Prussian blue analogue cobalt tetracyanonickelate hexacyanochromate decorated by CNTs: structural, morphological, optical characterization

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Abstract
Prussian blue analogues CoTCNi/HCCr and CoTCNi/HCCr/CNTs were stoichiometrically prepared by Co-precipitation method and the thin films deposited onto glass substrates via spin coater. XRD, Raman spectroscopy, EDX, SEM, and TEM techniques have been used to analyze the samples. The findings revealed the fabricated nanostructured materials of face-centered cubic (FCC) phase, in spherical shape decorated by CNTs. Transmittance (T\%) and reflectance (R\%) spectra of the thin films were measured in the wavelength range from 200 to 900 nm. The films exhibit high transparency more than 70\% within the visible spectrum. Besides, the optical band gap (E_g) was estimated showing blue shift caused by CNTs support.

1. Introduction
Prussian blue (Pb) contains transition metal ions linked together with neighboring nitrogen and carbon atoms are actively investigated based on the exceptional electron transfer mediators [1, 2]. Prussian blue often called hexacyanometallates [HCM] composed of ferric or ferrous ions has been characterized by the formula A_M_B(CN)_6.nH_2O where M and B are transition metals coordinated octahedrally to the nitrogen and carbon atoms of the cyanide group, A is the alkaline cation, x and y stoichiometric coefficients, and n the hydration intercalation molecules per unit formula [2, 3]. Since cyanide is highly reactive, it will easily bind metals as a strong ligand to form complexes of variable stability [4]. It is possible to vary the metal atoms that bond via nitrogen to other metals such as chromium, manganese, and copper produces new materials with novel aspects. Therefore, a series of complexes contain different combinations of metal ions were fabricated from metal salt and cyanide solutions [5, 6]. Recently, Prussian blue and their derivatives known as Prussian blue analogues (PbAs) have been prepared for electrochemical catalysis applications [7]. Generally, these materials possess low thermal and electrical conductivity that could be improved by adding appropriate dopants [8]. CNTs of unique abilities are candidate for this purpose. Incorporation of CNTs will produce new complexes having the properties of both components [9, 10]. Several chemical routes were employed for producing Prussian blue compounds. Among these methods, Co-precipitation was defined to be easily control of shape and particle size. In the present work, CoTCNi/HCCr and CoTCNi/HCCr/CNTs have been prepared by direct chemical reaction without using reducing agent and their physical properties were discussed for potential optoelectronic applications.

2. Experimental details
2.1. Chemicals
Potassium tetracyanonikelate (II) [K_2Ni(CN)_4], potassium hexacyanochromate (III) [K_3Cr(CN)_6], cobalt chloride hexahydrate (CoCl_2.6H_2O), and CNTs (≥95% as carbon nanotubes, average diameter 0.78 nm) were purchased from (Sigma-Aldrich).
2.2. Fabrication of CoTCNi/HCCr and CoTCNi/HCCr/CNTs
At first, 3 mol K$_2$Cr(CN)$_6$, 1 mol K$_2$Ni(CN)$_4$, and 4 mol CoCl$_2$.6H$_2$O were separately dissolved in 30 ml deionized water for 3 h using magnetic stirrer. Complex I (CoTCNi/HCCr) was stoichiometrically prepared by adding 15 ml K$_2$Ni(CN)$_4$ to 20 ml K$_2$Cr(CN)$_6$ under stirring. The precipitation process was directly occurred by adding 25 ml CoCl$_2$.6H$_2$O to the mixture with continuous stirring unto reach the neutral pH. The resulting precipitate was centrifuged many times using deionized water, dried at 80°C for 24 h and finally annealed at 180°C in a furnace for 12 h. A small part of the CoTCNi/HCCr powder was continued under heat treatment for 3 days. Complex II (CoTCNi/HCCr/CNTs) has been prepared by adding 10 ml (0.5 g l$^{-1}$) sonicating CNTs to 20 ml CoTCNi/HCCr solution then the mixture stirred until clear homogeneous solution formed. The product was centrifuged, dried, and annealed at the same preparation conditions. The thin films were fabricated by depositing the solution on glass substrates using spin coater (3000 rpm min$^{-1}$). The films were dried at 80°C for 24 h and heat treated in a microwave oven for 45 min (Scheme 1).

