FACILE SYNTHESIS OF MoS_2 NANOMATERIAL AS A PROMISING MICROWAVE ABSORBER

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Abstract

Lightweight, high-efficiency electromagnetic wave absorbers are being investigated as a desirable solution to electromagnetic emissions. MoS_2 nanostructure materials, which belong to the metal transition metal dichalcogenide materials group, have many advantages, including lower density, greater chemical stability, and special electronics transportation properties, and can be used as practical absorbers. In this study, one-step hydrothermal treatment was used to successfully prepare MoS_2 nanostructure materials. The obtained material was characterized by scanning electron microscopy, X-ray diffraction, and energy-dispersive X-ray spectroscopy. The microwave absorption properties of the MoS_2 materials were significantly influenced by their nanostructure. The best reflection loss was -55 dB at 9.6 GHz for a sample that was 2.7 mm thick and contained 25% wt%. The effective absorption bandwidth up to 7.1 GHz was successfully achieved with the thickness of only 1.5 mm. Considering the above advantages, MoS_2 can be used as a prospectively efficient microwave absorbent.

Keywords: *MoS_2; specific surface area; hydrothermal; microwave absorption.*

1. Introduction

The rise of electromagnetic waves (EMW) with the growth of electronic items and digital systems would create severe electromagnetic radiation on the environment and human health. Furthermore, the fast development of radar tracking systems poses a significant danger of conventional combat weapons. The development of stealth combat weapons can improve weapons's offensive and defensive capabilities [1]. As a result, finding a material with lightweight, high specific surface area, strong wideband, highly efficient EMW absorption capabilities has been received the focus interest [2]. Because of their unusual electrical characteristics, 2D transition metal dichalcogenides (TMDCs), particularly MoS_2, have garnered a lot of attention in recent years, making them interesting candidates for microwave absorbents [3].

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There are several methods for obtaining MoS_2 including mechanical cleavage [4], intercalation exfoliation [5], chemical vapor deposition [6], and hydrothermal technique [7]. The one-step hydrothermal technique is a straightforward and commonly used method for producing MoS_2 nanosheets among these strategies. Until now, the research on EM properties of MoS_2 is still in its infancy, and it still faces significant challenges for practical application. Li et al. [8] used a hydrothermal method to make MoS_2 nanosheets which had a reflection loss (RL) of -55.7 dB at 13.2 GHz and an effective absorption bandwidth (EAB) of 5.2 GHz. MoS_2, a typical flake-shaped nanoparticles prepared by Zhao et al. [9], had a reflection loss (RL) at 13.2 GHz of 43.9 dB and an EAB of 3.8 GHz. Zhao et al. [9] also designed another flower-shaped nanoparticles of MoS_2, had a reflection loss (RL) at 14 GHz of 29.9 dB and an EAB of 7.6 GHz.

However, comprehensive process optimization research is lacking. Only a few studies have looked at the effects of reaction temperature on the microwave absorption characteristics of MoS_2 so far, with little understanding into the process. Thus, in this study, we used a hydrothermal approach to synthesize MoS_2 nanosheets with various morphologies and evaluated their feasibility of microwave absorption. We found that the flower-like MoS_2 nanospheres had a broad effective absorption bandwidth and reduced thickness.

2. Experiment

2.1. Materials

All the chemicals used in this work are analytical grade. Sodium molybdate ($Na_2MoO_4.2H_2O$), Thioacetamide (CH_3CSNH_2) were obtained from Aladdin. Without additional purification, all compounds were utilized in their original state.

2.2. Preparation of MoS_2

The following was a typical procedure: Initially, under vigorous stirring 10 mmol Sodium molybdate and 35 mmol Thioacetamide were dissolved in 100 mL deionized water. The solution was continuously stirred for 1 h. Then, the solution was poured into a PTFE-lined autoclave with a capacity of 150 mL. The hydrothermal reaction was carried out at 160°C for 24 h. After cooling to room temperature, the precipitate was collected and washed repeatedly with distilled water and ethanol. Finally, in a vacuum oven at 50^oC for 12 h, the MoS_2 material was dried and named S1. Samples S2, S3 and S4 were heated at 180°C, 200°C and 220°C, respectively.

