

Research Article

Direct Preparation and Characterization of Copper Pentacyanonitrosylferrate Nanoparticles

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The present work describes the preparation of nanoparticles of copper pentacyanonitrosyl complexes starting from the compound sodium nitroprusside. Copper pentacyanonitrosylferrate (NCuNP) nanoparticles were successfully synthesized by using deionized water and formamide as solvent. The material was characterized by Fourier-transforming infrared spectroscopy (FT-IR), X-ray diffraction (XRD), ultraviolet-visible (UV-Vis) spectroscopy, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and cyclic voltammetry (CV). The results revealed that the electronic spectra of NCuNP exhibited a broad intervalence charge transfer band at 685 nm. An XRD peak broadening pattern of the NCuNP was verified, indicating a particle decrease when formamide is used. The particle size of NCuNP is estimated to be 80 nm. The cyclic voltammogram of the modified graphite paste electrode with NCuNP showed two redox pairs with formal potentials $E^{0'} = 0.36$ V and $E^{0'} = 0.78$ V ($\nu = 20$ mV s⁻¹; KCl 1.0 M), attributed to the redox process Cu^I/Cu^{II} and [Fe^{II}(CN)₅NO]/[Fe^{III}(CN)₅NO], respectively. The graphite paste electrode with NCuNP presents electrocatalytic response for Sulfite determination.

1. Introduction

Metallic nanoparticles (NPs) have attracted considerable attention on account of their intriguing properties and potential applications [1], due to their superior and advantageous functional properties for a wide range of technological applications, including catalysis, optics, microelectronics, and chemical, biological, and electrochemical sensors [1–7].

However, metallic nanoparticles (NPs) are materials that have received much attention due to their potential applications in areas such as chemistry, physics, biology, and engineering because of many magnetic properties, electrical, optical, and chemical properties that are dependent on particle size [1]. An important class of nanoparticles attracting considerable attention for their intriguing properties and potential applications is the hexacyano- and pentacyanonitrosylferrates metalates which are Prussian Blue analogues. Decreasing the size of these above particles plays an important role from an application point of view. The smaller or even nanoscale sizes improve the dispersibility of these cyanometalates in a particular solvent. This helps the thin

film formation process of the material, studying the optical properties, electrochromic behavior, and composite preparation. In order to achieve finely controllable synthesis of hexacyano- and pentacyanonitrosylferrate metalates, many synthetic methodologies have been obtained by using a microemulsion method [8]. Metal nitroprussides (MNP) have received much attention from the scientific community as electrochemical sensors due to their versatility and electrocatalytic activity [9–14].

Recently, a new protocol toward the synthesis of cobalt nitroprusside (CoNP) coordination nanoparticles was described based on drop-by-drop (DbD) method without the use of any additives. It was also prepared by sonication as well as by bulk mixing methods for comparison purposes [2]. This paper proposes a new facile and direct synthesis route to obtain nanoparticles of copper pentacyanonitrosylferrate (NCuNP).

The copper pentacyanonitrosylferrate (NCuNP), a Prussian Blue analogue, has been the subject of major investigations because of its excellent chemical and electrochemical [15] stability and due to an presence of the different oxidation

states that can be studied by various spectroscopic and electrochemical techniques, these insoluble binuclear complexes provide a wide range of analytical applications [15, 16].

Due to their intriguing properties and potential applications nanoscale size metallic particles are attracting considerable attention [17].

Recently, materials in the nanometer range have shown superior or advantageous functional properties for a wide range of technological applications, including catalysis, optics, microelectronics, and chemical/biological sensors. Metal nanoparticles as catalysts have been vigorously investigated because of their specific properties such as large surface area and their superior properties, which are different from their bulk counterparts [18]. Inorganic nanoparticles are very useful candidates for electrochemical studies [19, 20] owing to their outstanding activity and catalytic power [21–24].

