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Research Article

SYNTHESIS AND CHARACTERIZATION OF COPPER HEXACYANOFERRATE (II) NANOPARTICLES

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ABSTRACT

Nanoscale copper hexacyanoferrate (CuHF) is a low-cost material prepared via a chemical co-precipitation method. XRD diagram, FTIR spectrum, EDS image, HR-TEM image, surface area (BET), and pore volume parameters were used to determine the properties and morphologies of the CuHF. The synthesized nanomaterials have the following properties: nanoscale and cubic structure (space group F-43m). The CuHF molecular formula was $Cu_{13}[Fe(CN)_6]_{14}\cdot(2K)\cdot 10H_2O$. CuHF was a complex substance with a surface area of 12.80 m^2/g and average pore width of about 34.50 nm.

Keywords: copper hexacyanoferrate, cubic structure; nanoparticle

1. Introduction

The Prussian blue family (PB) is a complex compound. They have the general formula $M[Fe(CN)_6]$, where M is the transition metals (M= Fe, Cu, Ni, Co...). They have been utilized in various applications such as electrochemical sensing (Karyakin et al., 2001; Karyakin et al., 2017), energy storage (Qian et al., 2018; Yun et al., 2021), energy harvesting (Lee et al., 2014), and Cs^+ ions adsorption (Trung et al., 2021; Vipin et al., 2014; Kiener et al., 2019). The copper hexacyanoferrate (CuHF) is one of the most studied Prussian Blue's families. CuHF has been reported as a cubic structure where the Cu^{2+} ion is octahedrally coordinated to the N ends of CN groups. The porous and the framework of CuHF is stable, with narrow channels and a small volume (Avila et al., 2008). The nanoscale CuHF has been used as the nanochemistry materials have not yet been explored. Numerous publications are available on the application of this material. However, little information is available on this material's properties, chemical composition, and morphology. Many methods for synthesizing CuHF have been published, but the co-precipitation method is the most

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commonly applied because it is easy and inexpensive to perform (Firouzi et al., 2016). A protective agent such as citrate or polyvinylpyrrolidone can be added to the solution to improve the size and morphology of CuHF, when synthesizing this material (Ji et al., 2016, Wu et al., 2016). The chemical and physical properties of CuHF depend on the size and morphology of that material. This study aimed to introduce a cubic (Fm-3m) CuHF nanoscale prepared by a chemical co-precipitation method, which was easy to operate and low cost. The material was characterized by FTIR spectrum, XRD diagram, EDS image, surface area (BET) parameters, and HR-TEM image.

2. Experimental details

2.1. Materials

$K_4[Fe(CN)_6]\cdot 3H_2O$ (Merck, Germany), and $CuSO_4\cdot 5H_2O$ (Merck, Germany), the double-distilled water was used for all experiments.

2.2. Methods

2.2.1. Preparation of CuHF

CuHF is prepared according to the following equipment system (Figure 1)

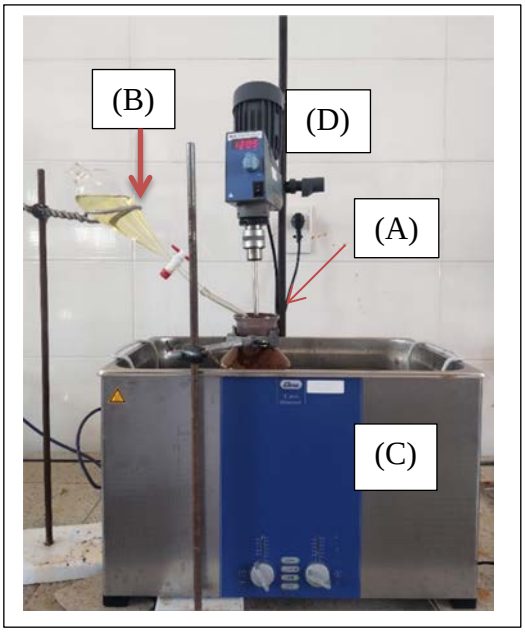

Figure 1. *Equipment system prepares CuHF*

(A) The reactor beaker containing 750mL $CuSO_4$ solution 0.15M

(B) The dropping funnel containing 250 mL ($K_4[Fe(CN)_6]$ 0.05 M)

(C) Ultrasonic bath (Elma S300H 1500W-50Hz)

(D) Stirring machine at 1200 rpm

Solution (B) was slowly dropped into a reactor beaker (A) in the ultrasonic bath (Figure 1). The temperature is maintained at 40 ºC, and the reaction time is 4 hours. After the end of the reaction, the products were separated by centrifuging (Universal 320-Germany) at 10.000 rpm, washed with double-distilled water, and then dried at 60 ºC.

