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Optical properties of Silver-Iron(II)nitrosyl cyanide thin films deposed on glass micro-slides using SILAR method

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This study is focused on the elaboration of Silver-Iron(II) nitrosyl cyanide thin films, using successive ionic layer adsorption and reaction (SILAR) method; the deposition has been performed on glass substrate after 120 dipping cycles using precursors solution of 10^{-2} mol.L^{-1} at room temperature. The elaborate $Ag_2[Fe(CN)_5NO]$ thin films have been characterized using infrared spectroscopy, optical microscope, scanning electron microscope, and XRD. The optical study using UV-Vis spectrometry indicates that the obtained thin films has a large absorbance bonds on 209, 257, 350, and 500 nm corresponding to the fundamental electronic transitions between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), with an optical band gap energy of 3.1 eV.

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1. Introduction

The elaboration of inorganic nanomaterials has gained much interest amongst the scientific community research activities, due to the multiplicity of their physicochemical properties such as chemical, magnetic, optical, electrical, and catalytical properties. Therefore, the preparation of these materials as thin films is considered as an important research topic in nanotechnology fields and related research subjects, photomagnetism, electrochromisme, photovoltaic [1-5]. The thin films can be elaborate from various materials, such as hybrid polymers [6], Chalcogenide compounds [7,8] and transition metallic complexes, like iron(II) diketonate-diamine complex [9], cobalt phthalocyanine complexes [10], Fe(II) spin-crossover complexes [11], Nickel(II) and Cobalt(II)-bipyridine-cyano-complexes [1,4], Eu(III)-phenylalanine complex [12], Zinc(II)-8-hydroxy-5,7-dinitroquinolate complexes [13], copper(II)-azo complexes [14], Mg(II) and Ca(II)-8-hydroxy-5,7-dinitroquinolate complexes [15-16]. Interestingly, the elaboration of metallic-complexes thin layers has been studied using various deposition techniques, such as successive ionic layer adsorption and reaction [1,4], chemical bath deposition [17] Langmuir–Blodgett method [18]; atomic layer deposition method [19], molecular self-assembly deposition [20], adsorption [21], spin-coating technique [22]. However, the using a simple and not expensive technique, such as the successive ionic layer adsorption and reaction method that allow us to obtain homogeneity films, along with controlled thickness of the hybrid molecular materials. In our work, we study the optical properties of Silver-Iron(II)-cyanide complex deposed on glass substrates using SILAR method. The aim of our study was to elaborate the hybrid thin films of the light-sensitive propriety, and the height quality and controlled thickness, as well as the deposition of these thin layers has been performed on micro-glass slides after 120 dipping cycles using cationic and anionic precursors solution of 10^{-2} mol/L at room temperature as shown in Fig. 1. The obtained Silver-Iron(II)-cyanide complex thin film were characterized using UV-Vis spectrometry, infrared spectroscopy, scanning electronic microscope, X-ray diffraction. The UV-V is spectral data which have been used to study optical properties, such as origin of electronic transition, gap's energy (E_g), and absorption coefficient (α) of as-deposed obtained Iron-Silver cyanide thin film [1,4].

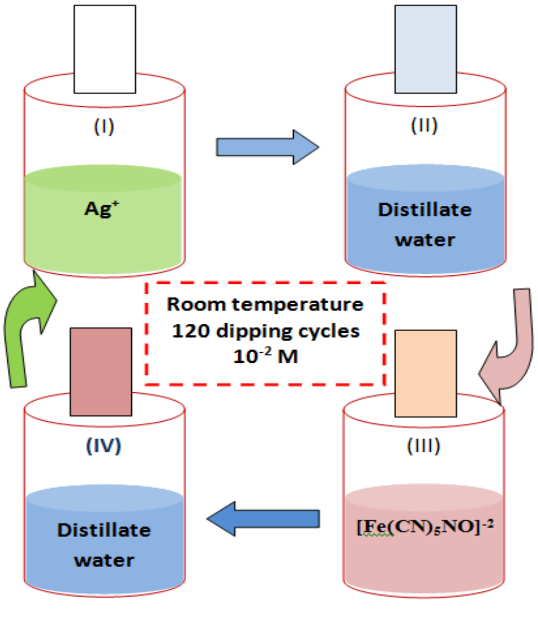

Fig.1. Deposition protocol of Silver-Iron(II)nitrosyl cyanide complex thin films using SILAR method

