



Synthesis, Characterization And Application Of Cobalt(II), Nickel(II) And Copper(II) Complexes As Sensitizer Dye In DSSC With 4-Cyanopyridine And Isothiocyanate Ligands

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Abstract:

Dye-sensitized solar cells (DSSCs) have been studied extensively for their advantages over conventional p-n junction devices, such as low cost, less toxic manufacturing, easy scale-up, light weight, and potential use of flexible panels. The sensitizer dye is a basic component in a DSSC which plays an important role in injecting the photo excited electron from valence band of the dye molecule into the conduction band of the wide band gap semiconductor such as TiO₂. Though a lot of work has been done using Ru complex as sensitizer for an efficient solar cell, only few works have been reported on other transition metal complex as a sensitizer in DSSC. Moreover, among all the semiconductor oxides, TiO₂ is preferred because of its excellent physicochemical properties. In the present study, we have prepared three complexes of cobalt(II), nickel(II) and copper(II) by reacting the respective metal nitrates with 4-cyanopyridine and isothiocyanate ligands at room temperature in aqueous medium. The complexes were characterized by elemental, FTIR and UV-visible spectroscopy technique and the results indicate that these complexes have the potentiality for application as a sensitizer in DSSC. One prototype solar cells were fabricated using one of the the as synthesized complexes as the dye sensitizers on nanoporous TiO₂ thin film and the photovoltaic parameters of the cells were compared. For the fabrication of the cells, TiO₂ thin films were prepared using commercially available TiO₂ nano powder on a transparent conducting oxide (TCO) glass substrate.

Keywords: DSSC, sensitizer dye, nanoporous, TiO₂Proton conductivity, Talc

Introduction

The dye sensitized solar cells (DSSC) have attracted wide attention as a cheaper alternative for converting solar energy to electricity than photovoltaic cells made from silicon and conventional p-n junction after the breakthrough discovery by O'Regan and Gratzel.[1-2] The most important parts in a DSSC are the sensitizer dye and the nanoporous wide band gap semiconductor which works as a photo anode in the device. Many efforts have been focussed on the synthesis and application of different dyes (both organic and inorganic). Numerous dye sensitizers have been proposed in recent years as it plays a key role in harvesting sunlight. [3]. Although, in the past few years, the most efficient cells have been obtained by using Ru-polypyridyl complexes as sensitizer dye due to its intense panchromatic behaviour and high MLCT, the need for an alternative still have a place owing to the high cost and complicated synthetic route of such complexes[4]. However, research has been extended to other charge transfer complexes such as Fe(II), Cu(II), Re (I), Os(II), Pt (II), Co(II) etc.[5-15] as potential sensitizers for DSSC. The efficiency of the sensitizing dye is also dependent on the electron injection from a photo excited state of the dye into the conduction band of a semiconductor. The most widely used semiconducting nanomaterial in a DSSC is TiO₂ due to its favourable properties like high photo catalytic activity, anticorrosion, stable chemical properties, high adsorption property and eco-friendliness [16-19].

In the present study, we have synthesized three complexes of cobalt, nickel and copper containing 4-cyanopyridine (4-CNpy) and isothiocyanate (-NCS) as ligand. The complexes were characterized by UV-vis, IR and elemental analyses. The as synthesized complexes were then adsorbed onto the TiO₂ thin films for the formation of the working electrode for application in DSSC. The performance of the as fabricated photoanode as well as the interaction between TiO₂ nanoparticle and the sensitizer dyes were also investigated through UV-vis spectroscopy. One prototype cell was fabricated by using KI and I₂ as electrolyte and carbon coated TCO as counter electrode. The photovoltaic parameter of the cell was measured with a Keithely 2400-source meter.

