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Structural and Optical Characterization of Curcumin Decorated on Exfoliated MoS_2 Nanosheets by Chemical Method

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In this study, we developed a simple and effective chemical method for preparing curcumin nanoparticles decorated on exfoliated MoS_2 nanosheets using solution blending method. Its structural and optical properties were studied. The structural results show that a uniform and homogeneous distribution of curcumin nanoparticles on MoS_2 nanosheets. From the absorption studies reveals that curcumin loaded on exfoliated MoS_2 nanosheets exhibits significantly higher absorption than bare exfoliated MoS_2 nanosheets. The photoluminescence spectroscopy results show that these samples have enhanced fluorescence and lifetime of this material is found to be 12.3ns. Because of its biocompatibility and fluorescence properties, it is a very promising material for biological applications such as bio imaging, drug delivery and so on.

Keywords: Curcumin nanoparticles, MoS_2

1 Introduction

The application of nanotechnology to biomedical concerns, known as nanomedicine, has the potential to change the landscape of disease diagnosis and treatment[1]. Nanomaterials are now being considered as an important alternative therapeutic agent for controlling drug resistance because they have demonstrated high bactericidal efficiency against drug resistant strains without causing resistance[2]. Aside from metal nanoparticles, two-dimensional (2-D) nanomaterials have recently received a lot of attention as potential biomedical applications. Molybdenum disulphide (MoS_2), a 2D-material, has emerged as a promising nanomedicine candidate, with applications in drug delivery, phototherapy, bio sensing, water disinfection, and antibacterial wound healing[3].

The medicinal plants are a copious source of new bioactive compounds with potential applications in medicine and other areas of human health promotion. In addition to their therapeutic effects, phytopharmaceuticals are widely used in general medicine to treat diseases of the cardiovascular, nervous, and immune systems[4]. Curcumin is the most important phenolic pigment extracted from turmeric, the powdered rhizome of Curcuma longa[5]. It is extensively used as a spice, food preservative, flavoring agent, and coloring agent. Curcumin has been proven in considerable research over the last few decades to have powerful antioxidant, anti-inflammatory, anticancer, anti-HIV, and antibacterial activities[6]. Curcumin is a strong ingredient in both traditional and modern medicine. It is a yellow, water-insoluble pigment derived from the turmeric root. Turmeric contains curcuminoids, primarily curcumin (diferuloylmethane), demethoxycurcumin, and bis-demethoxycurcumin[7]. We picked curcumin because it is biocompatible and non-toxic[8]. Despite its multiple bioactive and therapeutic properties, curcumin's pharmaceutical usefulness is limited by its low in-vivo bioavailability and poor water solubility. To overcome curcumin's limitations, several ways have been proposed, the most noteworthy of which are its encapsulation on nanoparticles, liposomes, hydrogels, and other polymers[9] as well as solid dispersion technology[10,11]. Curcumin contains two phenolic rings as well as active methylene groups, which can be used to attach bio-macromolecules to it. Other nanocarriers encounter considerable difficulties in translocation. These difficulties include the difficulty in producing nanocarriers that encapsulate a sufficient number of therapeutic drugs with active release, the difficulty in delivering them to the target molecule, the toxicity of designed nanomaterials, and the cost of production[1]. Exfoliated MoS_2 has a strong potential in biomedical applications, including their biocompatibility, high surface area, sheet-like structure and ease of synthesis. These properties make the exfoliated MoS_2 nanosheets an attractive platform

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for different biological applications such as drug delivery, cancer therapy, bio sensing and bio imaging.

It has been demonstrated that both MoS_2 and curcumin are capable of exerting therapeutic effects in a variety of biomedical contexts. By coating MoS_2 nanosheets with curcumin, it is possible to provide synergists effects. These effects result from the combination of the therapeutic properties of both materials. The synergist combination of these Curcumin-loaded MoS_2 nanosheets was synthesized using a solution-blending approach and this method is simple, cost effective and ecofriendly. Their structural, morphological, and optical properties were studied in this paper. For these studies, TEM, XRD, FTIR, UV-Vis, and PL spectroscopy were used.

2 Materials and Methods

2.1 Materials

The chemicals used for this experiment were of analytical grade. Curcumin($C_{21}H_{20}O_6$) and acetone were purchased from sigma Aldrich.