2. Experimental

The preparation of precursors solutions has been performed using potassium nitroprussideand silver nitrate, all chemical were provided by Merck. Therefore, to obtain good homogenous thin films, the micro glass substrates were cleaned in an ultra-sonic bath with a commercial detergent, and then rinsed with distilled water followed by dipping step in acetone for 10 min, to eliminate the organic waste. Finally, the whole was dried in vacuum at 105°C for 1 hour [1,4].

2.1. Thin films deposition

The preparation of $[Ag_2Fe(CN)_5NO_2]$ thin films has been realized as previously reported by Bendjeffal et al [1,4]. Briefly, the used substrate was immersed sequentially in a series of cationic and anionic solutions according to a well-defined elaboration procedure as shown in Figure.2; the glass substrate was dipped in beaker "**I**" containing the cationic solution of Ag^+ for 40s, then rinsed with distilled water in beaker "**II**" for up 10s, then immersed about 40s in beaker "**III**" containing the anionic solution of $[Fe(CN)_5NO]^{-2}$, and finally rinsed with distilled water in beaker “**IV**”. This protocol was repeated several times for 120 cycles. At the end of each deposition, the as-obtained pink complex thin film was dried in a oven at 105°C for few minutes [1,4]. The mechanism formation of Silver-Iron(II) nitrosyl complex thin films onto glass surface can be illustrated by Fig. 1 and via the following reactions:

$$Na_2Fe(CN)_5NO \rightarrow [Fe(CN)_5NO]^{-2}_{(aq)} + 2\ Na^+_{(aq)}$$

$$AgNO_3 \rightarrow Ag^+_{(aq)} + NO_3^-{}_{(aq)}$$

$$[Fe(CN)_5NO]^{-2}_{(aq)} + 2Ag^+_{(aq)} \rightarrow Ag_2[Fe(CN)_5NO_2]_{(S)}\downarrow$$

3. Resultants and discussion

3.1. Infrared analyses

The transition metals cyano-complexes can be easily studied using infrared spectroscopy following the cyano vibration band ($\upsilon_{\text{-CN}}$) in the region of 2200-1900 cm^{-1} [1,4,23]. The study of the presence of ($\upsilon_{\text{-CN}}$) was carried out using Shimadzu FTIR-8700 spectrometer. The infrared spectra of the Silver-Iron(II) nitrosyl cyanide thin films obtained at room temperature, 120 dipping cycles and 10^{-2} mol/L are given in Fig. 2. The FTIR spectra show vibration bands, respectively at 2100cm^{-1} according to cyano-vibration band ($\upsilon_{\text{-CN}}$) characteristics of these materials. Moreover, the $Ag_2[Fe(CN)_5NO_2]$ infrared specter show another vibration bands at 1950, 1663 and 658 cm^{-1} are assigned to ($\upsilon_{\text{-NO}}$),($\upsilon_{\text{-FeNO}}$), and ($\upsilon_{\text{Fe-NO}}$) [23].

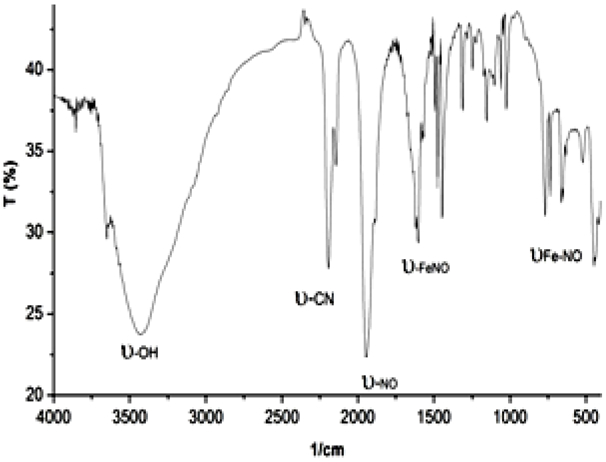

Fig. 2. Infrared spectra of Silver-Iron(II)nitrosyl cyanide thin film deposed on glass substrate at room temperature, 10^{-2} mol/L, and 120 depping cycles