2. Experimental

2.1. Instruments and Chemicals. All reagents and solvents were of analytical grade and were used as purchased. The vibrational spectra of materials were obtained by a Nicolet 5DXB FT-IR spectrometer (Nicolet Instruments, Madison, WI). 150 mg of previously dried KBr pellets and 1.5 mg (1.0% (w/w)) of each sample were prepared for the analysis. A minimum of 64 “scans” with a resolution of $\pm 4 \text{ cm}^{-1}$ in a band of 4000 to 400 cm^{-1} was used. The characterization by X-ray diffraction was performed using Rigaku Ultima IV diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Electronic spectra (UV-Vis) were obtained using Guided Wave model 260 spectrophotometer, in 350–1600 nm. The microstructure was observed by field-emission scanning electron microscope (FE-SEM, JSM-6700 F, Japan).

2.2. Preparation of Copper Pentacyanonitrosylferrate Nanoparticles (NCuNP). The nanoparticles were synthesized according to the procedure described in [8, 25] with some modifications and described as follows: two solutions, A and B; solution A consisted of 0.7 g of $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ dissolved in a solution of 30 mL of formamide and water mixture in a 6 : 4 ratio. Solution B was prepared by dissolving 0.7 g of $\text{CuCl}_2 \cdot \text{H}_2\text{O}$ in 20 mL of formamide and water mixture in a 6 : 4 ratio. After the solution was prepared, solution A was poured into solution B and stirred for 2 hours. The solid phase was filtered through a sintered plate funnel and washed thoroughly to eliminate the sodium chloride formed during the reaction.

3. Results and Discussion

3.1. The Vibrational Spectroscopy in the Infrared Region (FT-IR). Figure 1 illustrates the infrared spectra of the sodium nitroprusside (a) and NCuNP (b). The NCuNP exhibited two absorption bands at 2197 cm^{-1} and 1952 cm^{-1} (Figure 1(b)) which confirmed the formation of copper pentacyanonitrosylferrate nanoparticles. The absorption bands at 2197 and 1952 cm^{-1} , attributed to stretching of $\nu_s(\text{C}\equiv\text{N})$ and $\nu_s(\text{NO})$, were found to be in good agreement with the values for transition metal pentacyanonitrosylferrate [9–11], reported

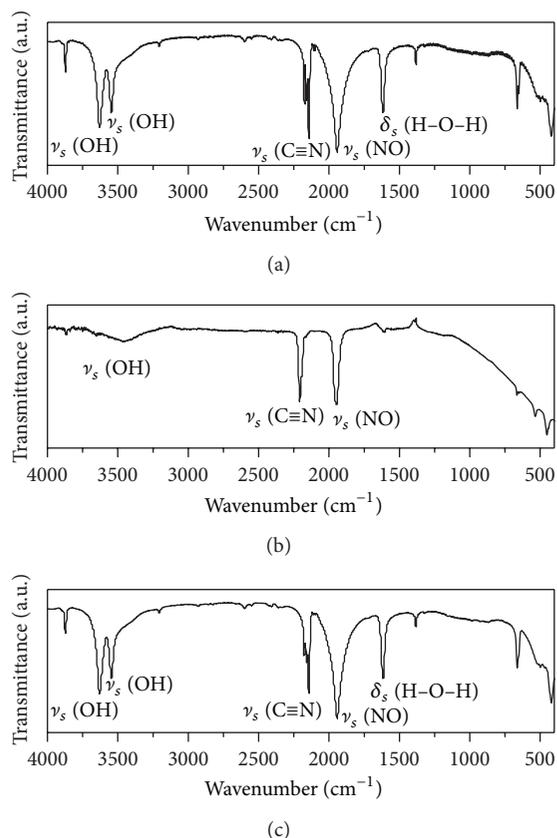


FIGURE 1: FTIR: (a) sodium nitroprusside, (b) NCuNP obtained in water (bulk), and (c) NCuNP obtained in water and formamide mixture (6 : 4).

in literature. A close comparison of the $\nu_{s(\text{C}\equiv\text{N})}$ and $\nu_{s(\text{NO})}$ band shifts and those obtained for sodium nitroprusside (NP) confirms a bathochromic (55 cm^{-1}) shift of the former relative to the latter (Figure 1(a)), thus characterizing the formation of the binuclear complex $-\text{Fe}^{\text{III}}-(\text{CN})-\text{Cu}^{\text{II}}$ [20].