2.2 Preparation of curcumin loaded MoS_2 nanocomposites

The exfoliated MoS_2 nanosheets were prepared according to the hydrothermal technique, which is previously published by our group[12]. 1.25mg of curcumin was dissolved in (1:10) water: acetone solvent mixture and stirred for 30 min. Under ultra-sonication condition, this dissolved curcumin was added dropwise to beaker containing 5.2mg exfoliated MoS_2 that was dispersed in 30ml acetone. Finally, the solution was poured into a Petri dish and allowed to evaporate the solvent overnight at room temperature. This dried powder was used for further studies.

2.3 Characterization

The surface morphology of the curcumin and curcumin loaded MoS_2 nanocomposites samples was examined using Transmission electron microscope (TEM) model JEM-HR 2100 with a 200 kV accelerating voltage and scanning electron microscope (JEOL JSM 6390LA). The elemental composition of the sample was analyzed by OXFORD EDAX (XMX N). The powder X-ray diffraction patterns of the samples were monitored using a Bruker X-ray diffractometer (Model D8 Advance, Bruker AXS with Cu Kα radiation (λ = 1.5406 Å) in the range 3 to 80°C. The fluorescence spectra of the samples were carried out by using Horiba QM 8075 11C. FT-IR spectra of the samples were collected on a Fourier transform infrared (FT-IR) instrument (Perkin Elmer L1600E) in the range of 400–4,000 cm^{-1} with a resolution of 4 cm^{-1}. The elemental composition of the curcumin sample was carried out by using CHNS analyzer (CHNS Analyzer: ELEMENTAR Vario EL III). Deionized water was used for the preparation of aqueous solutions.

3 Results and Discussion

3.1 Structural properties

Figure 1 shows the transmission electron micrograph images of exfoliated MoS_2 nanosheets, curcumin, and exfoliated nanosheets decorated with curcumin. Wrinkles appeared on large lateral sized MoS_2 nanosheets due to their low thickness, as shown in Fig. 1(a) & (b) depicts TEM images of curcumin nanoparticles clearly illustrating ultrafine spherical nanoparticles with diameters ranging from 4 to 12 nm, whereas in curcumin loaded MoS_2 nanosheets, curcumin nanoparticles are homogeneously distributed in the MoS_2 nanosheets and is depicted in Fig. 1(c). Fig. 2(a) shows SEM images of the prepared samples. SEM images are the supporting evidence of TEM and one can conclude that curcumin nanoparticles are decorated on exfoliated MoS_2 nanosheets.

Figure 2(b) depicts a typical energy dispersive x-ray spectrum (EDAX) of a curcumin-loaded MoS_2 nanosheets. Carbon, oxygen, molybdenum, and Sulphur have been detected in sample MSC. The S to Mo percentage atomic concentration is very close to the stoichiometric concentration (1:2). Other peaks in the EDAX spectra, such as carbon (C) and oxygen

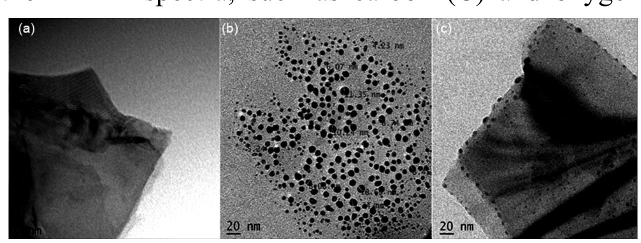

Fig. 1 — (a) TEM Image of exfoliated MoS_2 nanosheets, (b) TEM Image of curcumin nanoparticle, & (c) TEM image of MoS_2 - curcumin nanocomposite (MSC).

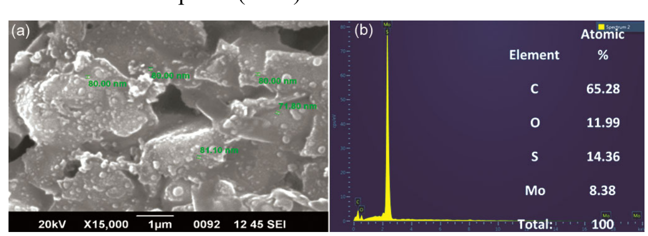

Fig. 2 — (a) SEM, & (b) EDX spectrum of curcumin loaded MoS_2 nanosheets (MSC).