2.2.2. Characterization of CuHF

Analysis of properties and morphology of materials based on a number of equipment systems are listed in Table 1

Table 1. *The measurements and their corresponding instruments*

Results of measurements	Instruments
XRD diagram	Scintag XDS-2000 diffractometer with CuKα radiation (λ = 1.54059) (Shimadzu XD-3A Japan)
FTIR spectrum	Thermo Scientific, Nicolet iS10, USA
TEM, HR-TEM image	JEM 2100, HSX: Jeol, Japan
Energy-dispersive X-ray (EDS) spectra	Field emission scanning electron microscopy (FESEM), JEOL JSM-6510LV, Japan
Surface area Brunauer–Emmett–Teller (BET)	Micromeritics - TriStar II 3020 3.02, USA

2.2.3. Calculated CuHF nanoscale size (D)

The main cubic cube was combined with eight sub-cubics (Sun et al., 2020). The CuHF nanoscale size (D) can be calculated from the XRD pattern based on the Scherrer formula as follows (Dan et al., 2014):

$$D = \frac{\lambda \times K}{\beta \times \cos\theta} \quad (1)$$

Where λ = 1.5405 Å is the wavelength of the incident XRD when using CuK_α radiation; K = 0.9, is a constant; β is the peak width in radians, often β measured as the full width at half maximum (FWHM), and θ is the diffraction angle of the (h, k, l) plane. θ is calculated using Bragg's law as follows (Bragg et al., 2013):

$$\theta = \arcsin\left(\frac{n\lambda}{2d(h,k,l)}\right) \quad (2)$$

In practice, the value of n can be considered 1 (Bragg et al., 2013). Therefore, the formula (4) becomes

$$\theta = \arcsin\left(\frac{\lambda}{2d(h,k,l)}\right) \quad (3)$$

Here, d is the spacing of cubic, $d(h,k,l) = \frac{a}{\sqrt{h^2+k^2+l^2}}$ and d(1, 1, 1) = 5.829Å (4)

3. Results and discussion

3.3. XRD diagram of the CuHF

The XRD data were analyzed by Fullfrop suite software with standard 101038.cif (Murray-Rust 2021) to identify the crystal structure of CuHF that has just been prepared. The red line is the XRD diagram of the $CuHF.10H_2O$ as prepared, and the blue line is the standard diagram Figure 2.

