spectra of solutions containing (b) 0.3 mM hqs and (c) 0.3 mM hqs, 0.1 mM Al^{3+} .

We have attempted to determine quantum efficiencies of PL of the hybrid thin films. The basis of the measurement depends on whether to consider the contribution of ZnO or not. As Case 1, light absorption only by the surface bound complexes was estimated by subtracting the light extinction by porous ZnO thin film without the complex from that of the hybrid thin film, assuming only the PL localized in the molecule. Case 2 takes both the molecular localized and ZnO/molecular cooperative processes into account, so that the efficiency is calculated from the total absorption of the film sample. Although precise evaluation of the light extinction by the molecule is difficult, because that by ZnO slightly differ from sample to sample, rather high quantum yields of 9.9 and 21.2% were determined in Case 1 for

dc bpy-Eu³⁺ complex bound to ZnO excited at 310 and 370 nm, respectively (Table 1). These results suggest more efficient energy transfer from dc bpy than CL1. PL measurements at 20 K and room temperature indicated that this sample retains PL intensity at room temperature being about half of that at 20 K, suggesting that non radiative decay of the excited state is effectively suppressed in the hybrid film [24]. For Case 2, however, these values drop to 1.1 and 0.7%, respectively, suggesting rather inefficient or no energy transfer from ZnO that then only filters UV light to be absorbed by the complex.

For the ZnO/hqs-Al³⁺ film, quantum yields were determined only for Case 2 as 4.5 and 9.6% for excitation at 400 and 355 nm, respectively. Because light absorption by ZnO at 400 nm is almost zero, the former can therefore be considered as reflecting the molecular localized PL, namely, the energy transfer from hqs. On the other hand, the latter originates from light absorption both by hqs and ZnO. The higher efficiency at 355 nm therefore indicates rather efficient energy transfer from ZnO to the hqs-Al³⁺ complex. In fact, a constant quantum efficiency independent on the excitation wavelength was found for the Al(hqs)₃ complex solution. The concerted action between ZnO and hqs-Al³⁺ complex to generate PL is a unique function of the ZnO/hqs-Al³⁺ hybrid thin film. Such a process may become operative because of the ligand localized PL mechanism of the hqs-Al³⁺ complex.

Table I. Quantum yields for PL of the hybrid films.

sample	excitation wavelength (nm)	Quantum Yield (%)	
		Case 1	Case 2
ZnO/dc bpy	310	21.2	0.7
-Eu ³⁺ -CL1	370	9.9	1.1
ZnO/hqs-	355	-	9.6
Al ³⁺	400	-	4.5

4. Conclusions

ZnO-based visible luminescent hybrid thin films were successfully obtained by electrodeposition of porous ZnO and post chemical treatments to attach luminescent molecules. While PL of fluorescent organic molecules was completely quenched, those with metal complexes were found to emit PL. The strategy to build up complexes by subsequent attachment of BLs, CMs and CLs successfully worked out. Especially efficient was the system combining Eu³⁺ complexes with a quantum efficiency exceeding 20%. The attachment of CL to Eu³⁺ complex enhanced PL intensity. While molecular localized PL is the main mechanism for the Eu³⁺ system, cooperative PL via energy transfer from ZnO to the complex seems to operate for the ZnO/hqs-Al³⁺ hybrid system.

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5. References

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