(O), could be attributed to the presence of curcumin molecules. The CHNS analyzer can be utilized to determine the elemental composition of the curcumin sample. The structure contains 69.5% carbon, 5.5% hydrogen, and the remainder is oxygen. These percentages are in good match with the sample's intended chemical composition. The abovementioned finding is supported by the CHNS data.

XRD spectrum of exfoliated MoS_2 nanosheet, curcumin and MSC nanocomposite (curcumin decorated on exfoliated MoS_2 nanosheet) are shown in Fig. 3. The observed XRD peaks at 14.4°, 32.7°, 33.5°, 39.6°, 49.8°, 58.5° and 60.2° are indexed as (002), (100), (101), (103), (006), (105), (110) and (008) planes, which are well matched with 2H-MoS_2 (JCPDS-No-37-1492). In curcumin sample, the XRD peaks were observed at 12.28°,17.30°, 18.20°, 19.48°, 21.29°, 24.71°, 25.70°, 27.44° and 28.55° corresponding to (010), (202), (013), (211), (212), (020), (120), (122) and (220) planes. This pattern is well matched with the JCPDS Card No 00-066-1420. When compared to curcumin nanoparticles, the XRD peaks of MSC nanocomposite are slightly shifted to a higher angle side, which suggests that the curcumin is dispersed on MoS_2 nanosheets. The degree of crystallinity was determined using these XRD data, and this value dropped to 66.4% after the decoration of curcumin nanoparticles on MoS_2 nanosheet.

Figure 4 shows FTIR spectra of MoS_2, curcumin, and curcumin-loaded MoS_2 samples in the 400-4000 cm^{-1} wavenumber range. As shown in Fig. 4(a), the peak at 3503 cm^{-1} and 1630 cm^{-1} for O-H stretching vibration and aromatic moiety C=C stretching. The peak at 1597 cm^{-1}, 1508 cm^{-1} corresponds to benzene ring stretching vibrations (C=O and C=C) vibrations. The absorption peak at 1427 cm^{-1} and 1278 cm^{-1} are attributed to olefinic C-H bending and aromatic C–O stretching vibrations. The peak at 1026 cm^{-1} corresponds to (C–O–C) stretching vibrations. These values are matched with previously reported fingerprint vibrations of curcumin[13].

3.2 Optical properties

Figure 4(b) depicts the comparative UV-visible absorption spectrum of curcumin, MoS_2 nanosheets,

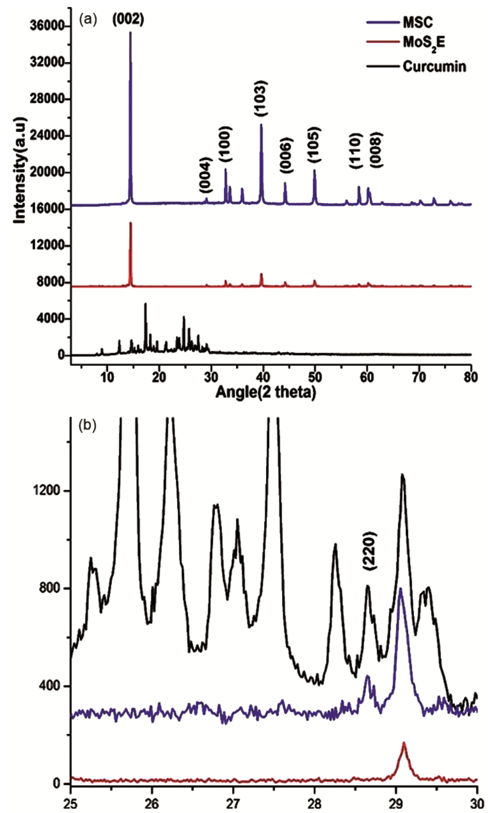

Fig. 3 — (a) XRD spectrum of exfoliated MoS_2 nanosheet, Curcumin and MSC nanocomposite, and (b) Magnified XRD spectrum of MoS_2 nanosheet, curcumin and MSC nanocomposite.