3.2. Surface morphological studies

The morphology of Silver-Iron(II)nitrosyl cyanide thin film surface was characterized by an optical microscope and scanning electron microscope, which are considered to be one of the most important instrumentations in studying surface morphology of solid materials by direct two dimensional surface imaging [1-4]. Hence, The typical SEM and OM images of the surface morphology show that the surface of Silver-Iron(II)nitrosyl cyanide film has a crystalline and homogeneous microstructure with a particle size above of 1µm as shown in Fig. 3.

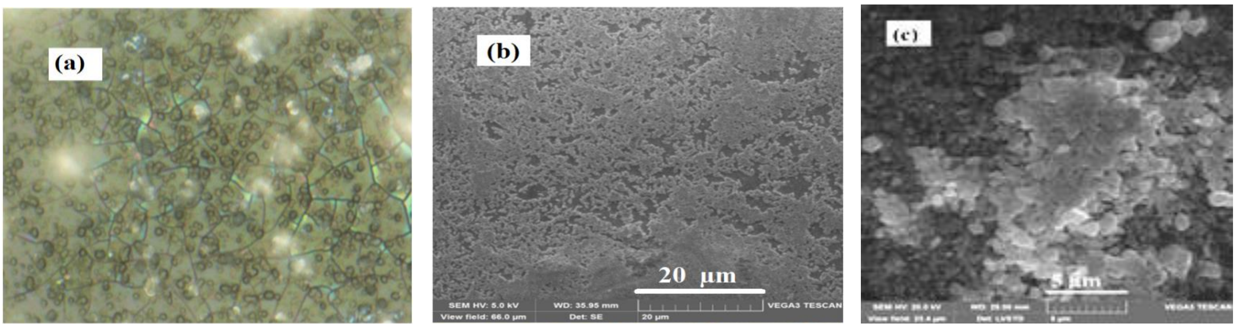

Fig. 3. Micrograph of optical microscope (a) and Scanning electron microscope (b,c) of Silver-Iron(II)nitrosyl cyanide thin film deposed on glass substrate at room temperature, 10^{-2} M, and 120 depping cycles

3.3. Structural study

The structure Silver-iron(II) nitrosyl cyanide thin film were studied using X-ray Bruker D8 advance diffractometer with varying diffraction angles between 8° and 80°. Fig.4 displays a typical X-ray diffraction patterns of $Ag_2[Fe(CN)_5NO]$ thin layer obtained at room temperature, with 120 dipping cycles and precursors concentration of 10^{-2} M. The observed diffraction peaks at 13.8°, 19.1°, 21.6°, 30.1°, and 35.5° correspond to the monoclinic structure of the deposed Iron-Silver thin film with indexed plans of (010), (111), (210), (301), (640), and (212) (JCPDS-ICDD#00-052-0366) [24]. However, the appearance of the broad peak between 15° and 24° may be depended on the amorphous structure of glass substrate [4].