2.3. The samples characterization
The crystal structure of the prepared samples was examined by XRD (Rigaku Smart Lab.), with Cu K$_\alpha$ radiation ($\lambda = 1.54056$ Å) and the phase content was analyzed using Raman spectroscopy (Horiba Lab RAM HR Evolution). EDX has been utilized for chemical composition analysis. The surface morphological distribution and mean particle size of the nanopowder were investigated from SEM (Helios Nanolab. 400) and TEM (Hitachi-H-7500) images. The optical properties of the thin films have been studied using spectrophotometer JASCO (V-570).

3. Results and discussions
3.1. Crystal structure and phase content analysis
The XRD pattern of synthesized Prussian blue analogues CoTCNi/HCCr and CoTCNi/HCCr/CNTs annealed at 180°C for 12 h are presented in figure 1. The reflection peaks of CoTCNi/HCCr located at $2\theta = 17.64^\circ$, 25.13°, 35.77°, 40.10°, and 44.04° attributed to (200), (220), (400), (420), and (422) planes respectively are identical to the face-centered cubic phase of Prussian blue cobalt hexacyanoferrate (CoHCF) and consistent with the standard card (JCPDS#82–2284)[11, 12]. Furthermore, CoTCNi/HCCr/CNTs exhibits similar pattern with relative low intensity broadening peaks shifted to higher angles without phase separation suggesting the structure disorder and small grain size. The peak detected at $2\theta = 26.71^\circ$ related to CNTs supports the change in phase [13, 14]. To approve the crystal structure, CoTCNi/HCCr was continued under annealing for 3 days. As seen in figure 1, the peaks become sharper and higher in intensity which completely well indexed to the pure Prussian blue face-centered structure (Fm3m) [15, 16]. The crystallite size has been determined from Scherrer
equation applied on the most intense peak (200) using the following formula [17]:

\[ D = \frac{K\lambda}{\beta \cos \theta} \]  

where, \( D \) the crystallite size, \( \beta \) the full width at half maximum FWHM measured in radians, \( \lambda = 1.540 \, \text{Å} \) the wavelength of incident x-ray, \( K = 0.94 \) the shape factor and \( \theta \) denotes the diffraction angle. The size of CoTCNi/HCCr and CoTCNi/HCCr/CNTs nanoparticles annealed for 12 h was found to be 18 nm and 15 nm, respectively [18]. Additionally, the crystallite size values of CoTCNi/HCCr annealed for 3 days was approximately 72 nm. It is clearly seen that the crystal size decreased by CNTs addition whereas significantly increased with long annealing time confirming the XRD behavior.

For further phase identification, Raman spectroscopy was examined in figure 2. Complex I exhibits two strong Raman shift peaks at 847 cm\(^{-1}\) and 2200 cm\(^{-1}\) attributed to hexacyanochromate (HCCr) and cobalt tetracyanonickelate (CoTCNi) respectively [14]. The two peaks located at 1360 cm\(^{-1}\) and 1584 cm\(^{-1}\) are related to the presence of CNTs. Furthermore, a slight shift to higher wave number was detected attributed to the change in energy level distribution into the band gap [19]. The element chemical composition has been recorded by EDX shown in figures 3(a), (b). As observed, CoTCNi/HCCr contains carbon, nitrogen, oxygen, cobalt,
nickel, and chrome with atomic percent (at.%) 8.52, 24.26, 16.36, 20.46, 14.23, and 16.17, respectively. Besides, CoTCNi/HCCr/CNTs depicts similar chemical composition with high carbon percent 17.52 (at.%) influenced by CNTs addition. No impurities were observed in the spectrum however the oxygen peak has been detected because of the thermal annealing in air.

3.2. SEM and TEM study
The surface morphology of the nanopowder was analyzed from SEM images in figures 4(a), (b). The nanoparticles of complex I are aggregated in random distribution with slight voids. These voids almost disappeared in complex II, and the particles were grown in nanospheres with high density decorated by CNTs [19]. On the other side, the average particle size and morphological distribution were investigated from TEM images in figures 4(c), (d). The particle size of complex I was varied between 25–40 nm while the morphology of complex II formed from aggregated particles covered by CNTs [20]. As can be seen, the estimated crystallite size from XRD shows smaller values compared to TEM calculations which may be owing to that the XRD analysis provides the average crystallite size of whole powder whereas TEM technique gives shape and size distribution of individual particles. Also, because of the one particle contains multiple crystals [21].