3.2. X-Ray Diffraction (XRD). The material was also characterized by XRD technique (Figure 2). The XRD analysis was compared to the crystallographic cards (references 01-0244 and 30-0483) and in accordance with findings in [26, 27]. Therefore, by the Scherrer equation [27], the particle sizes were estimated to be 80 nm. Peak broadening was verified indicating a decrease in particle size when formamide is used [25].

3.3. The Electronic Spectra (UV-Vis). Another strong indication of the formation of nanoparticles was verified by electronic spectroscopy. As shown in Figure 3, the NCuNP obtained from formamide (a) and NcuNP (in water) shows two absorption processes with λ_{max} at 655 and 696 nm, respectively, attributed to the intervalence charge transfer, absent in pure sodium nitroprusside, Figure 3(a). Figure 3(b) shows a widening of the band and shift bathochromically by about 51 nm for the NCuNP for the complex prepared in

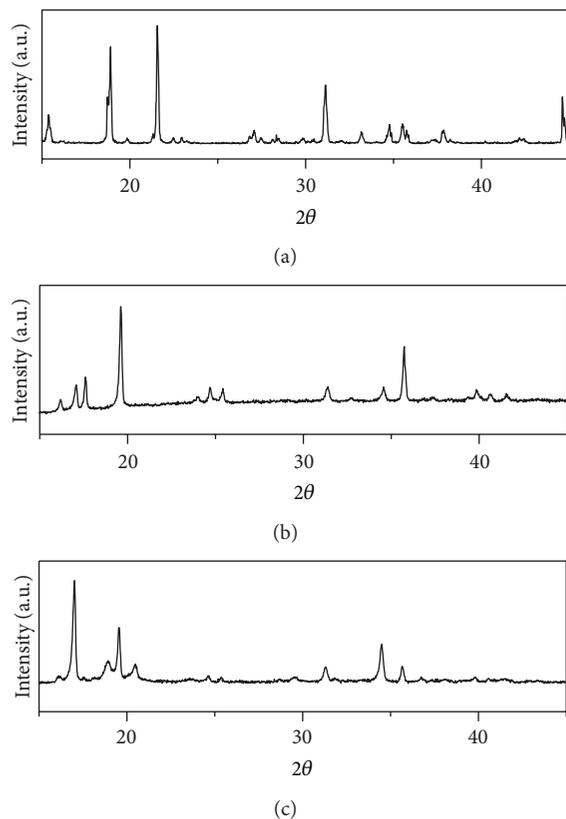


FIGURE 2: X-ray diffractogram of (a) sodium nitroprusside, (b) NCuNP obtained in water (bulk), and (c) NCuNP obtained in water and formamide mixture (6 : 4).

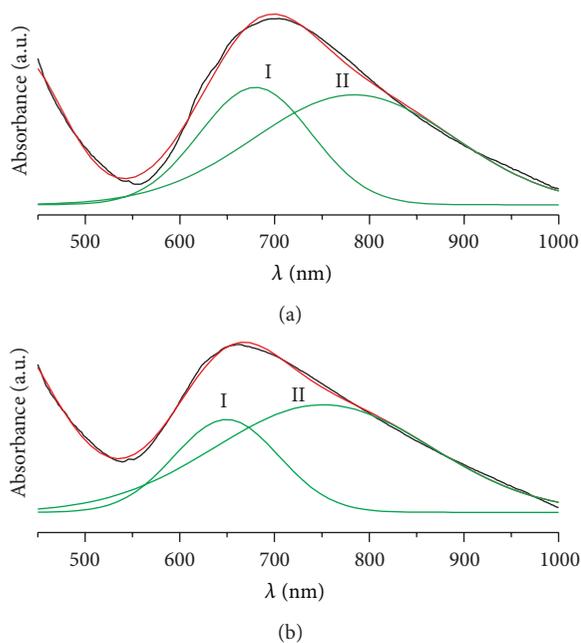


FIGURE 3: Electronic spectrum (UV/Vis): (a) NCuNP obtained in water and formamide mixture (6 : 4) and (b) NCuNP obtained in water (bulk).