2.3. Characterization

The morphology and crystal structure of obtained MoS_2 were determined using scanning electron microscopy (SEM - S4800), X-ray diffraction (XRD, Bruker D5 with Cu Kα1 radiation $\lambda = 1.54056$ Å) and Energy-dispersive X-ray spectroscopy (EDX).

2.4. Electromagnetic measurements

The homogeneous mixture was made by mixing the MoS_2 material with paraffin wax in a typical experiment. The substance accounted for 25% of the total weight in the mixture. The finished mixtures were pressed into a toroidal shape with an inner diameter of 3.04 mm and an outside diameter of 7.0 mm. The microwave absorption properties were measured by utilizing Keysight PNA-X N5242A vector network analyzer. The microwave absorption properties were determined using the transmission line principle [10]. The RL was calculated using the following equations in detail:

$$RL\,(\mathrm{dB}) = 20.\log\left|\frac{Z_{in}-1}{Z_{in}+1}\right| \tag{1}$$

$$Z_{in} = \sqrt{\frac{\mu_r}{\varepsilon_r}}\tanh\left(j\frac{2\pi fd}{c}\sqrt{\mu_r\varepsilon_r}\right) \tag{2}$$

where Z_{in} is the input impedance of the absorber, ε_r and μ_r are the complex relative permitivity and permeability, respectively, c is the velocity of electromagnetic waves in vacuum, f is the frequency of electromagnetic wave, and d is the thickness of samples.

3. Results and discussion

3.1. Morphology and structure characterization of material

The morphologies of the MoS_2 materials were observed by SEM and shown in Fig. 1. All of nanospheres have the size at the range of 200 ÷ 300 nm. The structure of the sample S1 (160^{o}C) was shown in Fig. 1a to be a random stacking of 2D nanosheets. For S2 (Fig. 1b), the structure presented a more regular morphology of flower-like nanospheres. When the temperature was up 200^{o}C, the density of flower-like nanospheres increased markedly (Fig. 1c). Furthermore, the structure of flower-like nanospheres was largely damaged and the stack was partially disordered for S4 (Fig. 1d).