Experimental

Material And Methods

All reagents and solvents viz. cobalt nitrate, copper nitrate, nickel nitrate, ammonium thiocyanate, 4-cyanopyridine, titanium dioxide, isopropyl alcohol, acetic acid, nitric acid, ammonia, ethanol etc. used in this work were of ACS grade and obtained from Aldrich and Merck (India) Ltd and used as received unless otherwise stated. C,H,N analyses were carried out using a Perkin Elmer 2400 Series II CHNS/O Analyzer. Chemical analyses of cobalt and nickel were done gravimetrically and copper was done iodometrically by following standard procedures. FT-IR spectra were recorded in a Shimadzu FTIR-8400 spectrophotometer in the mid-IR region (4000 to 400 cm^{-1}) for KBr pellets. The solution UV-vis spectra were obtained using a Shimadzu UV-1700 spectrophotometer. Deionised water was used as a reaction medium throughout the experiments.

Synthesis Of Complexes

For the synthesis of $[\text{Co}(4\text{-CNPY})_2(\text{SCN})_2(\text{H}_2\text{O})_2]$ (**1**), a mixture of cobalt nitrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2.91g) and 4-cyanopyridine (2.04g) dissolved in water (20 mL) was mechanically stirred at room temperature. Ammonium thiocyanate, NH_4SCN [(1.52 g) dissolved in 5 mL water] was then added drop wise to the mixture with continuous stirring and the stirring was continued for 5 hours. The pink precipitate formed was filtered, washed with small volumes of water under suction and then dried in a vacuum desiccator containing fused CaCl_2 . Yield: 3.5 g (83.5%). Anal. calcd. for $\text{C}_{14}\text{H}_{12}\text{CoN}_4\text{O}_2\text{S}_2$: C, 40.63; H, 2.84; N, 16.70 (%); Co, 14.07 (%). Found: C, 40.10; H, 2.88; N, 20.05 (%); Co, 15.30 (%).

Similar procedure was applied for the synthesis of $[\text{Ni}(4\text{-CNPY})_2(\text{SCN})_2(\text{H}_2\text{O})_2]$ complex (**2**) Yield: 3.47 g (82.8%). [Anal. calcd. for $\text{C}_{14}\text{H}_{12}\text{NiN}_4\text{O}_2\text{S}_2$: C, 42.35; H, 2.55; N, 17.88 (%); Ni, 14.01 (%). Found: C, 40.18; H, 2.88; N, 20.06 (%); Ni, 15.02 (%).] and

$[\text{Cu}(4\text{-CNPY})_2(\text{SCN})_2(\text{H}_2\text{O})_2]$ complex (**3**) [Yield: 3.55 g (83.7%). Anal. calcd. for $\text{C}_{14}\text{H}_{12}\text{CuN}_4\text{O}_2\text{S}_2$: C, 42.54; H, 1.82; N, 16.14 (%); Cu, 15.00 (%). Found: C, 39.60; H, 2.85; N, 19.83 (%); Cu, 14.43 (%)] with Nickel nitrate, $\text{Ni}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ and copper nitrate $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as precursors.

Result And Discussion

Optical Studies Of The Complexes

Infrared Spectral Studies

The mid-IR spectra of 1, 2, and 3 are shown in Figures 1, 2 and 3 respectively. The most important IR absorption bands of the metal complexes are summarized in Table 1. For all three compounds the absorption due to the nitrile group present in the 4-CNpy ligand appears near 2240 cm^{-1} and indeed the spectra shown by the three compounds are quite similar to suggest close structural similarity of the species. The infrared spectra of the complexes present strong absorption bands at around 2100 cm^{-1} for the νCN vibration and medium bands in the range $790\text{--}905\text{ cm}^{-1}$ for the νCS vibration. The stretching vibrations of the CN and CS groups shift significantly to higher frequencies in the complexes as indicated by $\Delta\nu$ in Table 1, compared to free SCN group ($\nu\text{CN} = 2045\text{ cm}^{-1}$ and $\nu\text{CS} = 751\text{ cm}^{-1}$) [20]. These findings indicate the coordination of the NCS group through the nitrogen resulting in the formation of isothiocyanate complexes [21]. The absorptions appearing at around 1600, 1540, 1410 and 1000 cm^{-1} for all the three compounds may be attributed to the pyridine ring vibrations. The bands assigned to the pyridine ring vibrations are shifted to lower frequencies, which is a good indication of the coordination of the heterocyclic nitrogen atoms. All the IR spectrum of the complexes showed in addition to the O–H stretching vibration at $3500\text{--}3400\text{ cm}^{-1}$ (not shown here) and a band of moderate intensity at around 470 cm^{-1} , which is usually assigned to wagging or rocking modes of coordinated water [22, 23]. The formation of co-ordination complex of the ligands with the metal ions (Co, Cu and Ni) is important from the point of view of energy transfer in a DSSC. The coordination complexes generally make the energy transfer possible from the excited state of the ligand to the metal ions, thus increasing the nonradiated transition of the ligand excited state and decreasing the fluorescence emission.