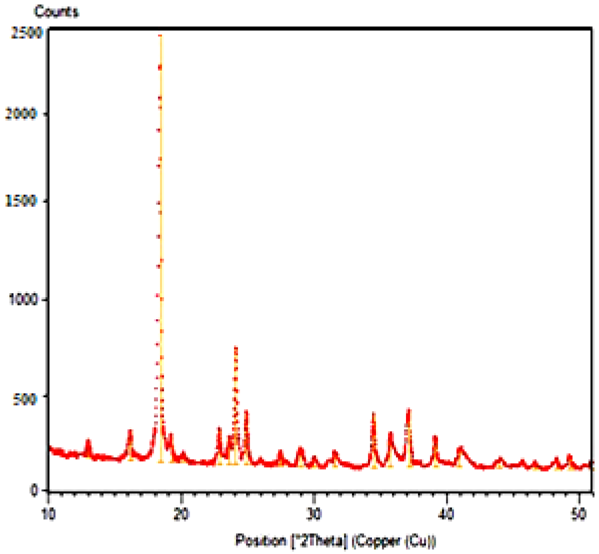

Fig. 4. X-ray diffraction patterns of Silver-Iron(II)nitrosyl cyanide thin film deposed on glass substrate at room temperature, 10^{-2} mol.L^{-1} , and 120 dipping cycles

3.4. Optical properties

UV-Vis spectrophotometry was used to study the optical properties, such as light absorption, electronic transition and optical band gap of Iron-Silver nitrosyl cyanide thin films. The UV-Vis absorption spectra of the as-deposited thin films synthesized in optimal conditions Fig.5 show that all Iron-Silver cyanide thin films samples have large and intense bands between 200 nm - 300 nm. The strong absorption bands observed in this area are basically due to principle electronic transition states (d→d, d→π*, π→d, π→π* and n→π*) as previously reported [1,25]:

From the coordination of the ligand along with the metallic central atom, there is a splitting of the "d" orbital resulting in excited d→d states, leading to the promotion of an electron within d orbital, which are essentially confined to the central metal. In the case of the "d→π*" states, electronic transitions are due to charge transfer between an excited electron of central metal and an anti-bonding orbital of the ligand. Meanwhile, the charge transfer starts from π bonding ligand system to the central metal (d) orbital in case of the "π→d" electronic transition. However, in the case of "π→π*" or "n→π*" states, electronic transitions are observed within ligand system orbitals. Noteworthy, the transition of an electron from a π-bonding or non-bonding orbital to the lowest unoccupied molecular orbital (π*) gives rise to these electronic transitions [1,4].

As reported, the Silver-iron(II) nitrosyl cyanide thin layer has a maximal absorbance with large absorbance bonds on 209, 257, 350, and 500 nm due to the fundamental electronic transitions ranging between 200 nm - 600 nm, corresponding to n→π*, π→π*, d→π*and d→d electronic transition between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) [25,26].

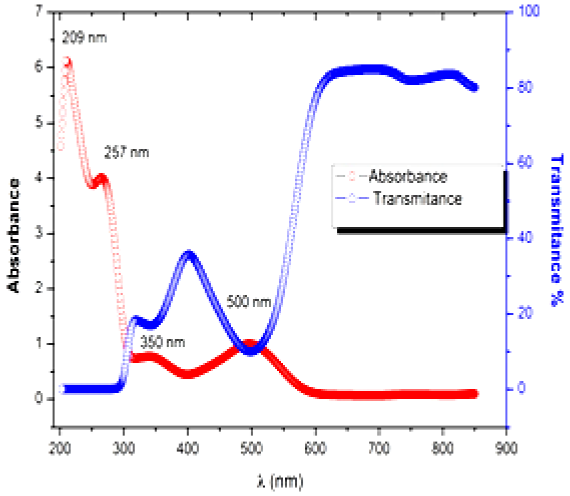

Fig. 5. Transmitance and absorption UV-Vis spectra of Silver-iron(II) nitrosyl cyanide thin layer deposed on glass substrate at (room temperature, 10^{-2} mol/L, and 120 dipping cycles)

The gap's energy and absorption coefficient were determined using the Transmitance and absorption spectra of as-obtained thin films at optimal conditions (room temperature, 10^{-2} mol/L, and 120 dipping cycles). Additionally, the information about direct transitions was determined from the analysis of the spectral dependence of the absorption near the fundamental absorption edges within the frame work of one electron [4]. Equations that relate the absorption coefficient (α) and the gap's energy (E_g) are as follow [1,3]:

$$\alpha = (1 / d) \ \ln (100 / T_{(\%)}) \qquad (1)$$

$$\alpha (h\upsilon) = A (h\upsilon - E_g)^{1/2} \qquad (2)$$

Where "α" the absorption coefficient (cm^{-1}), "T" is the transmittance (%),"d" the thickness of the thin film (cm). The factor (A) depends on the transition probability, and it is assumed to be constant within the optical frequency range, and E_g is the energy band gap value (eV) of the indicated transition (n→π*, π→π*, π→d, d→π* and d→d). The extrapolation of the straight line graphs $[(\alpha h\upsilon)^2 = f(h\upsilon)]$ to zero absorption ($\alpha = 0$) provides the gap's energy value.