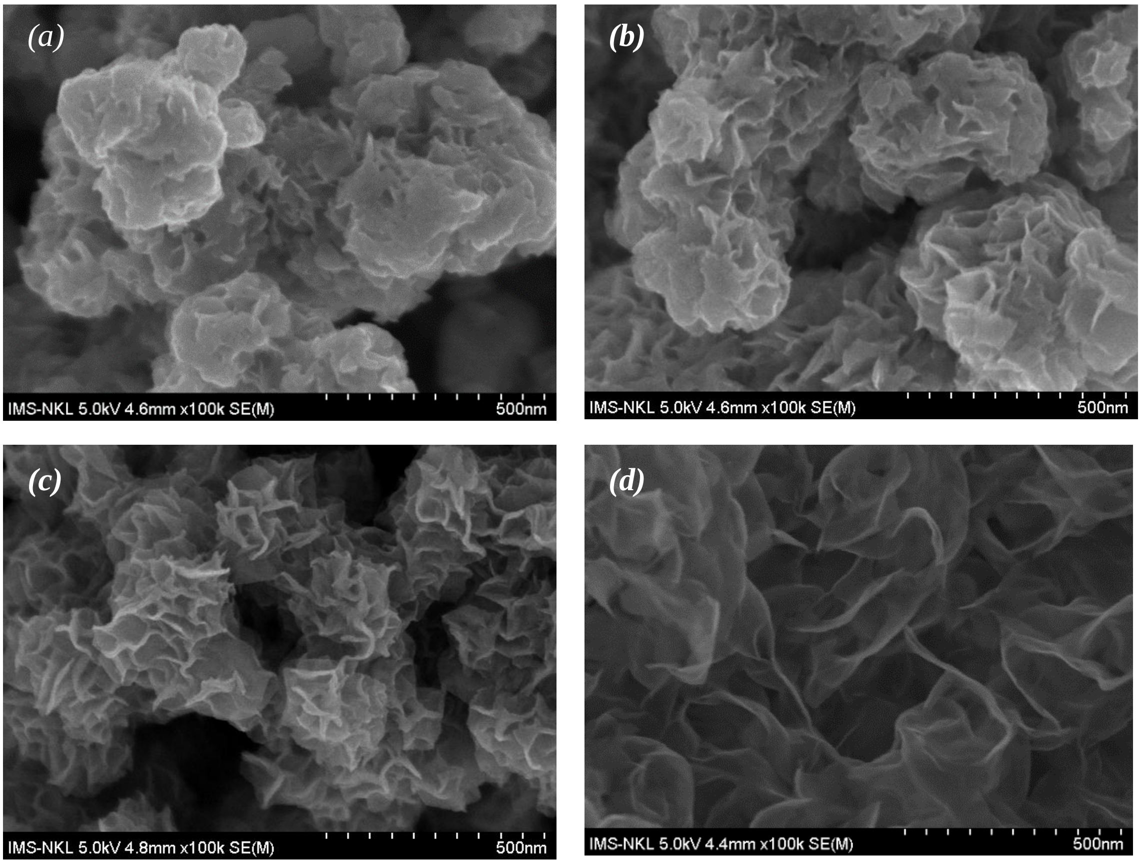

Fig. 1. SEM images of MoS_2: S1 (a), S2 (b), S3 (c) and S4 (d).

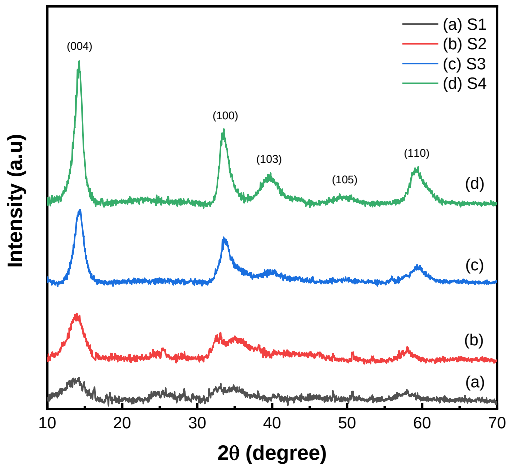

Fig. 2. XRD patterns of MoS_2: S1 (a), S2 (b), S3 (c) and S4 (d).

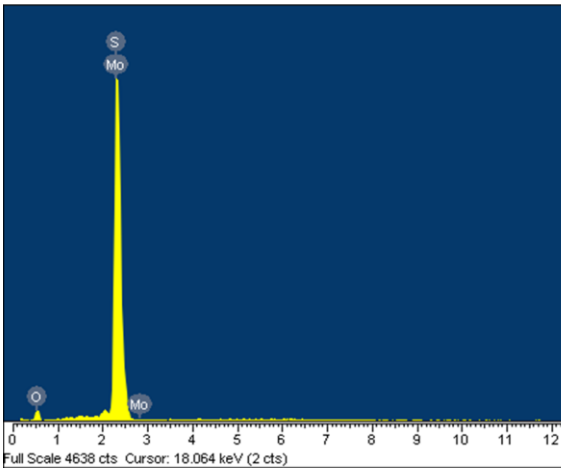

Fig. 3. EDX spectrum of S3 (MoS_2 - 200°C)

Figure 2 shows the XRD patterns of MoS_2 samples. This figure shows that the MoS_2 peaks were indexed to a pure phase of the compound. At 160°C, the diffraction peaks are less defined, but as the hydrothermal temperature rises, they get stronger, showing that the high temperature samples have better crystallinity. It was shown that the specific diffraction peaks correspond to (004), (100), (103), (105) and (110) of the S4 sample (JCPDS No. 73-1508) [11]. The MoS_2 flower-like nanospheres are discovered to match to the 2H phase of MoS_2.

