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Novel organic-inorganic nanohybrids (MnO_2 and Ag nanoparticles functionalized 5-methoxy-2-mercaptobenzimidazole): One step synthesis and characterization

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ABSTRACT

The study included the synthesis of manganese dioxide nanoparticles using the nitric acid by oxidation method. Moreover, the work involved the chemical synthesis of Ag metal nanoparticles using sodium citrate for reducing Ag ion into Ag metal in its nanoscale form. These nanoparticles were diagnosed using FTIR, XRD, and AFM. The maximum height was 5 nm and 2.5 nm for Ag NPs and MnO_2 NPs, respectively. In addition, the novelty lies in the use of the organic compound 5-methoxy-2-mercaptobenzimidazole (MMBI) to synthesis the organic–inorganic nanohybrids which were characterized using FTIR and XRD.

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1. Introduction

Heterocyclic compounds are one of many types of organic compounds which are containing sulfur, nitrogen or/and oxygen atoms in the three-, four-, five- or six-membered ring, as well as carbon atoms [1–7]. Notably, organic researchers have been interested in heterocyclic compounds due to their pharmacological importance and their applications in different fields. Many antibiotics, dyes and drugs were obtained by the laboratory synthesis of heterocyclic compounds [8,9]. In addition, many important extracted antibiotics, such as penicillin, contain in their composition heterocyclic ring systems [10]. Benzimidazoles are important heterocyclic compounds containing nitrogen atoms as well as carbon and hydrogen atoms in a figure as a six-membered ring of phenyl and a five-membered ring of imidazole [11]. Furthermore, the benzimidazoles have a significant role in the medical field due to their biological effectiveness [12–14]. The most important uses are antimicrobial [15] anti-inflammatory [16] anti-cancer [17] antioxidant [18] anti-bacterial [19] for ulcers [20] anesthetic [21] antineoplastic [22] and antimalarial [23]. Due to the biological effects of benzimidazole and its derivatives, it received great attention from researchers [24–26]. On the other hand, the inorganic nanoparticles showed good chemical and physical properties, and embody a very important substance due to its great role in developing new nanoscale devices that important in physical, medical and biological applications [27–31]. Recently, great achievements have provided in producing new structures or types of nanomaterials that have an appropriate surface leading to improved antimicrobial applications [31,32]. The great interest at the present time can be attributed to the development of new antimicrobial agents due to the bacterial resistance to the prepared treatment and to the newly emerging diseases [33,34]. Recently, work has been done on loading nanomaterials on the surfaces of organic compounds to increase their biological effectiveness towards microbes, as these new materials showed high efficacy against bacteria and fungi that were not previously observed in both basic compounds [35–37]. Among the nanomaterials that grafted and functionalized with organic compounds are silver [35] gold [38] platinum [39] manganese oxide [40] ZnO [41] titanium dioxide [42] nickel oxide [43] and others. The new nanocomposites containing organic molecules showed unique properties in inhibiting the activity of microbes. In particular, we will deal with nanocrystalline silver, which has been widely used due to its wide applications, its cheap price, and the possibility of preparing it easily using green methods during short reaction time [44–48]. The different methods of

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preparing silver metal in nanoscale make us more attracted to its frequent use, as the result is often indifferent geometric nano shapes and with different nanoscale sizes [45,46] which gives different results even for the same application. However, nanosilver has many nanostructures such as nanowires, nanosquares and nanohexagons, but the shape remains the most common is nanospheres [44–47]. This may be attributed to the growth mechanism depending on the crystalline planes which is determined by the reaction conditions.

Manganese dioxide nanoparticles are characterized by being harmless to the environment, non-toxic to living cells and high surface area but more importantly, it can be obtained easily at a very low cost [49,50]. It is also distinguished by the possibility of preparing it in different ways, such as sol–gel [51] hydrothermal [52] and thermal degradation [53] using different precursors such as potassium permanganate or manganese acetate and sulfate, but the most specific for the geometry is the use of manganese-containing complexes, which gave the structure of nanoscale flowers [49]. In this study, silver nanoparticles and manganese nanoparticles were prepared and then the organic compound 5-methoxy-2-mercaptobenzimidazole was incorporated on them separately. In general, this type of compounds has not been studied extensively despite its many uses and the characteristics of the obtained products. Therefore, the study aimed at preparing and carefully diagnosing it. In addition, 5-methoxy-2-mercaptobenzimi dazole (Chart) specifically used because the number of researches on it is very few, and therefore this work will also expand the chemistry of this compound.