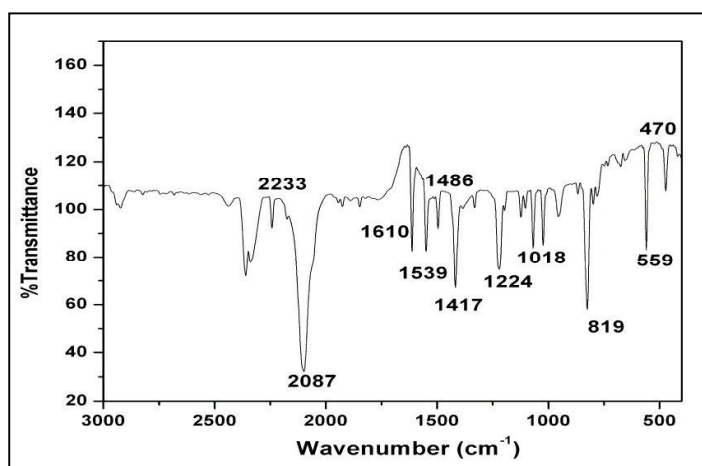


Figure 1(a): KBr phase Infrared spectra of compound 1

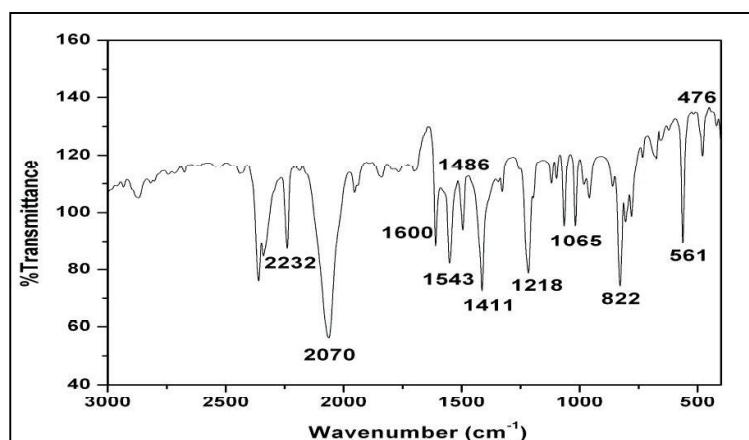


Figure 1(b): KBr phase Infrared spectra of compound 2

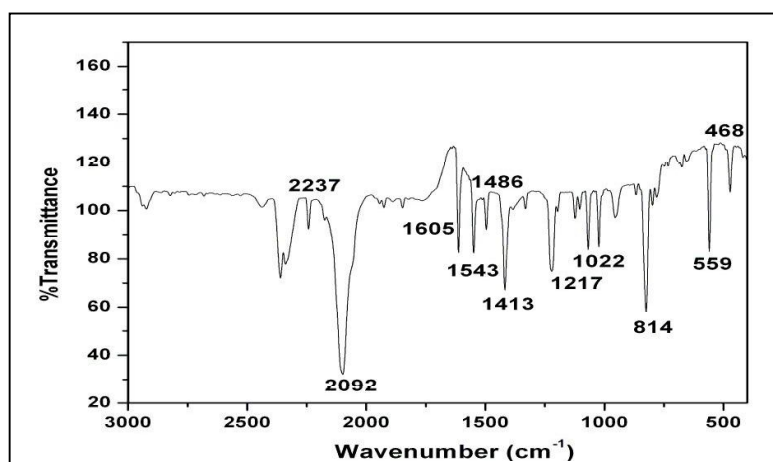


Figure 1(c): KBr phase Infrared spectra of compound 3

Complexes	ν (C–N)	$\Delta\nu$ (C–N)	ν (C–S)	ν (NCS)
Co(4-CNPy) ₂ (SCN) ₂ (H ₂ O) ₂] (1)	2087	42	819	559
[Ni(4-CNPy) ₂ (SCN) ₂ (H ₂ O) ₂] (2)	2070	25	822	561
[Cu(4-CNPy) ₂ (SCN) ₂ (H ₂ O) ₂] (3)	2092	47	814	559

Table 1: IR spectral data for the metal complexes

The UV-Vis And Photoluminescence Spectra Of The Complexes

The UV-vis spectra of the complexes are shown in Fig 2(a), 2(b) and 2(c). All the three complexes Co(II), Ni(II) and Cu(II) show expected absorption bands in the UV-vis region. In case of complex 1 and complex 3, three peaks were observed while for complex 2 only one peak was observed.