Figure 3 shows the X-ray energy dispersive spectrum of S3. The results demonstrate that the material has particular signals for Mo, S, and O elements proving that the material has been successfully synthesized. Furthermore, the Mo:S ratio in the sample material does not reach the specified 1:2 value. This is because the surface of the material, which has particular surface roughnesses that might lead to measurement inaccuracies, is where the EDX measurement is carried out.

3.2. Microwave absorption properties of material

The frequency dependency curves of real and imaginary complex permitivity of samples are shown in Fig. 4 and Fig. 5. As can be shown in these figures, the real and imaginary parts of relative complex permitivity consistently show a decreasing trend with frequency. The sample S3 (MoS_2 - 200°C) has the highest value of ε’, indicating that it had the greatest ability to spread and store electromagnetic waves.

The high values of *ε’* of MoS_2 indicate that the flower-like structure implanted on nanospheres has significantly improved the dielectric properties of this material. It was also approved for the enhancement of dipolar and interfacial polarization, as well as low resistivity, which contributed to the effective electronic transmission proficiency in the material [12]. Additionally, the ε’’ value of S3 was the highest, implying the greatest capacity to attenuate electromagnetic waves, and hence the best microwave absorption capability.

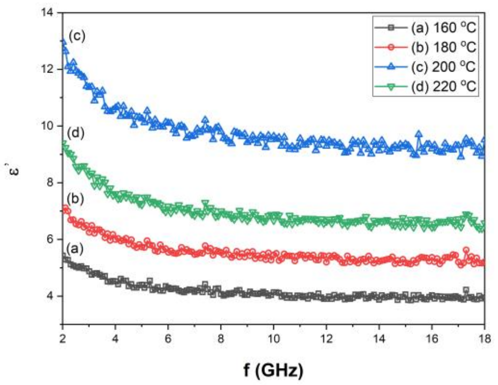

Fig. 4. The real part of complex permittivity of S1 (a), S2 (b), S3 (c) and S4 (d).

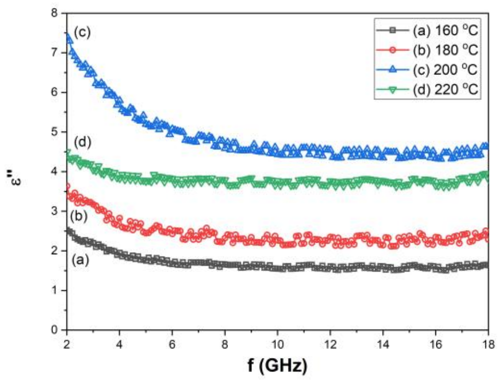

Fig. 5. The imaginary part of complex permittivity of S1 (a), S2 (b), S3 (c) and S4 (d).

Additionally, the attenuation constant contributed to the improved microwave absorption capabilities as expressed in the following equation [13]:

$$\alpha = \frac{\sqrt{2}\pi f}{c}\sqrt{(\mu''\varepsilon''-\mu'\varepsilon')+\sqrt{(\mu''\varepsilon''-\mu'\varepsilon')^2+(\mu'\varepsilon''+\mu''\varepsilon')^2}} \tag{3}$$

where μ', μ'' are the real, imaginary part of complex permeability.

It should be emphasized that the attenuation constant reflects the capacity to absorb integrally [14]. As may be seen in Fig. 6, the S3 has a higher attenuation constant. It corresponds to the comparatively large dielectric loss. As a result, the larger attenuation constant of MoS_2 is advantageous for the development of microwave absorption. Furthermore, the greater conductivity of MoS_2 promotes electronic polarization, which improves microwave absorption performance. As a result, the S3 has superior microwave absorption capabilities.

