

Magnetic Properties of Melanin Doped with Copper Oxide Nanoparticles [†]

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Abstract: In this study, the analysis of XRD patterns reveals that both natural melanin and copper oxide-doped melanin exhibit amorphous structures. The absence of new peaks for Cu₂O confirms that the copper oxide nanoparticles are effectively integrated into the melanin matrix. Utilizing Scherrer's equation, we calculated the crystallite size, which increased from 2.02 nm for natural melanin to 3.01 nm after doping, suggesting a significant influence of copper ions on melanin structure. Additionally, the VSM measurements demonstrate a shift from ferromagnetic behavior in the natural melanin to paramagnetism in the doped samples, highlighting the impact of copper oxide on the magnetic properties of melanin. These findings provide valuable insights into the biological and functional transformations of natural melanin, furthering our understanding of its role in various medical applications.

Keywords: natural melanin; nanocomposites; paramagnetism; copper oxide-doped melanin

1. Introduction

Natural eumelanin is a hybrid bio-polymer found in various living organisms. It protects humans' skin. Melanin can be categorized into different types based on its molecular precursors. Eumelanin, or black melanin, consists primarily of oligomers originating from 5,6 di-hydroxy-indole and 5,6 dihydroxy-indole-2-carboxylic acid. It demonstrates remarkable antioxidant capabilities in lipid peroxidation inhibition and in standard chemical assays. In contrast, pheomelanin, known for its orange-red color, is formed from benzothiazine ring units [1–3]. Neuro-melanin, a dark type, is believed to be a combination of dihydroxy-indole and benzothiazine.

One of the primary biological functions of melanin is its capacity to chelate metals, which helps reduce oxidative stress in the human body. By binding to reactive metal ions, melanin exhibits high antioxidant activity [4,5]. The amine, carboxyl, and hydroxyl groups within melanin are crucial for its metal-binding properties. It is essentially a reservoir for metal ions that permits their exchange, re-release, and storage. Moreover, it effectively sequesters reactive metals, thereby mitigating their potential to induce oxidative stress.

Melanin demonstrates a high binding capacity for ions such as Ca and Zn ions [6]. Sepia melanin can release heavier metals, functioning as a sink [7,8]. The Fenton and Haber-Weiss reactions are two processes that catalyze transition metals to produce reactive oxygen species (ROS). Our previous research has shown that natural melanin can bind to transition metals such as zinc, iron, and copper, with their binding capacities determined [8,9]. These metals can interchangeably bind to the carboxyl groups in melanin. Notably, the binding capacity for certain transition metals (TMs) is often used as an indicator of the ratio amount of dihydroxy- carboxylic acid molecules in natural melanin. As individuals age [10], a decrease in binding capacity suggests a reduction in carboxyl groups or DHICA content, leading to diminished antioxidant efficiency.



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2. Materials and Methods

Copper oxide nanoparticles were synthesized using the chemical co-precipitation technique. In a typical procedure, 5 g of $\text{CuCl} \cdot 2\text{H}_2\text{O}$ and 10 g of $\text{Cu}_2\text{Cl}_3 \cdot 6\text{H}_2\text{O}$ were combined in distilled water under a nitrogen gas vacuum. The mixture was subjected to vigorous stirring and heated to 100°C . Subsequently, 10 mL of NaOH was gradually introduced. The mixture was continuously stirred for 1 h. Afterward, the nanoparticles were repeatedly rinsed with distilled water and dried under vacuum for 24 h. Herbal eumelanin in this work was extracted from black seed (*Nigella sativa*). A total of 10 gm of seeds was solubilized in a solution of NaOH (pH 10) for 1 h then this was stirred with copper oxide for 3 h. The resulting nanoparticles were then washed twice with distilled water and dried in an oven for 48 h. For the XRD results for the nanoparticles, a Bruker D8 Discover diffractometer (Bruker, Karlsruhe, Germany) with $\text{Cu-K}\alpha$ radiation of wavelength $1.54 \text{ \AA}$ was used. Magnetic measurements were performed by using a vibrating sample magnetometer (VSM, 7404 model-1.8T magnets, Lake Shore Cryotronics, Westerville, OH, USA).

3. Results and Conclusions

Figure 1 presents the XRD curves of both the melanin and copper oxide-doped (Cu_2O) melanin samples. The XRD pattern shows both samples have a broad peak, indicating an amorphous structure. The peak at ($2\theta = 22^\circ$) indicates the formation of melanin. Furthermore, no new peaks for Cu_2O appear in the XRD result, confirming that the Cu_2O nanoparticles bonded well to the melanin molecules. The Scherrer equation is used to calculate the crystallite size ($D = \frac{k\lambda}{\beta \cos\theta}$), where D is the crystallite size of the nanoparticles, ($k = 0.9$) is the constant for the spherical particles, λ is the wavelength of the XRD ($\sim 0.154 \text{ nm}$), and β is the FWHM of the Bragg angle. The average crystallite size of the melanin nanoparticles before doping with copper oxide is 2.02 nm and the average size increased significantly to 3.01 nm . The significant increase in the crystallite size of the melanin doped with copper oxide is related to the size of copper ions [8].

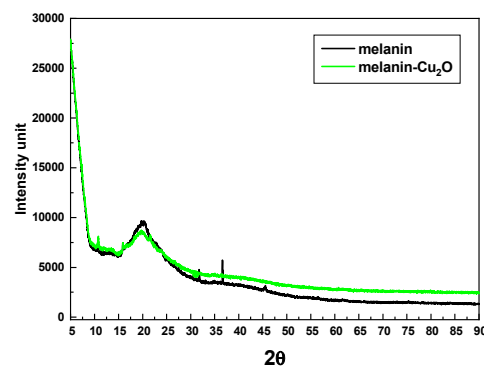


Figure 1. XRD pattern of natural melanin and natural melanin doped with Cu_2O .

Figure 2 shows a hysteresis loop at 300K° . The measured magnetization (M) per gram of all the samples was measured as a function of the magnetic field (H). The results show the ferromagnetic behavior of natural melanin becomes paramagnetic after doping with copper oxide. This change in magnetic behavior allows us to gain insight into certain biological and vital transformations of melanin.

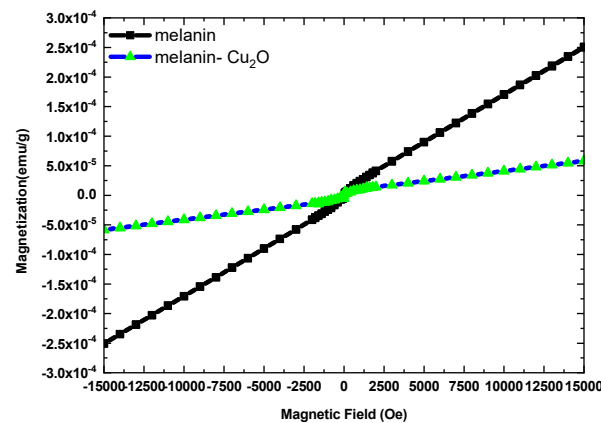


Figure 2. Magnetization hysteresis loops of natural melanin and natural melanin after it was doped with Cu_2O versus applied magnetic field at room temperature.

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