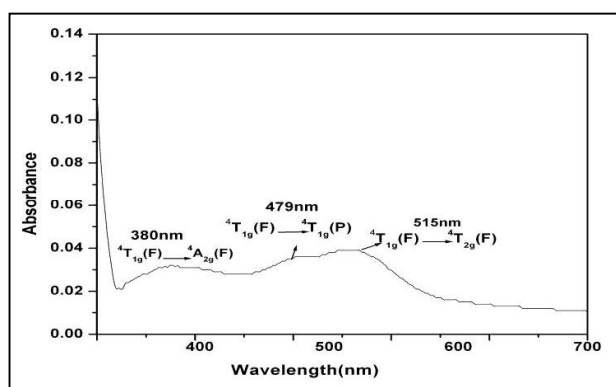


Figure 2 (a): Electronic spectra of compound 1 in methanol

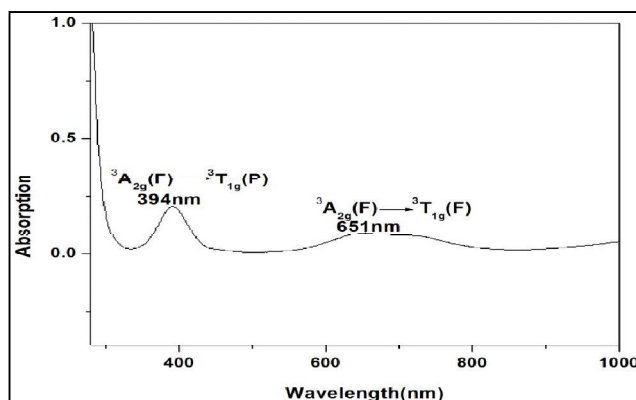


Figure 2(b): Electronic spectra of compound 2 in methanol

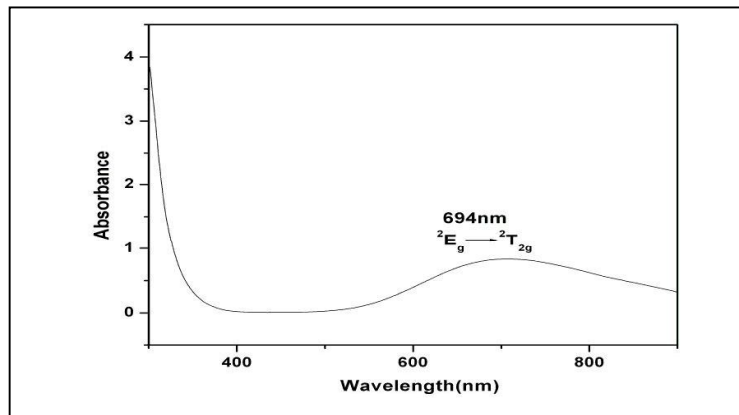


Figure 2 (c): Electronic spectra of compound 3 in methanol

Fabrication Of TiO₂ Photoanode

Fig.3 (a)-3(b) show the comparison of UV-Vis absorption spectra of the TiO₂ thin film and dye loaded TiO₂ thin film (soaked with complex 1,2 and 3). From the spectra it is observed that, the percentage of absorption in the dye loaded TiO₂ thin film increases significantly in comparison to unsoaked TiO₂ thin film. This indicates the good anchorage of the dye on the surfaces of TiO₂ thin film and hence it is found suitable for the fabrication of photoanode for DSSC. It is also clear from the spectra that although the three complexes show similar sensitization, complex 1 has little more shifts in the position of the peaks compared with the other two which can be attributed to a better HOMO- LUMO interaction between the dye and TiO₂.