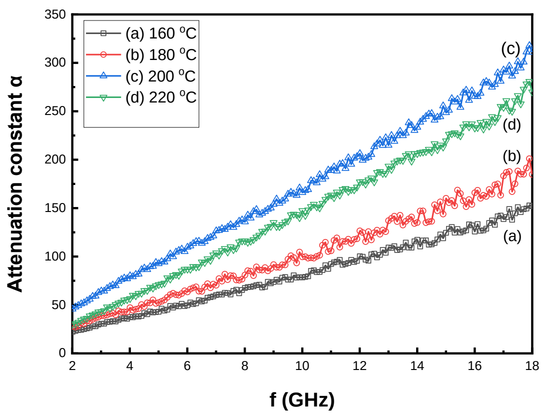

Fig. 6. Attenuation loss of S1 (a), S2 (b), S3 (c) and S4 (d).

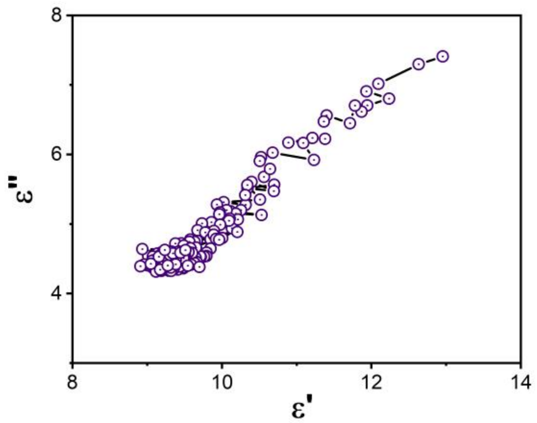

Fig. 7. The typical Cole-semicircle curve of S3.

On the basis of Debye relaxation theory [15], the dielectric properties of the material are further examined by the association between real part and imaginary part of complex permittivity. One relaxing mechanism can be carried out using the Cole-Cole equation as follows:

$$\left(\varepsilon' - \frac{\varepsilon_s + \varepsilon_\infty}{2}\right)^2 + \left(\varepsilon''\right)^2 = \left(\frac{\varepsilon_s - \varepsilon_\infty}{2}\right)^2 \tag{4}$$

where ε_s, ε_∞ are the static permittivity and the relative permittivity at the high-frequency limit.

The plot of *ε'* versus *ε''* would be displayed whole semicircle. Each semicircle corresponds to a Debye relaxation process. As shown in Fig. 7, multiple distinct semicircles can be noticeably observed, which indicates that the multi-dielectric relaxation process occurs in the composite material. Furthermore, the distorted Cole-Cole semicircles indicate the presence of dielectric loss-enhancing mechanisms such as defect polarization and interfacial polarization [16]. Under the external electromagnetic field, the heterogeneous interfaces in MoS_2 may produce further polarization centers, increasing interfacial polarization and improving relevant relaxation.

The microwave reflection loss of the samples at different thickness is presented in Fig. 8 ÷ Fig. 11. With rising thickness, the RL curve gradually changes to lower frequency. The phenomenon is explained by the matching relationship between frequency and the matching thickness t_m of the absorption materials [17]:

$$t_m = \frac{k.c}{4f\sqrt{|\varepsilon_r|.|\mu_r|}} \qquad k = 1, 3, 5... \tag{5}$$

The RL value of sample S1 (MoS_2 - 160°C) is shown in Fig 8. It is apparent that a minimum RL of -18.9 dB at 13.7 GHz with a thickness of 1.8 mm and the effective bandwidth of RL values less than -10 dB (90% of electromagnetic wave absorption) is 6.0 GHz. The sample S2 (MoS_2 - 180°C) has an effective broad EMW absorption bandwidth of 5.7 GHz at 1.5 mm thickness and a low RL of -18.7 dB at 8.6 GHz at 2.1 mm thickness. For sample S4 (MoS_2 - 220°C), it can be clearly seen that a minimum RL of -21.5 dB at 14.0 GHz and the effective bandwidth of RL values below -10 dB (90% of electromagnetic wave absorption) is 5.5 GHz with a thickness of 1.5 mm. It is obvious that, among the three samples, sample S3 has the highest microwave adsorption capacity. The best minimum reflection loss of MoS_2 flower-like nanospheres is -55.0 dB at the frequency 9.6 GHz with a small thickness of 2.7 mm. The best effective absorption bandwidth which is 7.1 GHz (10.2 ÷ 17.3 GHz) exhibited at the thickness of 1.5 mm. Furthermore, the effective absorption bandwidth in both the X and Ku bands (8.0 ÷ 18.0 GHz) can be achieved by changing the thickness of the MoS_2 material.