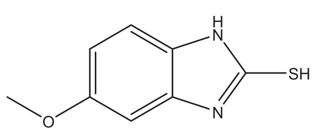

Chart. Chemical structure of 5-methoxy-2-mercaptobenzimidazole.

2. Experimental

2.1. Materials and instrumentations

Potassium permanganate ($KMnO_4$), silver nitrate ($AgNO_3$), and manganese sulfate dihydrate ($MnSO_4 \cdot 2H_2O$) were used as precursors for Ag NPs and MnO_2 nanoparticles, respectively, which supplied from Aldrich. Sodium citrate ($Na_3C_6H_5O_7$) was used as a reducing agent for converting silver ion into silver nanometal which was purchased from Fluka. Nitric acid (HNO_3) was used as an oxidation agent for converting Mn ions into manganese oxide nanoparticles which was purchased from Alfa-Aesar. 5-methoxy-2-mercaptobenzimidazole ($C_8H_8N_2OS$) was used purchased from Aldrich for grafting on the as-prepared nanoparticles. The device of the type Perkin-Elmer was used for conducting FTIR spectra. X-ray diffraction (XRD) for the materials were recorded using a Shimadzu-XR-6000 device. The morphology of the as-prepared nanomaterials was recorded by atomic force microscopy (AFM) using PHYW type with tip scanner type (linear low-voltage electro-magnetic).

2.2. Methods

2.2.1. Synthesis of Ag NPs

34 mg of $AgNO_3$ was dissolved deionized water (100 ml) in a three-neck flask by vigorous stirring with heating until the boiling, thereafter, sodium citrate (35 mM, 10 ml) was added slowly under vigorous stirring, the solution gradually turned to greenish yellow, which indicates the formation of silver nanoparticles. The solution remains on the boil for 7 min. The resulting mixture was then left to cool to 25 °C with continuous stirring. The mixture was centrifuged for 20 min at 5000 rpm and the precipitate washed and centrifuged again for further using [35,36].

2.2.2. Synthesis of Ag NPs - MMBI

The solution of the 5-methoxy-2-mercaptobenzimidazole (35 mg) in ethanol (5 ml) was carefully added to silver nanoparti-

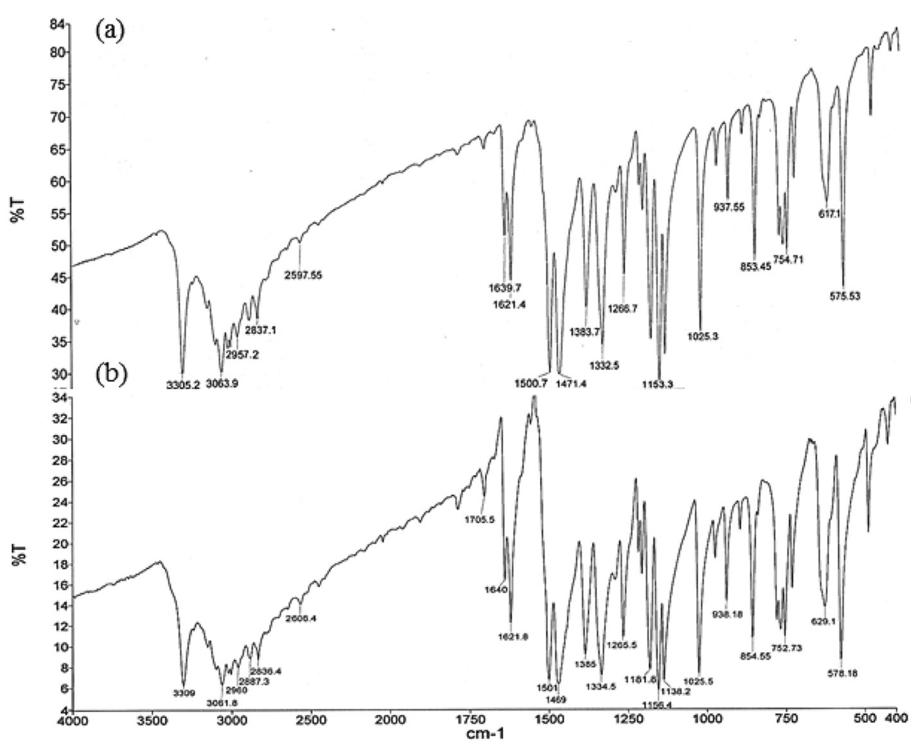

Fig. 1. FTIR spectra of MMBI (a); Ag NPs-MMBI (b).

cles solution (10 mg) in deionized water (100 ml). The organic and inorganic mixture was then left to react at 25 °C for a day. Thereafter the product was separated by centrifuge the mixture for 20 min at 5000 rpm and the precipitate washed with ethanol/water mixture, centrifuged again and then dried at 80 °C for 8 hr.

