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Spectral, thermal and optical–electrical properties of the layer-by-layer deposited thin film of nano Zn(II)-8-hydroxy-5-nitrosoquinolate complex

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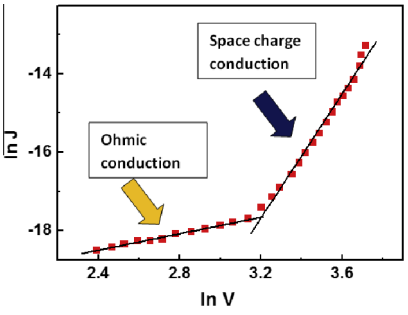
HIGHLIGHTS

- Nano [**Zn(II)-(HNOQ)$_2$**] complex thin films were synthesized by the rapid direct simple efficient LbL technique.
- The nano complex structure was confirmed by EI-MS and FT-IR.
- SEM images indicate a particle size of 23–49 nm.
- TGA of the nano [**Zn(II)-(HNOQ)$_2$**] reflects its high thermal stability.
- Nano thin films have two direct allowed transitions with transport and optical gaps of 2.4 and 1.0 eV, respectively.

GRAPHICAL ABSTRACT



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ABSTRACT

Zinc(II)-8-hydroxy-5-nitrosoquinolate, [**Zn(II)-(HNOQ)$_2$**], was synthesized and assembled as a deposited thin film of nano-metal complex by a rapid, direct, simple and efficient procedure based on layer-by-layer chemical deposition technique. Stoichiometric identification and structural characterization of [**Zn(II)-(HNOQ)$_2$**] were confirmed by electron impact mass spectrometry (EI-MS) and Fourier Transform infrared spectroscopy (FT-IR). Surface morphology was studied by using a scanning electron microscope imaging (SEM) and the particle size was found to be in the range of 23–49 nm. Thermal stability of [**Zn(II)-(HNOQ)$_2$**] was studied and the thermal parameters were evaluated using thermal gravimetric analysis (TGA). The current density–voltage measurements showed that the current flow is dominated by a space charge limited and influenced by traps under high bias. The optical properties of [**Zn(II)-(HNOQ)$_2$**] thin films were found to exhibit two direct allowed transitions at 2.4 and 1.0 eV, respectively.

Introduction

Nano-sized metal complexes can be readily attached to a solid surface by several modes of synthetic approaches for the design, assembly, and formation of deposited thin films by selection of one of the well-known molecular engineering processes [1,2]. These include: Chemical bath deposition, magnetron sputtering, organic vapor phase deposition method (OVPD), microwave heating, spin coating, electrochemical deposition, spray pyrolysis technique, Langmuir–Blodgett, pulsed laser deposition and Layer-by-Layer (LbL) chemical deposition technique [3]. The LbL technique has been recently used as a potentially rapid, direct, efficient, and simple method that is based on sequential immersion of neutral or charged substrate into neutral or oppositely charged electrolytic solutions for synthesis of nano-materials as well as nano-composite materials and nano-sized metal complexes in the form of thin films [4,5]. In addition, the LbL technique affords a great utility of wet chemistry for self-assembly and fabrication of thin films [6,7]. This opens a large field of possibilities for the design of various important classes of compounds [8].

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Metal complexes of 8-hydroxyquinoline (8HQ) derivatives are commonly used as important components in designing and manufacturing various electronic devices such as light-emitting diodes and photoluminescence devices [9–11]. In addition, improvement in characteristics of photovoltaic and solar cells were also demonstrated and reported using derivatives of tris(8-hydroxyquinoline) aluminum (Alq_3) [12,13].

The aim of this work is devoted to study and evaluate the potential implementation of the LbL chemical deposition technique for design, synthesis and assembly of nano-sized Zn(II)-8-hydroxy-5-nitrosoquinolate complex, [**Zn(II)-(HNOQ)$_2$**], based on the direct and wet reaction of Zn(II) with 8-hydroxy-5-nitrosoquinoline. The structural characterization and confirmation of the deposited thin films were explored. The thermal stability, optical and electrical properties were also investigated and interpreted.

Experimental

Instrumentations

Scanning electron microscope (JSM-6360 LA, JEOL Ltd.), (JSM-5300, JEOL Ltd.) and an ion sputtering coating device (JEOL-JFC-1100E) were used to examine and image the assembled thin films of the [**Zn(II)-(HNOQ)$_2$**] complex. SEM specimens were coated with gold to increase the conductivity. The metal analysis of zinc content after acid digestion and suitable dilution of the [**Zn(II)-(HNOQ)$_2$**] complex was determined by complexometric titration. The results were further confirmed using a Shimadzu model (AA-6650) flame atomic absorption spectrophotometer at the appropriate wavelength. A Finnigan MAT 95, equipped with a DIP, ionization energy of 70 eV, electron multiplier voltage 1800 V, was used to acquire the electron impact mass spectra. The FT-IR spectrum of the [**Zn(II)-(HNOQ)$_2$**] complex was measured by a BRUKER Tensor-37 Fourier Transform infrared spectrophotometer in the range of 400–4000 cm^{-1}. Thermal gravimetric analysis (TGA) was measured using a Perkin–Elmer TGA7 Thermobalance. The operating temperature heating range, heating rate and flow rate parameters were selected as 20–600 °C, 10 °C min^{-1}, 20 ml min^{-1}, respectively and the experiment was accomplished in the presence of pure nitrogen atmosphere and the sample mass was in the range of 5–12 mg.