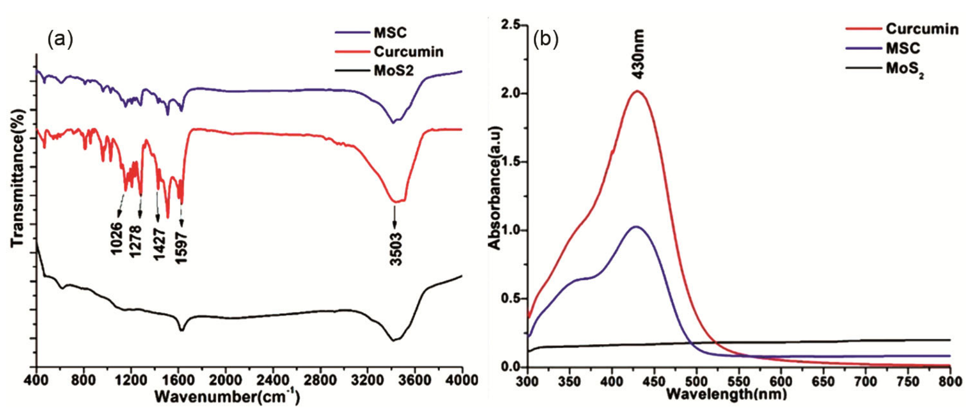

Fig. 4 — (a) FTIR spectra of curcumin, MoS_2 and MoS_2 – Curcumin (MSC) samples, & (b) UV-Vis absorption spectrum of curcumin, MoS_2 and MoS_2-Curcumin samples.

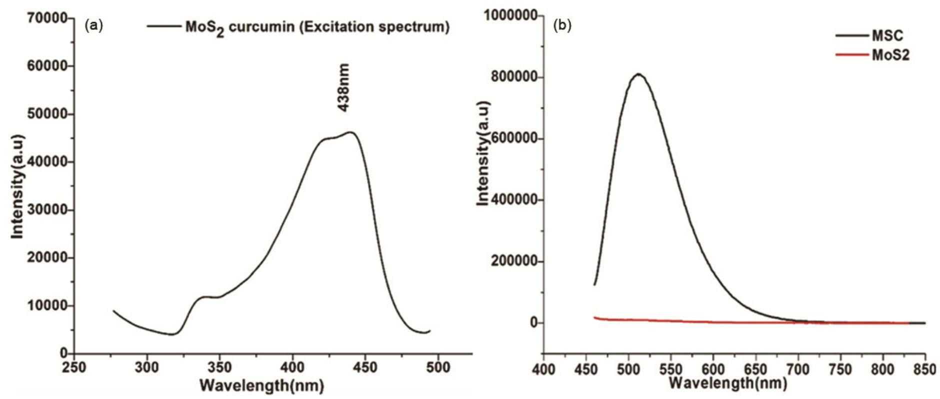

Fig. 5 — PL spectrum of (a) Excitation spectrum of curcumin loaded MoS_2, and (b) Emission spectrum of curcumin loaded MoS_2 and MoS_2.

and curcumin loaded on exfoliated nanosheets. Acetone, acetonitrile, methanol, ethanol, and 2-propanol were chosen as possible process solvents due to their low toxicity. Curcumin is primarily soluble in acetone[14]. In a water/acetone (5:1) mixture solution, curcumin exhibits a distinct UV-Vis absorption peak at around 300-500 nm. The maximum wavelength of this broad absorption peak is 430 nm, with a shoulder peak at 360 nm. The peak at 430nm is due to the electronic dipole allowed π-π* type excitation of its extended conjugation system. Because the polar solvent (water: acetone) electrostatically interacts with the curcumin molecule's polar chromophores, it tends to stabilize both the bonding electronic ground states and the π* excited states[15].

We found that the excitation spectrum of MSC had its predominant peak at a wavelength of 438 nm, so we decided to choose that value as the excitation wavelength. Figure 5(b) depicts the emission spectrum of MSC with an excitation wavelength of 438 nm. The emission peak in this figure is centered at 513nm, implying the formation of curcumin nanoparticles deposited on the surface of an exfoliated nanosheets. The aggregation of curcumin molecules or their adsorbed state can also cause significant changes in their fluorescent properties. This fluorescence enhancement is due to Aggregation-Induced Emission (AIE)[16].