Fig.6 displays the variation of the absorption coefficient (α) versus photon energy (hυ) of the deposed complex thin film, this study shows that the obtained Silver-Iron(II) nitrosyl cyanide thin film present an height absorbance between 4 and 6 eV. Also, This study shows that the energy gap for Silver-Iron(II) nitrosyl cyanide thin film equals to 3.1 eV as shown in Fig.7. This value is similar to the obtained results of Bendjeffal [1]. These findings indicate that this complex has characteristics of semi-conductors. Moreover, the value of energy gaps belongs to the range of highly efficient photovoltaic materials. Hence, the studied complex can be considered as potential material for many optical applications [1].

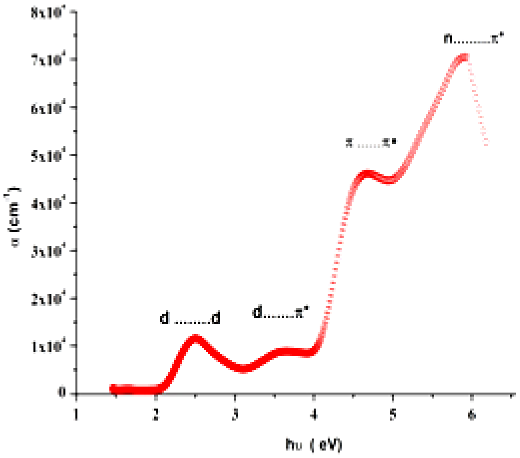

Fig. 6. Variation of the absorption coefficient (α) as a function of photon energy of Silver-Iron(II)cyanide thin film deposed on glass substrate

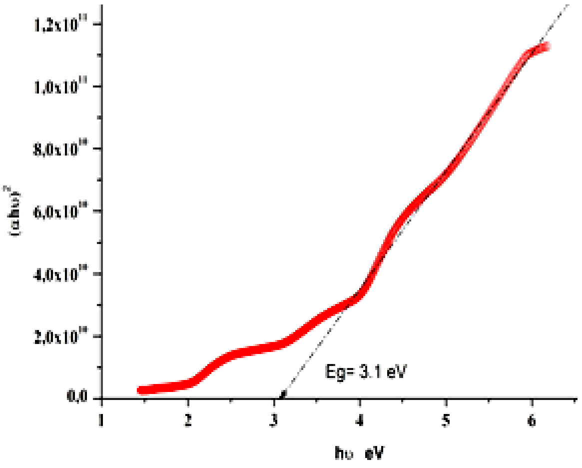

Fig. 7. Variation of $(\alpha h\upsilon)^2$ as a function of photon energy of Silver-Iron(II)cyanide thin film deposed on glass substrate

4. Conclusion

In conclusion, thin films of Silver-Iron(II) nitrosyl cyanide were successfully deposed on glass slides using successive ionic layer adsorption and reaction method. A good deposition results were obtained after 120 cycles of dipping, with precursor's concentration of 10^{-2} mol/L at room temperature. The SEM characterization showed that as-deposited thin films have a crystalline microstructure with a grain size of more than 1μm.

The XRD structural characterization also showed that the as-deposed complex thin layers have polycrystalline structure. On the other hand, the optical absorption analyses showed that the studied Silver-Iron(II)nitrosyl cyanide thin films have strong absorption bonds in UV-Vis area on 209, 257, 350, and 500 nm due to the fundamental electronic transitions (n →π*, π→π*, d→π*and d→d) electronic transition between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) with optical gap's energy (E_g) above 3.1 eV.

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