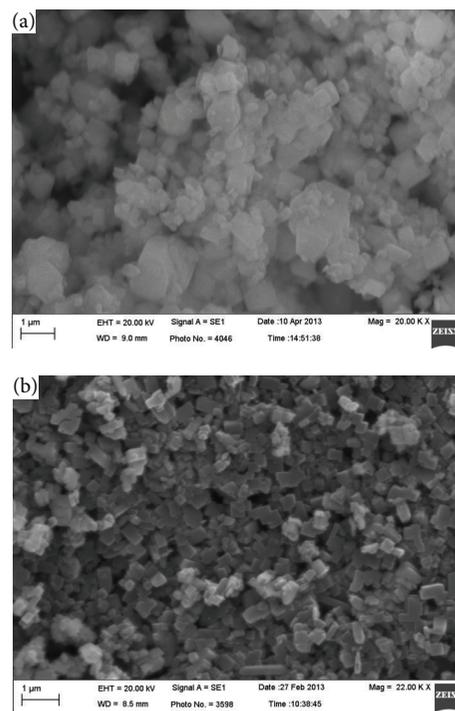


FIGURE 4: FE-SEM images of the (a) NCuNP obtained in water and (b) formamide mixture (6 : 4).

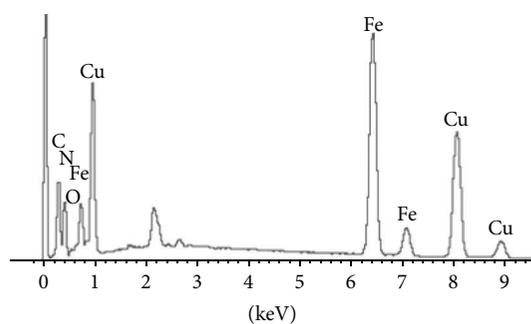


FIGURE 5: Energy-dispersive X-ray spectroscopy (EDX) of the NcuNP obtained in formamide mixture (6 : 4).

aqueous medium. These indicate that the particles exhibited size-quantization effects [25].

3.4. Scanning Electron Microscopy and Energy-Dispersive X-Ray Spectroscopy (SEM and EDX). Figure 4 illustrates SEM images of NCuNP obtained in water (a) and in formamide mixture (b). The NCuNP in formamide mixture show cubic particles with size in the range of 8.5 nm. Figure 5 shows the energy-dispersive X-ray spectroscopy (EDX) of NCuNP that exhibited the presence of elements (Na, Fe, and Cu) in the nanoparticle, thereby confirming the formation of the binuclear complex.

3.5. Cyclic Voltammetry (CV). NCuNP was characterized by cyclic voltammetry as shown in Figure 6. With

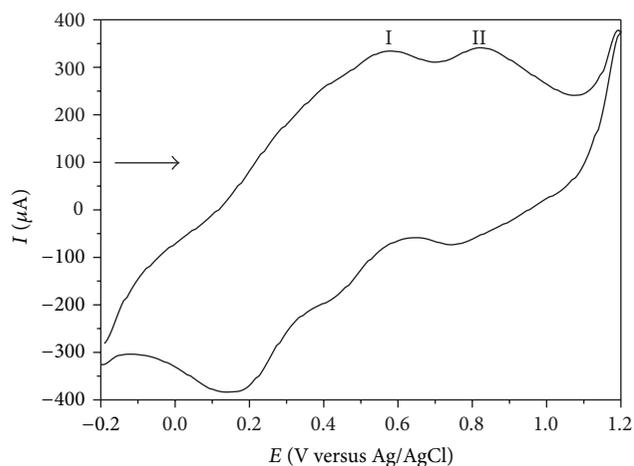


FIGURE 6: Cyclic voltammogram of graphite electrode modified with NCuNP ($\text{KCl } 1.0 \text{ mol L}^{-1}$; $\nu = 20 \text{ mV s}^{-1}$; 20% (w/w)).