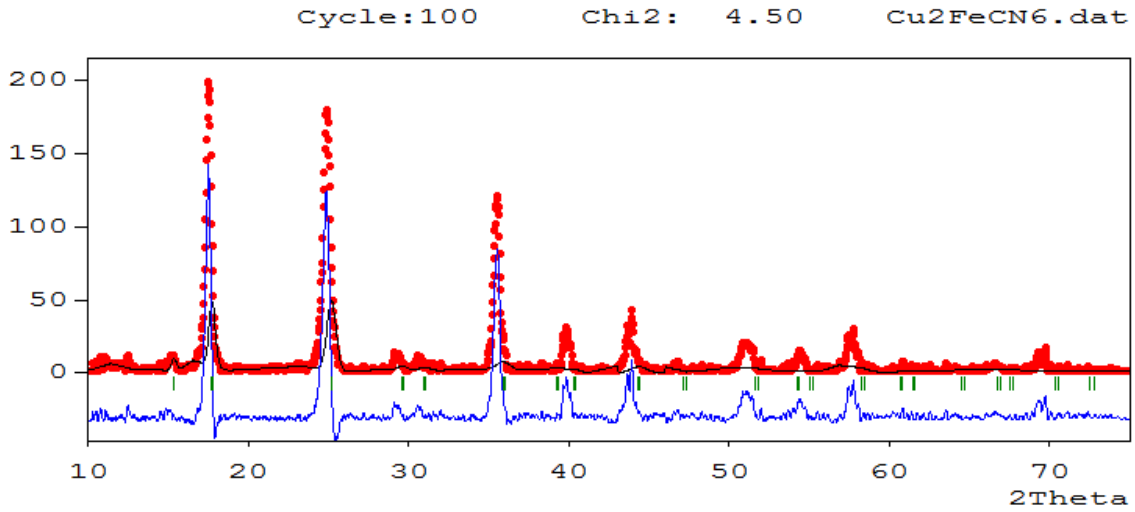

Figure 2. *XRD diagram of the CuHF compares with the standard*

The parameter results of Rietveld refinement were shown below:

Information on Space Group: CuHF

Number of Space group: 216; Hermann-Mauguin Symbol: F 43m

Hall Symbol: F 423; Crystal System: Cubic; Laue Class: m-3m

Point Group: 43m; Bravais Lattice: F; Lattice Symbol: cF

Reduced Number of S.O.: 24; General multiplicity: 96

Asymmetric unit: $0.000 \leq x \leq 0.500$; $0.000 \leq y \leq 0.250$; $-0.250 \leq z \leq 0.250$

List of S.O. without inversion and lattice centering translations

The interaction parameters (SYMM) at the binding sites in a single crystal are shown in Table 2.

Table 2. *The interaction parameters (SYMM) in a single crystal*

Number of SYMM	Interaction direction	Number of SYMM	Interaction direction
1	x,y,z	13	y,x,z
2	x,-y,-z	14	-y,x,-z
3	-x,y,-z	15	y,-x,-z
4	-x,-y,z	16	-y,-x,z
5	y,z,x	17	z,y,x
6	-y,-z,x	18	-z,-y,x
7	y,-z,-x	19	-z,y,-x
8	-y,z,-x	20	z,-y,-x
9	z,x,y	21	x,z,y
10	-z,x,-y	22	x,-z,-y
11	-z,-x,y	23	-x,-z,y
12	z,-x,-y	24	-x,z,-y

The result (Fig. 2) shows that the XRD peaks of the prepared CuHF nanomaterials coincide with the peaks of the standard.

Using the Scherrer equation and parameters determined from formulas (3) and (4), the crystal size of CuHF is calculated to be about 5.6 nm.

3.2. FTIR of CuHF

The FTIR spectra feature three vibrations within an octahedral unit: $[Fe(CN)6]^{4-}$: ν(CN), δ(Fe-CN), ν(Fe-C), and water, ν(OH), and δ(HOH) (Avila et al., 2008). The analytical parameters of the infrared spectrum (FTIR) of CuHF materials are presented in Fig. 3 and Table 3. This result indicates one type of crystal binding to water molecules, demonstrating the successful preparation of CuHF. xH_2O. The FTIR spectra obtained in this study are also related to the research results by the Avila group (Avila et al., 2008) (Table. 3).

Table 3. *Frequency (in cm^{-1}) for the FTIR absorption bands observed in CuHF*

ν(CN) cm $^{-1}$	**δ(Fe-CN)** cm $^{-1}$	**ν(Fe-C)** cm $^{-1}$	**ν(OH)** cm $^{-1}$	**δ(HOH)** cm $^{-1}$	
2099.59	590	472	3609.12; 3452	1623.14	This study
2106	597	499	3621; 3506	1602	Avila group