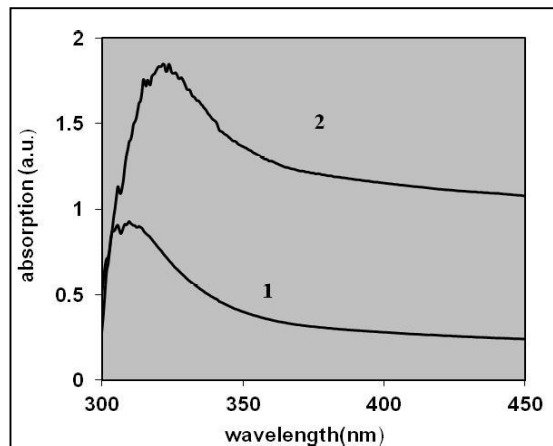


Figure 3(a): UV-Vis absorption spectra of TiO₂ thin film (1) and UV-Vis absorption spectra of TiO₂ thin film soaked with the complex 1(2)

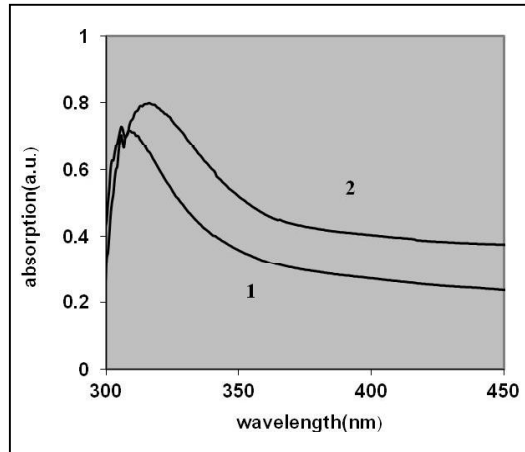


Figure 3(b): UV-Vis absorption spectra of TiO_2 thin film (1) and UV-Vis absorption spectra of TiO_2 thin film soaked with the complex 2(2)

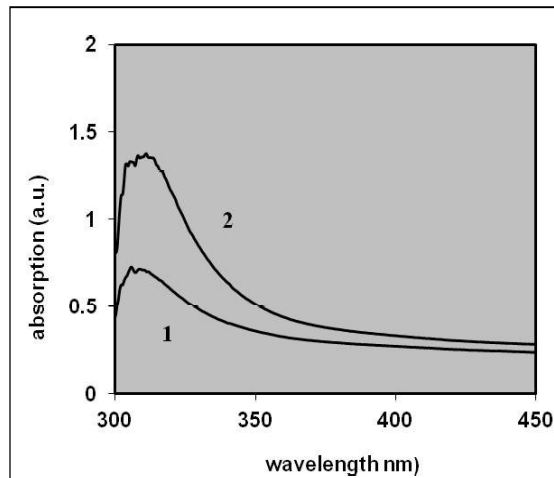


Figure 3(c): UV-Vis absorption spectra of TiO_2 thin film (1) and UV-Vis absorption spectra of TiO_2 thin film soaked with the complex 3(3)

Fabrication Of Cells

For the fabrication of the cells, first, TiO_2 thin film was deposited onto transparent conducting oxide (TCO) glass substrate which is tin oxide in the present study. Commercially available TiO_2 nano powder was mixed with acetic acid and surfactant and then stirred for 30 minutes to get a uniform paste. The paste was then deposited on the TCO and was sintered at 450°C for 2h.