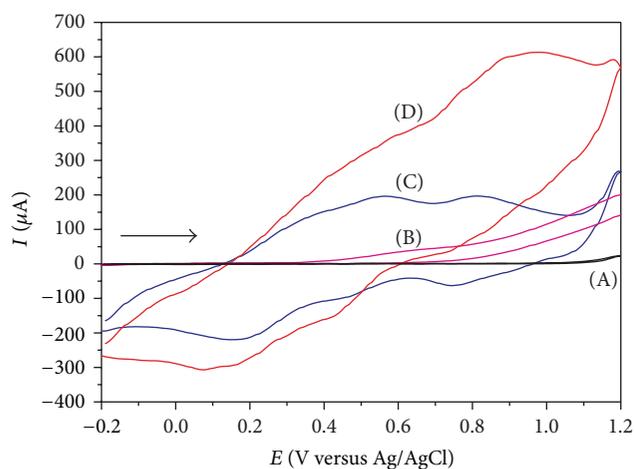


FIGURE 7: Cyclic voltammograms of (A) the graphite paste electrode; (B) graphite paste electrode and $4.0 \times 10^{-2} \text{ mol L}^{-1}$ of Sulfite; (C) graphite paste electrode modified with NCuNP; and (D) graphite paste electrode modified with NCuNP and $4.0 \times 10^{-2} \text{ mol L}^{-1}$ of Sulfite ($\text{KCl } 1.0 \text{ mol L}^{-1}$; 20 mV s^{-1} ; 20% (w/w)).

the voltammogram of NCuNP (20% w/w), a redox pair (peak I) was observed with a midi potential $E^{0'} = 0.36 \text{ V}$ and a redox pair (peak II) was observed with a midi potential $E^{0'} = 0.78 \text{ V}$ ($\nu = 20 \text{ mV s}^{-1}$; $\text{KCl } 1.0 \text{ M}$), attributed to the redox process $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$ and $[\text{Fe}^{\text{II}}(\text{CN})_5\text{NO}]/[\text{Fe}^{\text{III}}(\text{CN})_5\text{NO}]$.

Figure 7 illustrates the voltammetric behavior of the graphite paste electrode modified with NCuNP for the electrooxidation of Sulfite in 1.0 mol L^{-1} KCl. The unmodified graphite paste electrode in a solution of $\text{KCl } 1.0 \text{ mol L}^{-1}$ in the absence (curve A) and presence of Sulfite (curve B) did not show a redox pair in the potential range studied between -0.2 and 1.2 V . After the addition of Sulfite there was an increase in the anodic peak current intensity (curve D) when compared with the graphite paste electrode modified with NCuNP in the absence of Sulfite (curve C). There was an increase in the anodic current intensity of the peak at 0.80 V . Thus, it was

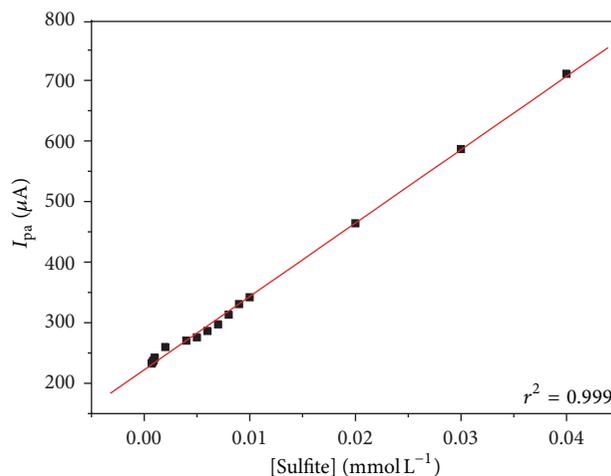
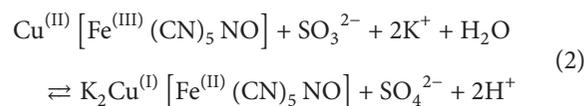
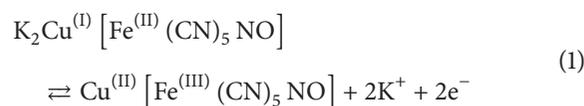


FIGURE 8: Analytical curve for the determination of Sulfite using the graphite paste electrode modified with NCuNP ($\text{KCl } 1.0 \text{ mol L}^{-1}$; 20 mV s^{-1} ; 20% (w/w)).

determined that, by adding aliquots of the Sulfite, the analyte was oxidized at the electrode surface by an electrocatalyst oxidation process.