The microwave absorption properties of MoS_2 materials are compared in Table 1. According to these comparisons, MoS_2 flower-like nanospheres material has particularly strong microwave absorption properties, including high reflection loss, effectively broad absorption bandwidth, and a thin thickness.

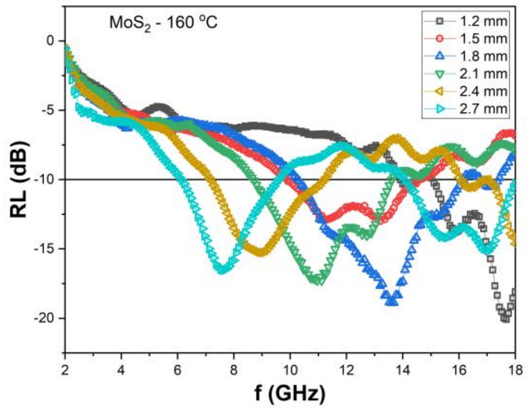

Fig. 8. Reflection loss of S1.

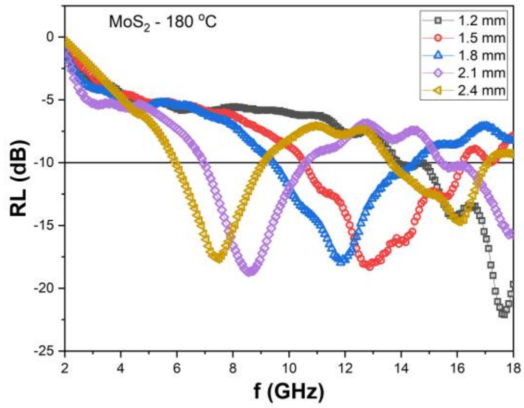

Fig. 9. Reflection loss of S2.

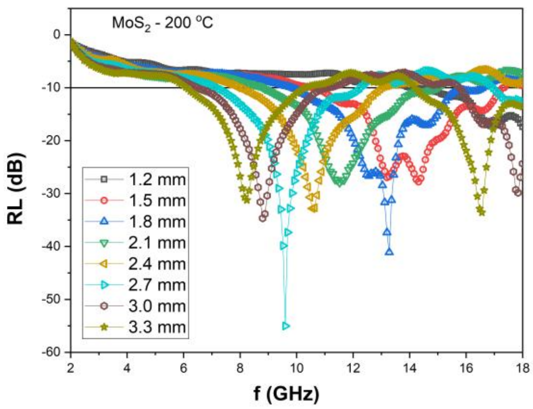

Fig. 10. Reflection loss of S3.

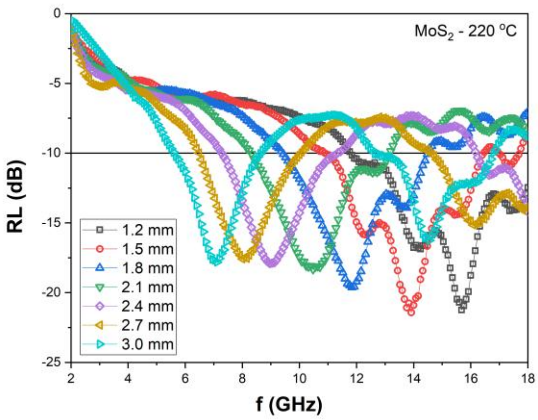

Fig. 11. Reflection loss of S4.