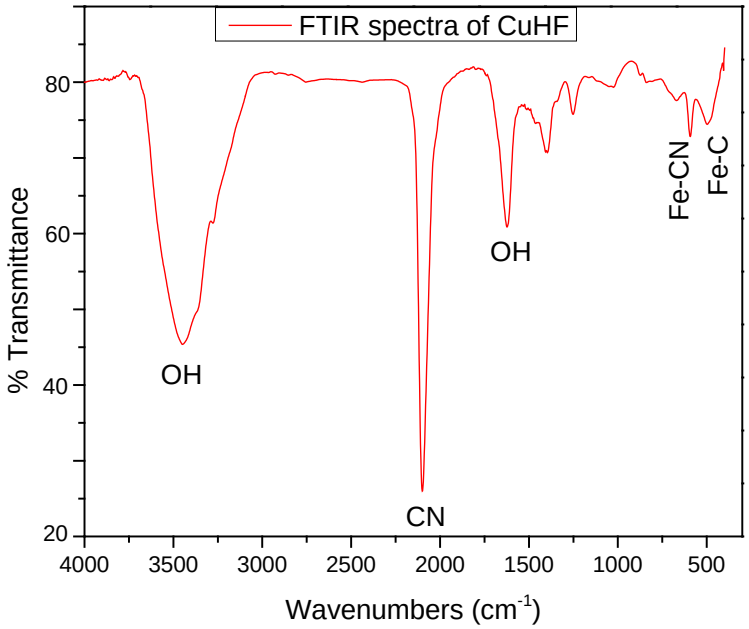

Figure 3. *The FTIR spectra of the CuHF*

3.3. The EDS of CuHF

The elemental composition of the CuHF was examined using Field emission scanning electron microscopy (FESEM), JEOL JSM-6510LV. The EDS spectrum of CuHF is shown in Figure 4.

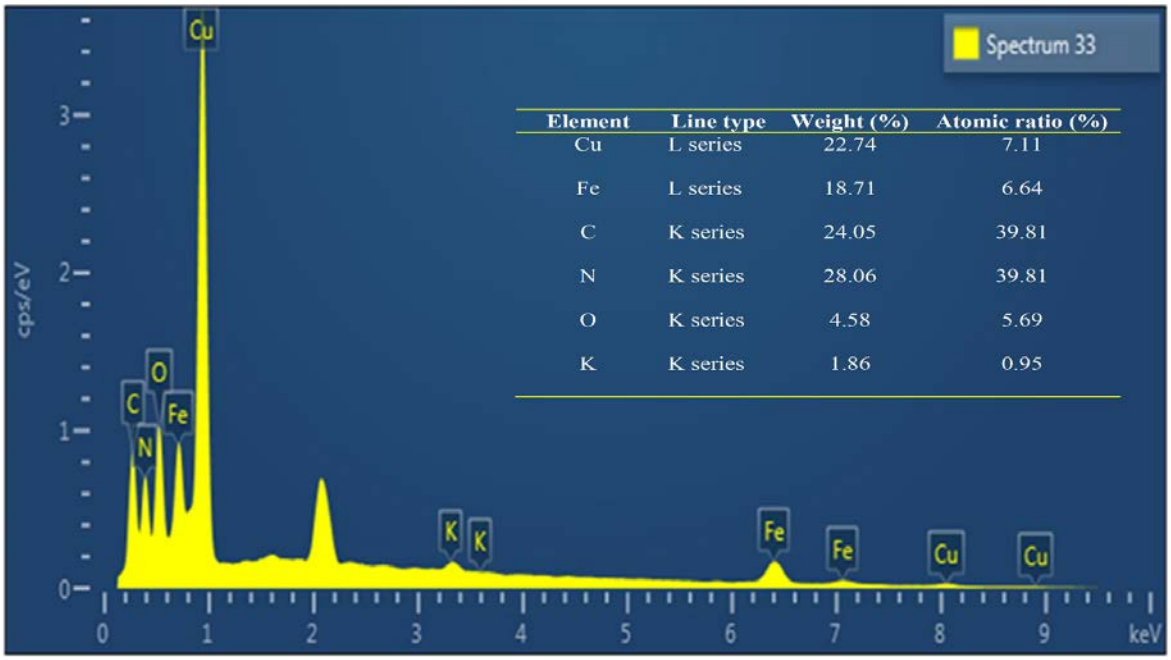

Figure 4. *The EDS spectrum of CuHF*

The atomic percentages of different elements of the CuHF are described in detail in Fig 4; the formula of the CuHF can be $Cu_{13}[Fe(CN)_6]_{14}\cdot(2K)\cdot 10H_2O$. The composition of the elements, the morphology, the structure, and the size of the materials depend significantly on the conditions and the preparation method (Kiener et al., 2019).