The average lifetime (t_{avg}) of the synthesized curcumin-loaded MoS_2 nanosheets (MSC) sample is studied using a diode laser of wavelength of 330 nm with pulse duration of 1 ns and is given in equation 1

$$T_{avg} = \sum_{i=0}^{n} fi_i \, t_i$$

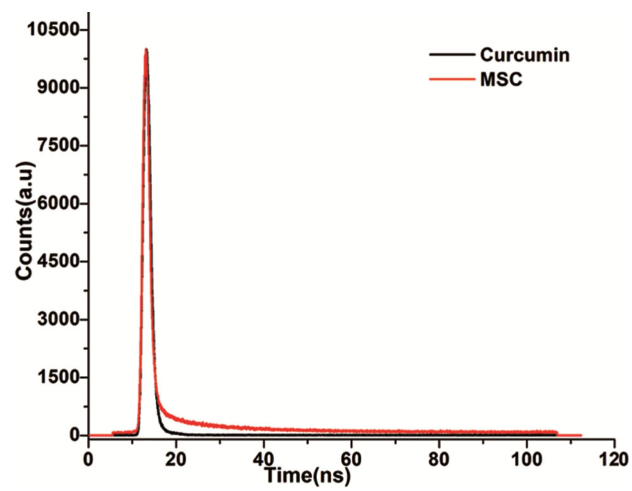

Fig. 6 — Time resolved fluorescence spectra of the MSC and curcumin.

$$\text{Where, } fi = \frac{\propto_i}{\sum_i \propto_i t_i} \quad (1)$$

where, the fitted parameter is α_i. t_i represents the fluorescence lifetime of excited state at i^{th} component and n is the number of emissive components[17].

Here, the lifetime values of Curcumin sample, t_1= 0.70 ns, t_2= 3.22ns; The fitted parameter values are B_1= 98.21, B_2= 1.79. The average fluorescence lifetime is estimated to be 0.9 ns. In MSC sample, t_1= 0.62 ns, t_2= 13.72ns; The fitted parameter values are B_1= 72.83, B_2= 27.17. The average fluorescence lifetime is estimated to be 12.3ns.

Figure 6 depicts the time resolved spectra of the MSC and curcumin. The spectrum was obtained by exciting the synthesized MSC sample at 330 nm with a 1 'ns' diode laser, and the emission wavelength is at 510 nm. Compared to curcumin nanoparticles, lifetime of the MSC sample is found to be 12.3ns. The fact that the MSC sample has a longer life time suggests that the curcumin molecule self-assembles into a nanostructure on an exfoliated nanosheets. The fluorescence emission from MSC is known as Aggregation Induced Enhanced Emission (AIEE), which is known to limit the rotation and vibration of molecules, thereby increasing the MSC's lifetime[18]. 2D TMDs have much lower toxicity than graphene oxide[19]. As a result of its low cytotoxicity, exfoliated MoS_2 is a very promising material for human exposure applications.

4 Conclusion

Curcumin loaded on exfoliated MoS_2 nanosheets was successfully synthesized using solution blending method. Its structural, morphological, and optical properties were carried out using XRD, SEM, TEM, FTIR, UV-Vis and PL. The surface morphology of the sample illustrates that a uniform distribution of spherical curcumin nanoparticles is deposited on exfoliated MoS_2 nanosheets. The average size of the curcumin nanoparticle is found to be 6nm. FTIR result reveals that the fingerprint vibrations of curcumin were present in curcumin loaded on MoS_2 sample. According to the absorption studies, curcumin loaded on exfoliated MoS_2 nanosheets exhibits significantly higher absorption than bare exfoliated MoS_2 nanosheets. PL results show that curcumin loaded on exfoliated MoS_2 nanosheets fluoresces significantly more than exfoliated MoS_2.This is due to the emission of curcumin nanoparticles caused by aggregation. Curcumin loaded on exfoliated MoS_2 nanosheets has a fluorescent lifetime of 12.3 ns. As a result, this enhanced fluorescence of this synergistic material ensures its potential applications such as bio imaging, drug delivery, etc.

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