2.2.3. Synthesis of MnO_2 NPs and its derivative MnO_2 NPs- MMBI

Potassium permanganate (1.8400 g) in deionized water (100 ml) and manganese sulfate dihydrate (2.7500 g) in deionized water (150 ml) were mixed together and thereafter, concentrated nitric acid was added to maintain the pH to equal to approximately 1. This acid-manganese mixture was then stirred at 75-85̊C for a day. The precipitate was separated by centrifuge, washed with water to maintain the pH equal to 6–7 and dried at 60–80 °C for a day [54,55].

2.2.4. Synthesis of MnO_2 NPs- MMBI

35 mg of manganese dioxide nanoparticles were dispersed in 200 ml of deionized water in three-necked flask under vigorous stirring for 15 min at room temperature. Thereafter, the solution of the 5-methoxy-2-mercaptobenzimidazole (17 mg in 5 ml of ethanol) was added to the dispersed solution of manganese oxide. The resulted mixture was stirred for 24 hr and then the product was filtered and washed several times with deionized water and hot ethanol to remove unreacted MMBI and then dried at 80 °C for 8 hr.

3. Result and discussion

3.1. FTIR

3.1.1. FTIR of MMBI

The FTIR spectrum of 5-methoxy-2-mercaptobenzimidazole in Fig. 1 (a) shows a band at 3305 cm^{-1} of the vibrations of amine group υ(N–H). The band at 1639 cm^{-1} attributed to the bending vibration of amine groups. Furthermore, the bands at 2957 and 2837 cm^{-1} assigned to the stretching vibration of methoxy group. The bands at 2597 and 617 cm^{-1} can be assigned to the vibration of (S–H) and (C–S), respectively. Moreover, the band centered at 1266 and 1500 cm^{-1} assigned to the stretching vibration of (C–O–C) and (C = N) groups, respectively. Finally, the bands at 1639 and 1921 cm^{-1} represented the stretching vibrations of (C = C) of aromatic ring [56].

3.1.2. FTIR of Ag NPs - MMBI

As in Fig. 1 (b), the spectrum shows the same number of bands to that appears in the free MMBI. However, some bands shifted towards higher frequency to that found in free MMBI. The shifted bands are that assigned to the stretching vibration of amine and thiol groups which appeared at 3309 and 2605 cm^{-1}, respectively. This is a good evidence for the success grafting of MMBI on the chose nanoparticles via the electron pairs of sulfur and nitrogen atoms of thiol and amine groups, respectively. Notably, FTIR of Ag NPs was not illustrated as it shows no vibrations because that IR energy is not enough to cause Ag-Ag vibrations.

3.1.3. FTIR of MnO_2 NPs

FTIR of this nanoparticle is illustrated in the Fig. 2 (a). At the range 400–800 cm^{-1}, the three bands that centered at 718, 520.6 and 462 cm^{-1} are attributed to υ(Mn–O). The low intense bands at 3444 and 1625 cm^{-1} are attributed to the stretching and bending vibrations of (O–H) of the absorbed water on MnO_2 nanoparticles due to high surface area [44].

3.1.4. FTIR of MnO_2 NPs - MMBI

The spectrum displays the following bands at; 3247, 1680 and 1458 cm^{-1} represented the stretching vibration of (N–H), (C = C) and (C = N), respectively. It is clearly note that the stretching vibrations of (N–H) and (C = N) bands were shifted towards lower frequency than that found in free MMBI. This is a good evidence for the grafting of MMBI onto manganese oxide nanoparticles as shown in Fig. 2 (b).