When the material was prepared to follow the chemical equation:

$$2CuSO_4 + K_4[Fe(CN)_6] \rightarrow Cu_2[Fe(CN)_6] + 2K_2SO_4 \quad (5)$$

$$CuSO_4 + K_4[Fe(CN)_6] \rightarrow K_2Cu[Fe(CN)_6] + K_2SO_4 \quad (6)$$

The $K_2Cu[Fe(CN)_6]$ dissolved in the solution (Vincent et al., 2015), so they were discarded after the product was washed several times with distilled water. Thus, the K^+ ions in the CuHF (Figure 4) may be the ions which were adsorbed by CuHF that had just been prepared.

3.4. TEM and HR-TEM images of CuHF

The morphology of CuHF is shown in Fig. 5a. It has a zeolitic structure which is a combination of cubic blocks. Figure 5b is an image of one crystal.

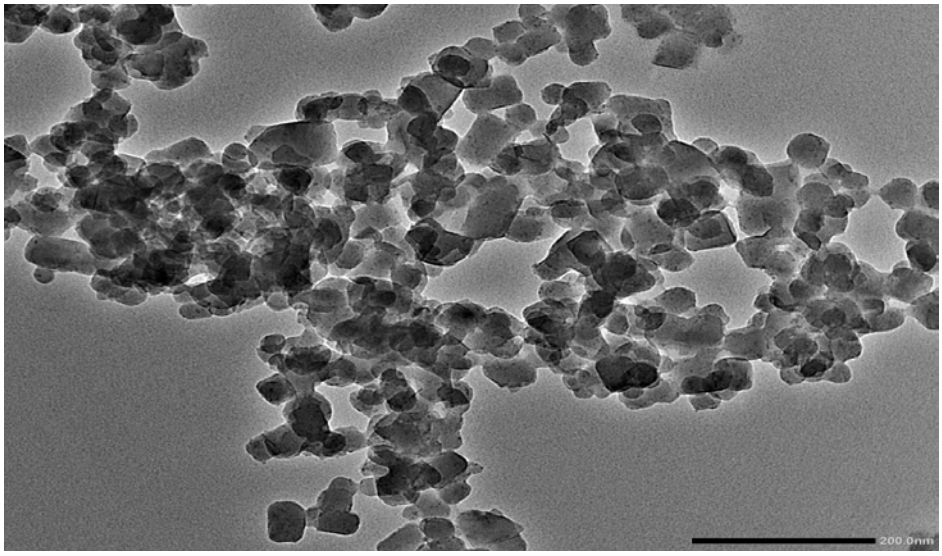

Figure 5a. *The HR-TEM image of CuHF*

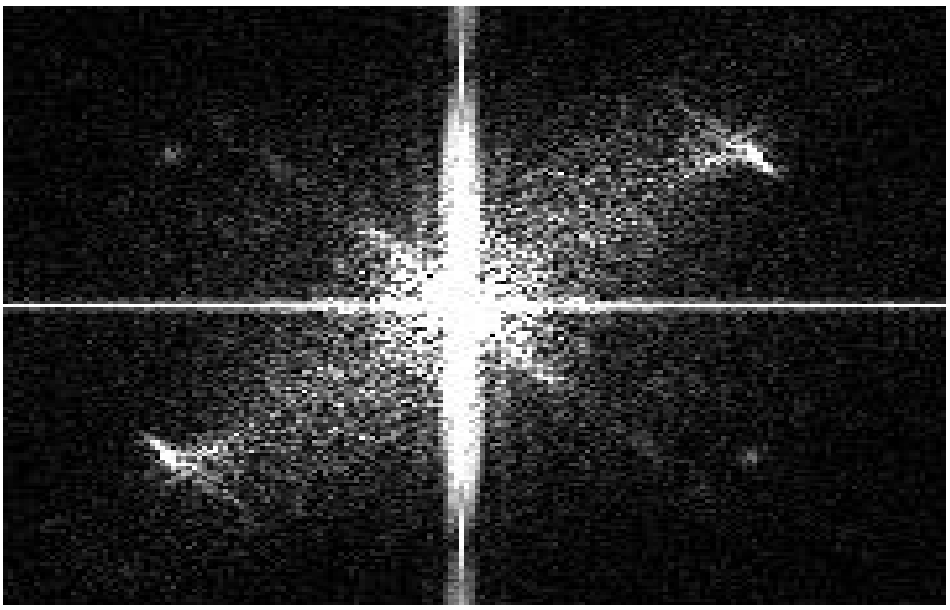

Figure 5b. *The HR-TEM image of one unit cell of CuHF*

3.5. Surface area (BET) and pore volume of CuHF