3.3. Optical properties of the thin films
Transmittance and reflectance spectra of the films were done in the wavelength range from 200 to 900 nm as illustrated in figures 5(a), (b). As can be seen, the films of high transparency (70%–75%) within the visible region, virtually decreases by CNTs associated to the increase of optical scattering [22]. A strong absorption edge was detected within the UV spectrum related to the interaction between photon energy and the electrons of the thin film material [23]. The reflectance spectra of the films were measured in the UV–vis region. As shown, the reflectance is less than 30% in the visible region decreases by CNTs dopant. The optical properties of semiconducting materials were defined by the optical band gap expressed as [24]:

![Figure 3. EDX spectra of (a) complex I and (b) complex II nanoparticles annealed at 180 °C.](image-url)
where, $\alpha$ the absorption coefficient, $A$ is independent constant, $h\nu$ the photon energy, $n = 1/2$ for allowed direct transition, and $E_g$ the optical band gap was given from $(\alpha h\nu)^n$ versus $h\nu$ plot in figure 6. The values of $E_g$ for complex I and complex II were calculated from extrapolating the linear region to the photon energy axis to be 4.20 and 4.40 eV, respectively. The blue shift in the optical band gap based on the excess of free electrons occupy the lowest states in the conduction band according to Burstein–Moss (BM) effect [25]. The Urbach energy describes the width of localized states into the energy gap was defined by the equation [26, 27]:

$$\alpha = \alpha_0 \exp(h\nu/E_u)$$

where, $\alpha_0$ is a constant and $E_u$ the Urbach energy was given from the reciprocal gradient of linear portion between $\ln \alpha$ against $h\nu$ depicted in figure 7. The $E_u$ values of complex I and complex II have been estimated to be 232 meV and 256 meV respectively. The increase in Urbach energy related to the structure disorder and presence of localized states inside the energy gap [27, 28]. As known, the refractive index $n$ and extinction coefficient $k$ are essential optical parameters used for studying the behavior of light through the films can be obtained from the equation [26–28]:

$$n = \left(1 + \frac{R}{1 - R}\right) + \frac{4R}{\sqrt{1 - R^2} - k^2}$$

where, $k = \frac{\alpha \lambda}{4\pi}$ the extinction coefficient and $R$ the reflectance. Figures 8(a), (b) describes $n$ and $k$ as a function of photon energy. The films show direct refractive index in the visible region sharply increases in the UV region depends on the strong optical interaction [28, 29]. Moreover, the extinction coefficient decreased suggesting the weak in optical absorption. The optical dielectric properties were investigated from real $\varepsilon'$ and imaginary $\varepsilon''$ parts of dielectric constant using the formulas [30, 31]:

$$\varepsilon' = n^2 - k^2 \quad \text{and} \quad \varepsilon'' = 2nk$$

\[\text{Figure 4.} \ (a), (b) \text{ SEM and (c), (d) TEM images of CoTClNi/HCCr and CoTClNi/HCCr nanoparticles annealed at 180 °C.}\]
Figure 5. (a) Transmittance and (b) reflectance spectra of CoTCNi/HCCr and CoTCNi/HCCr films.

Figure 6. $(\alpha h\nu)^2$ versus $(h\nu)$ plot of complex I and complex II films.
Figure 7. Urbach energy of complex I and complex II films.

Figure 8. (a) Refractive index and (b) extinction coefficient (k) of the films as a function of photon energy.
Figures 9(a), (b) shows both $\varepsilon'$ and $\varepsilon''$ sharply increased vicinity the fundamental absorption region supporting the high dispersion rate [29]. The optical conductivity of the films was described as follow [30, 31]:

$$\sigma' = \omega\varepsilon''\varepsilon_0$$ and $$\sigma'' = \omega\varepsilon'\varepsilon_0$$

(6)

where, $\sigma'$ the real and $\sigma''$ imaginary part of optical conductivity, $\omega$ the angular frequency and $\varepsilon_0$ the free space dielectric constant. Figures 10(a), (b) presents $\sigma'$ and $\sigma''$ with low values in the visible region drastically increased dependent on the electrons transition from the valence band to conduction band [32, 33].

4. Conclusions

Prussian blue analogues CoTCNi/HCCr and CoTCNi/HCCr/CNTs were successfully prepared by direct chemical reaction using precipitation method. The samples were examined by XRD exhibiting cubic-face centered structure. Raman spectroscopy confirmed the phase content and EDX spectra show high purity complexes. The morphological characteristics were studied from SEM and TEM images indicating the influence of CNTs on both size and shape of nanoparticles. The optical constants like optical band gap, dielectric constants, and optical conductivity were evaluated from transmittance and reflectance spectra dependent on photon energy and CNTs.
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Figure 10. (a) Real and (b) imaginary optical conductivity of the films as a function of photon energy.
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