The optical transmittance and absorbance were measured using a double beam UV–Vis spectrophotometer type LABOMED in the spectral range 190–1100 nm with scan step 2 nm using glass substrate as reference. Measurements of the current–voltage characteristics were made using a high internal impedance electrometer (Keithely 617A) with internal voltage source. The temperature of the device was recorded by chromel–alumel thermocouple (Type-K) connected to the temperature controller.

Chemicals and materials

Zinc acetate dihydrate, $Zn(OAc)_2{\cdot}2H_2O$, of analytical grade was purchased from Aldrich Chemical Company, USA. 8-Hydroxyquinoline (8-HQ, 99% min.), ethanol and methanol were obtained from BDH limited, Poole, England and were used as received. Sodium hydroxide, sulfuric acid, glacial acetic acid and sodium nitrite, were all of analytical grade and purchased from Aldrich chemical company, USA and BDH limited, Poole, England. A 0.1 M solution of metal ion was prepared in doubly distilled water (DDW). Another ethanolic solution of 8-hydroxy-5-nitrosoquinoline [HNOQ] (0.1 M) was also prepared. Micro-slide glass substrates of the dimensions 76.2 mm, 25.4 mm and 1.0 mm were cleaned as previously described by washing them with double distilled water and chromic acid (1 M) and finally ultra sonically cleaned [14] and used to assemble the thin films of the [**Zn(II)-(HNOQ)$_2$**] complex.

Synthesis and assembly of the nano-sized [Zn(II)-(HNOQ)$_2$] complex

8-Hydroxy-5-nitrosoquinoline was synthesized as previously reported [15]. Synthesis and assembly of thin films of the nano-sized [**Zn(II)-(HNOQ)$_2$**] complex were carried out according to the following procedure. A clean glass substrate was vertically immersed into the metal ion solution for 8 min. period to deposit the Zn(II) ion on the substrate surface (first step). The substrate was then immersed into the ligand solution for another 8 min. period whereas the pre-adsorbed metal ion on the glass substrate was allowed to react with the ligand (second step). These two deposition steps represent a deposition cycle and were carried out at room temperature. A colored and uniform thin film of the [**Zn(II)-(HNOQ)$_2$**] complex was formed after few dipping cycles. The substrate was rinsed with distilled water after each reaction cycle. This procedure was repeated to increase thin film thickness and homogeneity. The desired thin film was obtained at a number of dipping cycles equals to 10 cycles.

Results and discussion

Characterization of chemical structure and surface morphology of assembled thin film of nano-sized [Zn(II)-(HNOQ)$_2$] complex

The Stoichiometry of Zn(II):[HNOQ] was evaluated on the basis of metal analysis for determination of the experimental percentage of Zn(II) in the complex after the digestion using metal analysis with EDTA – titration as well as atomic absorption spectrophotometric determinations. This value was identified as 15.882% based on triplicate analysis and is considered to be in a good agreement with the theoretical percentage of Zn(II) in the complex (15.895%) based on a 1:2 stoichiometric ratio. The electron impact-mass spectroscopic (EI-MS) study was also used to confirm the structure of the ligand and metal complex molecules. EI-MS of the ligand, [HNOQ], was found to produce the molecular ion peak at m/z 174 as the base peak. The loss of the NO group was evident by the formation of the fragment ion peak at *m*/*z* 144 amu. Several other fragment ions were also characterized in the EI-MS of [HNOQ] at *m*/*z* 130, 116, 89, and 63 amu which are related to the ligand molecule. On the other hand, the EI-MS of [**Zn(II)-(HNOQ)$_2$**] complex is shown in Fig. 1 and it is characterized by the presence of a characteristic molecular ion peak at *m*/*z* 411 amu. The fragment ion peak at *m*/*z* 238 amu is corresponding to the loss of 173 amu from the molecular as the coordinated ligand molecule. In addition, several other characteristic fragment ions related to the ligand molecule, are evident in the EI-MS of the [**Zn(II)-(HNOQ)$_2$**] complex as shown in Fig. 1.

The mode of bonding of Zn(II) to the ligand molecule was also studied and evaluated by comparison of the FT-IR spectrum of the free ligand with that of the deposited nano-sized metal complex. The FT-IR spectrum of the [HNOQ] ligand was found to produce several characteristic peaks at 3464, 3093, 1601, 1382, and 1280 cm^{-1} corresponding to OH, $CH_{aromatic}$, C=N, NO and CO, respectively, as the major functional groups. On the other hand, the FT-IR spectrum of the deposited thin film of the [**Zn(II)-(HNOQ)$_2$**] complex was found to confirm the complexation of Zn(II) to the [HNOQ] ligand *via* the coordinate bond contribution of the ring nitrogen donor atom. This was evident from the shift in the C=N peak (1550 cm^{-1}). The participation of the hydroxyl group in coordination was confirmed by the disappearance of the OH peak from the FT-IR spectrum. In addition, no evidence for the contribution of the nitroso functional group in the complexa-