To examine the surface area and the pore characteristics of CuHF, N_2 adsorption/desorption measurements were performed in the condition: analysis adsorptive: N_2 (Nitrogen); analysis bath temperature: 77.350 K; sample mass: 0.3587 g; warm free space: 9.4024 cm^3 measured; cold free space: 28.2383 cm^3, calibration interval: 10 s; sample density: 1.000 g/cm^3. The obtained gas (N_2) adsorption-desorption curves are shown in Figure 6. The isothermal plots of N_2 adsorption/desorption for the CuHF show type IV isotherms. The absorption process is monolayer at low pressure, but at high pressure, absorption occurs in multilayers.

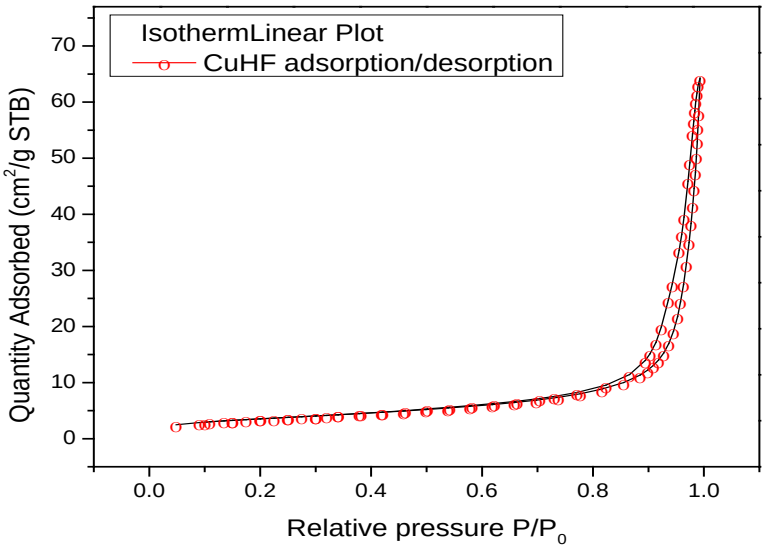

Figure 6. *Isothermal plots of N_2 adsorption/desorption for CuHF*

The pore size distributions of the CuHF were calculated from adsorption and desorption data using the Barrett–Joyner– Halenda (BJH) model, showing a broad peak centered from 2-50 nm Fig.7a and Fig. 7b, respectively. The pore size of the CuHF is distributed from mesoporous to macroporous.