Table 1. Comparison of the microwave absorption properties with other absorbers.

Absorber	**RL_{min} (dB)**	**Bandwidth (GHz) (RL ≤ -10 dB)**	**Thickness (mm) Filled ratio (wt%)**	**Ref.**
MoS_2 nanosheets	-55.7	5.2	2.3 (40%)	[8]
MoS_2 flower-shaped nanoparticles	-29.9	7.6	3.0 (30%)	[9]
MoS_2 flake-shaped nanoparticles	-43.9	3.8	3.0 (30%)	[9]
MoS_2 flower-like nanospheres	**-55** **-**	**-** **7.1**	2.7 (25%) 1.5 (25%)	This work

The remarkable microwave absorption performance of the MoS_2 flower-like nanospheres material is correlated to its original structure and composition. Firstly, MoS_2 is a semiconductor material so that a great number of dipole polarization and defected centers are appearing [3]. Secondly, due to a high specific surface area of MoS_2 flower-like nanospheres, the abundant oxygen vacancies and significant lattice defects in the porous structure will behave as dipoles in the alternating electromagnetic field, causing a strong dipole polarization effect [17]. Finally, the electromagnetic wave dissipation is aided by the unique multi-channel pore in the petals of flowers and nanospheres of MoS_2 material [15].

4. Conclusion

In this study, the structure of MoS_2 flower-like nanospheres has exhibited a significant microwave absorption performance. The crystal structure of obtained material was belonged to 2H-MoS_2 phase. The size of nanospheres is in the range of 200 ÷ 300 nm. The optimal value of reflection loss of -55.0 dB was obtained at 9.6 GHz with the sample which had thickness of 2.7 mm. The maximum effective bandwidth reached 7.1 GHz (10.2 ÷ 17.3 GHz) when thickness was 1.5 mm. Therefore, the MoS_2 flower-like nanospheres prepared herein would have an excellent EMW absorption properties in X - Ku bands.

Acknowledgements

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TỔNG HỢP VẬT LIỆU NANO MoS_2 LÀM CHẤT HẤP THỤ VI SÓNG TIỀM NĂNG

Trần Quang Đạt, Nguyễn Văn Tuấn, Nguyễn Vũ Tùng, Phạm Văn Thìn

Tóm tắt: *Các vật liệu hấp thụ sóng điện từ nhẹ, hiệu năng cao đang được nghiên cứu như một giải pháp đầy hứa hẹn với sự phát xạ điện từ. Vật liệu cấu trúc nano MoS_2, thuộc nhóm vật liệu dichalcogenide kim loại chuyển tiếp kim loại, có nhiều ưu điểm, bao gồm mật độ thấp, độ ổn định hóa học cao, có các đặc tính đặc biệt về chuyển dời điện tử, và có thể được ứng dụng làm chất hấp thụ sóng vô tuyến. Trong nghiên cứu này, một quy trình thủy nhiệt đã được tiến hành để tổng hợp thành công vật liệu cấu trúc nano MoS_2. Vật liệu được nghiên cứu các tính chất đặc trưng bởi kính hiển vi điện tử quét, phổ nhiễu xạ tia X và phổ tán xạ năng lượng tia X. Các đặc tính hấp thụ vi sóng của vật liệu MoS_2 bị ảnh hưởng đáng kể bởi cấu trúc nano của chúng. Tổn hao phản xạ tốt nhất là -55 dB ở 9,6 GHz đối với mẫu dày 2,7 mm và chứa 25% trọng lượng. Băng thông hấp thụ hiệu quả lên đến 7,1 GHz với độ dày chỉ 1,5 mm. Với những ưu điểm trên, MoS_2 có thể được ứng dụng như một vật liệu tiềm năng để hấp thụ vi sóng.*

Từ khóa: MoS_2; diện tích bề mặt riêng; thủy nhiệt; hấp thụ vi sóng.

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