As all the three complexes show almost similar kind of sensitization, only one synthesized complex (complex 1) was used to fabricate the photoanode by adsorbing the dye onto the surfaces of TiO_2 thin films by continuous dip coating technique. The films were dipped vertically with the help of a substrate holder into the baths

containing the dye solution. The films were withdrawn after 24 hour dip time, washed in distilled water and dried in an oven at 40°C for 5h. The color of the film was found to change from transparent to pink indicating the anchorage of the dyes on the surface of TiO₂ thin film. The Carbon coated counter electrode was prepared by exposing the TCO to the flame of a candle until it was turn into black in colour. Then, the photo-anode and counter-electrode was pressed together with the help of blinder clips and finally the electrolytic solution (KI/I₂) was added.

Characterization Of The Cell

The current-voltage (I-V) characteristics of the as fabricated DSSC was measured with keithley Electrometer(Model No:2400)and is shown in Fig. 4. The intensity of illumination was measured with a Lutron LX-101 lux meter. The solar cell parameters were measured under illumination with a 50 mW Cm⁻² (0.5 SUN) tungsten lamp. The observed photovoltaic parameters of the cells are tabulated in Table 1. A conversion efficiency of 0.72% (*Voc* = 0.25mV, *Jsc* = 1.2 μA/cm², FF = 0.19) has been achieved for the cell.

Solar Cell	I (mW Cm ⁻²)	Voc (mV)	Jsc (mA Cm ⁻²)	FF (%)	η (%)
Co(II)Complex	50	0.25	1.2	0.19	0.72

Table 2: Current –Voltage parameters for the Cell-2 under 50 mWcm⁻² illumination intensity

The parameters shown are the open circuit voltages (*Voc*), short circuit current density (*Jsc*), fill factor (FF) and efficiency (η).

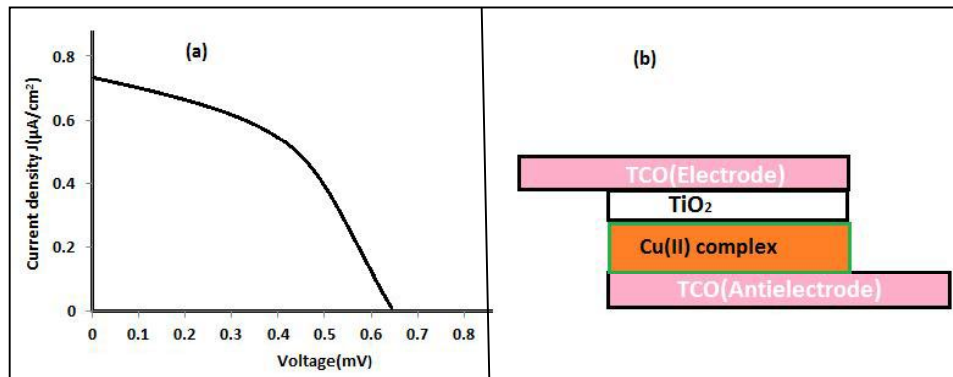


Figure 4: (a) I-V Characteristic of cell (b) Schematic Diagram of a DSSC

Conclusion

Three complexes of cobalt, nickel and copper involving 4-cyanopyridine and isothiocyanate as ligand were synthesized and characterized by UV-vis, IR and elemental analyses. Three photoanodes were fabricated by adsorbing the complexes onto the prepared TCO/TiO₂ thin films and their efficiency was investigated with the help of UV-vis absorption spectroscopy which shows that these complexes may be a suitable candidate for application in DSSC. One prototype cell was fabricated and efficiency was evaluated.

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