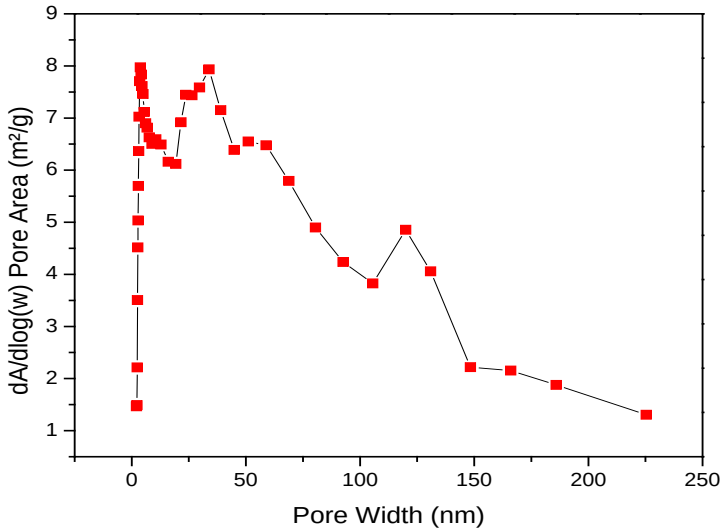

Figure 7a. *BJH Adsorption dV/dlog(w) Pore Volume*

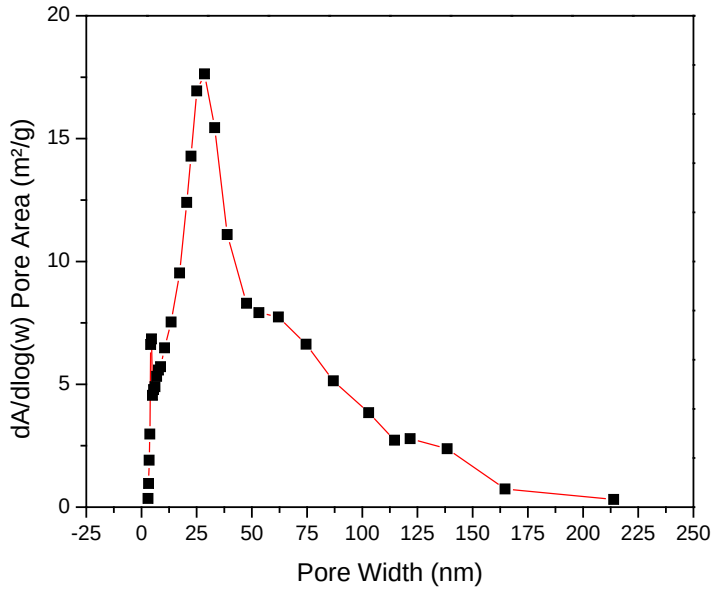

Figure 7b. *BJH desorption dV/dlog(w) Pore Volume*

The results of the physical properties analysis of CuHF materials by the BET method are shown in Table 4

Table 4. *The physicochemical characteristics of the CuHF*

BET Surface Area	**12.80 m^2/g**
BJH Adsorption cumulative surface area of pores	11.657 m^2/g
BJH Desorption cumulative surface area of pores	12.853 m^2/g
BJH Adsorption cumulative volume of pores	0.101 cm^3/g
BJH Adsorption average pore width (4V/A):	34.499 nm
BJH Desorption average pore width (4V/A):	31.466 nm

The Copper hexacyanoferrate has a zeolitic cubic structure, BET surface area 12.80 m^2/g was prepared.

4. Conclusions

Copper hexacyanoferrate (CuHF) nanoscale was prepared by a chemical co-precipitation method, which was easy to operate and low cost. The CuHF was characterized by an XRD diagram, FTIR spectrum, EDS image, HR-TEM image, surface area (BET) and pore volume parameters. The results show that the CuHF has a cubic structure (space group F-43m), and the calculated crystal size was about 5.6 nm. The CuHF molecular formula was $Cu_{13}[Fe(CN)_6]_{14}\cdot(2K)\cdot 10H_2O$. Micrographs of complex substances (CuHF) were zeolitic structure, and surface area of 12.80 m^2/g, average pore width of about 34.50 nm was demonstrated.

❖ ***Conflict of Interest:*** *Authors have no conflict of interest to declare.*

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TỔNG HỢP VÀ TÍNH CHẤT CỦA VẬT LIỆU NANO ĐỒNG HEXACYANOFERRATE

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TÓM TẮT

Đồng hexacyanoferrate kích thước nano (CuHF) là loại vật liệu có giá thành thấp, được điều chế bằng phương pháp đồng kết tủa hóa học. Thông qua các kĩ thuật nhiễu xạ tia X (XRD), quang phổ hồng ngoại biến đổi Fourier FTIR, quang phổ tia X phân tán năng lượng(EDS), kĩ thuật kính hiển vi điện tử truyền qua có độ phân giải cao (HR-TEM) và diện tích bề mặt (BET) để xác định các tính chất và hình thái của CuHF. Vật liệu được tổng hợp có các đặc tính sau: tinh thể có cấu trúc lập phương (F-43m) và kích thước khoảng 5,6 nm. Công thức phân tử của CuHF là $Cu_{13}[Fe(CN)_6]_{14}\cdot(2K)\cdot 10H_2O$*. CuHF là một chất phức hợp có diện tích bề mặt (BET) là 12,80* m^2 */ g, và có độ rỗng trung bình khoảng 34,50 nm.*

Từ khóa: copper hexacyanoferrate; cấu trúc lập phương; vật liệu nano