The electrocatalytic oxidation of Sulfite occurs as follows: Fe^{3+} is produced during anodic scan, and the Sulfite molecule is chemically oxidized when it is reduced to Fe^{2+} , which will again be electrochemically oxidized to Fe^{3+} .

The electrocatalytic process in this system can also be represented according to (1) and (2):



Thus Sulfite is oxidized at the electrode surface, and this process occurs in the potential of 0.80 V . The oxidation process does not occur in this potential when glassy carbon electrode or unmodified graphite paste is used (Figure 7(B)).

The peak potential is not affected by the concentration of Sulfite and the catalytic current is also linear with the square root of scan rate. Figure 8 illustrates the analytical curve used to determine Sulfite. The modified electrode showed a linear response from 7.0×10^{-4} to $4.0 \times 10^{-2} \text{ mol L}^{-1}$ with the corresponding equation $Y(\mu\text{A}) = 0.112 + 134.187 (\text{Sulfite})$ and a correlation coefficient of $r^2 = 0.999$. The method showed a detection limit of $3.20 \times 10^{-4} \text{ mol L}^{-1}$ with a relative standard deviation of $\pm 2\%$ ($n = 3$) and amperometric sensitivity of $0.134 \text{ mA mol L}^{-1}$.

3.5.1. Interference Study. Interferences in the determination of 56 ppm sulfite using the graphite paste electrode modified with NCuNP were examined by testing the effect of several species frequently found with Sulfite. The effects of several

organic acids such as citric acid, oxalic acid, and ascorbic acid, the sugars such as glucose, fructose, and sucrose, and some inorganic ions such as thiosulfate, persulfate, nitrite, nitrate, and chloride were carried out by adding 300-fold of sulfite concentration ($1.0 \times 10^{-2} \text{ mmol L}^{-1}$) of some of the compounds mentioned. Of the compounds tested only ascorbic acid caused a negative interference in the electrode response. The other compounds did not show any interference (at 300-fold of sulfite concentration) to detect Sulfite using the modified electrode.

4. Conclusions

The nanoparticles were synthesized by using deionized water and formamide as solvent. The structure of NCuNP and its composites were confirmed by FT-IR, XRD, UV-Vis, FE-SEM, and EDX techniques. The nanoparticle sizes can be influenced according to the solvent used. It is concluded that the use of formamide as solvent and water is much more advantageous than using only water as solvent. A smaller size of the material with the use of formamide was observed. The cyclic voltammogram of the graphite paste electrode modified with NCuNP showed two redox pairs with formal potentials $E^{\theta'} = 0.36 \text{ V}$ and $E^{\theta''} = 0.78 \text{ V}$ ($\nu = 20 \text{ mV s}^{-1}$; KCl 1.0 M), attributed to the redox process $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$ and $[\text{Fe}^{\text{II}}(\text{CN})_5\text{NO}]/[\text{Fe}^{\text{III}}(\text{CN})_5\text{NO}]$, respectively. The redox pair $[\text{Fe}^{\text{II}}(\text{CN})_5\text{NO}]/[\text{Fe}^{\text{III}}(\text{CN})_5\text{NO}]$ presents a notable electrocatalytic response for the determination of Sulfite. The modified electrode gives a linear range from 7.0×10^{-4} to $4.0 \times 10^{-2} \text{ mol L}^{-1}$ ($r^2 = 0.999$) for the determination of Sulfite with detection limit of $3.20 \times 10^{-4} \text{ mol L}^{-1}$ with a relative standard deviation of $\pm 2\%$ ($n = 3$) and amperometric sensitivity of $0.134 \text{ mA mol L}^{-1}$ for Sulfite.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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