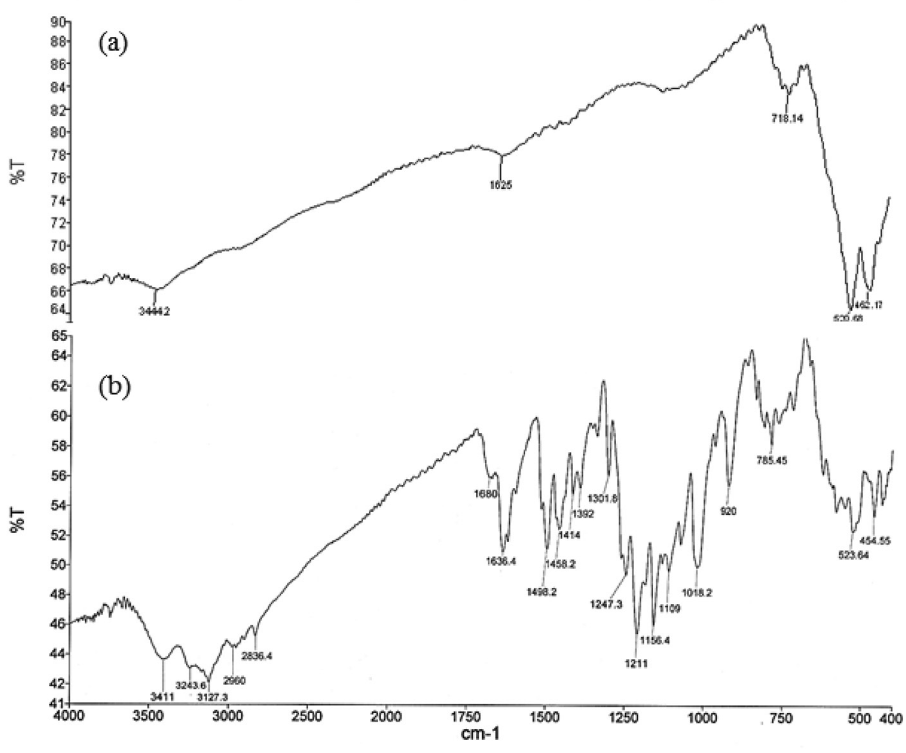

Fig. 2. FTIR spectra of MnO_2 NPs (a); MnO_2 NPs- MMBI (b).

3.2. X-Ray diffraction XRD

3.2.1. XRD of Ag NPs

Fig. 3 (a) shows the XRD of nano silver. The diffraction displays four peaks at 2θ = (38.2408°), (44.4235°), (64.5903°) and (77.5154°), of the (111), (200), (220) and (311) reflections of the fcc structure of AgNPs, respectively. The diffraction pattern is in well agreement with the standard powder diffraction card (JCPDS file No. 04–0783). The appearance of single isolated and sharp peaks at this diffraction is clear evidence of the preparation of silver particles with excellent crystal structure and high purity [36].

3.2.2. XRD of Ag NPs-MMBI

Throughout XRD pattern in Fig. 3 (b), the diffraction peaks of Ag NPs at the planes (111), (200), (220) and (311) were noticed in the same position as minor material. Additionally, the new peaks at 10.7, 13.6 and 27.4 are a good evidence for the formation of silver nanoparticles anchored MMBI as a new organic–inorganic nanohybrid [37]. The peaks of silver nanoparticles were

3.2.3. XRD of MnO_2 NPs

As shown in the Fig. 3 (c) of XRD related MnO_2. Powder XRD pattern was obtained, which presented number of peaks located at (2θ = 12.7530, 18.0830, 28.7999, 37.6007, 42.1174, 49.8883, 56.4056, 60.1143, 65.6025, 69.0715, and 72.9804°) can be assigned to the planes; [(101), (200), (301), (211), (310), (411), (600), (512), (020), (514), and (312)] respectively. These peaks were matched with peaks of α –MnO_2 standard data [51]. The absence of other peaks, demonstrating the purity of the prepared nanoparticles [57].

3.2.4. XRD of MnO_2 NPs-MMBI

Fig. 3 (d) displays the XRD of 5-methoxy-2-mercaptobenzimidazole functionalized MnO_2 NPs. The XRD of this nanohybrid shows the MnO_2 NPs diffraction peaks at the planes; [(101), (200), (301), (211), (310), (411), (600), (512), (020), (514), and (312)] but with various intensities. Moreover, the XRD displays new diffraction peaks, suggesting, the organic compound (MMBI) was successfully react with MnO_2 NPs and a new 5-methoxy-2-mercaptobenzimidazole functionalized manganese nanoparticles was formed [49].

3.3. AFM

3.3.1. AFM of Ag NPs

This technique is important for studying the morphology of the prepared materials, as it gives a good idea of the geometric compositions of the prepared nanomaterials. 3D image AFM of pure Ag NPs is illustrated in Fig. 4. In the AFM, the highest rise for the particles in the measured sample was found to be 5 nm, this value gives a good proof that the silver nanoparticles were prepared at the nanoscale.

3.3.2. AFM of MnO_2 NPs

The 3D-AFM investigations of pure MnO_2 NPs was shown in Fig. 5. In the three-dimensional figure, the highest rise for the particles in the measured sample was found to be 2.3 nm. This value proves that the manganese oxide particles were prepared at the nanoscale and in very small particle sizes.

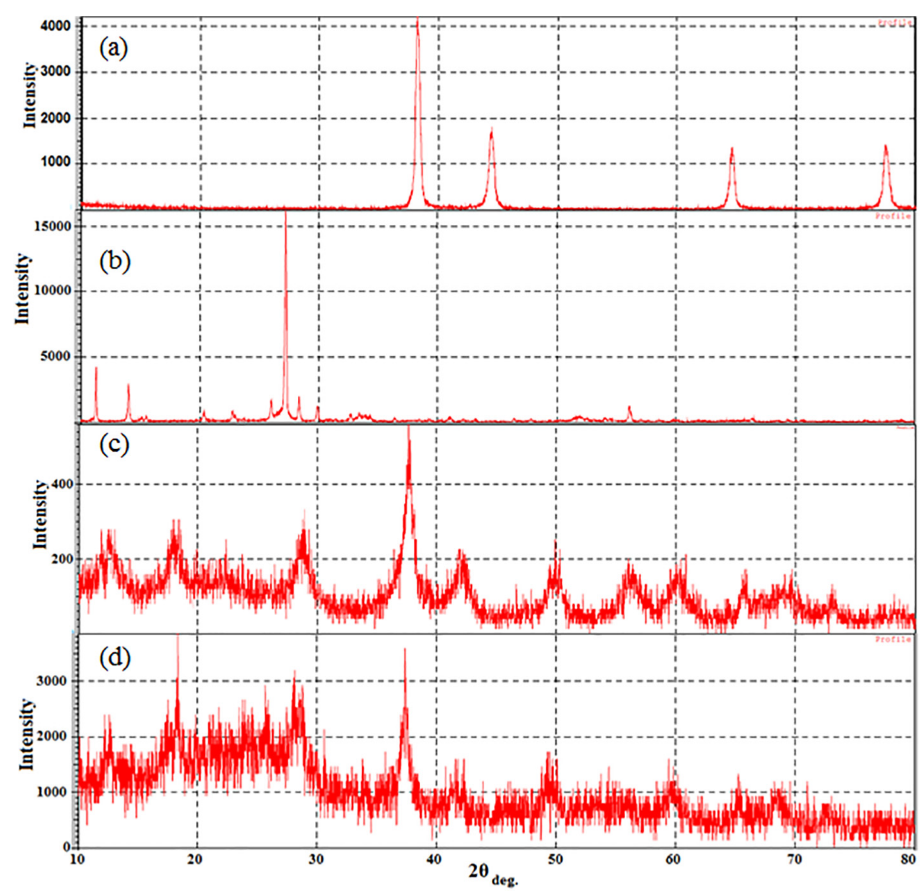

Fig. 3. XRD patterns of Ag NPs (a); Ag NPs-MMBI (b); MnO_2 NPs (c); MnO_2 NPs-MMBI (d).

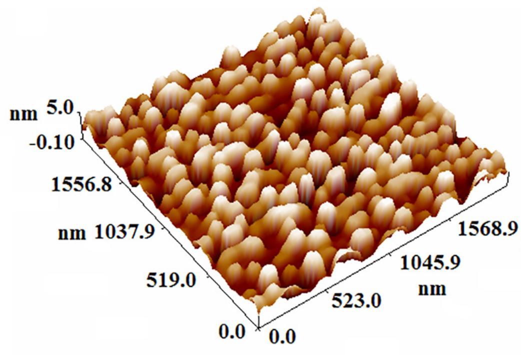

Fig. 4. 3D-AFM of Ag NPs.

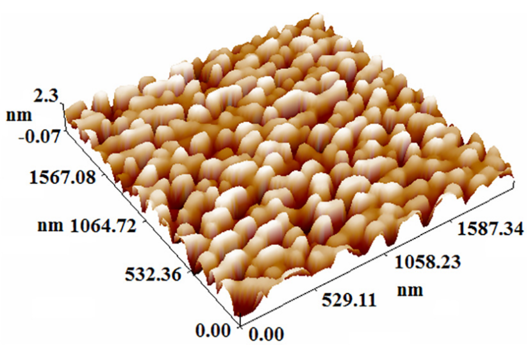

Fig. 5. The 3D-AFM of MnO_2 nanoparticles.

4. Conclusion

Organic-inorganic nanohybrids were successfully synthesized by simple method. These hybrids conclude MnO_2 NPs (2.5 nm) or Ag NPs (5 nm) as inorganic part and 5-methoxy-2-mercaptobenzi midazole as organic part. In addition to preparing new nanocomposites, but the most important thing is that this research expanded the chemistry of the 5-methoxy-2-mercaptobenzimida zole, which has not been extensively studied.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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