High absorption efficiency of WS$_2$/CNTs hybrids with conductive network for high performance EMI shielding

H H Wang$^{1,2}$, D Q Zhang$^{1,2}$, H B Zhang$^1$, T T Liu$^1$, J Y Xu$^1$ and M S Cao$^{2,*}$

$^1$ School of Materials Science and Engineering, Qiqihar University, Qiqihar 161006, China
$^2$ School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China

*Corresponding author.

E-mail addresses: caomaosheng@bit.edu.cn (M.S. Cao)

‡ These authors contribute equally to this work.

Abstract. In order to reduce the environmental pollution caused by the secondary reflection of electromagnetic interference (EMI) shielding materials, the WS$_2$/CNTs hybrids with high absorption efficiency were successfully prepared by using a one-step hydrothermal method. The WS$_2$/CNTs heterostructure, which combines the unique excellent dielectric properties of WS$_2$ with the high conductivity of CNTs, promotes the effective absorption and reflection of EMW. The excellent EMI shielding performance of 5WS$_2$/CNTs-25 can reach up to 27.8 dB, which was analyzed by the dielectric properties of the WS$_2$/CNTs hybrids. The conductive network composed of CNTs makes the multiple reflection and absorption of EMW, which makes the WS$_2$/CNTs hybrids promising candidates for the field of EMI shielding.

1. Introduction

Proliferation of large data has led to the electromagnetic (EM) pollution when entering the information age, which may be harmful for humane health promoting the development of electromagnetic interference (EMI) shielding materials$^{[1-2]}$. In addition, EM radiation can interfere with the normal operation of the equipment on which people depend, further severe cases can lead to the paralysis of the city$^{[3]}$. Therefore, scholars at home and abroad are committed to finding high-performance EMI shielding materials.

So far, carbon based materials such as carbon cloth, carbon nanotubes (CNTs), carbon fiber and graphene were usually used for substrates or filler of EMI shielding materials due to their high conductivity and characteristics of easy processing$^{[4-6]}$. Zhan et al.$^{[7]}$ has prepared the natural rubber/CNTs composite foam (F-NR/CNTs) with high electrical conductivity and excellent EMI properties by introducing CNTs to F-NR. The F-NR/CNTs has a three-dimensional separated CNTs network resulting in a more significant absorption efficiency. As we all know, the conductivity is an important factor to determine the EMI shielding performance, which is beneficial to improve the reflection efficiency$^{[8]}$. A large number of electromagnetic waves (EMW) reflected back to free space will cause secondary pollution. Therefore, it is an inevitable trend to prepare the EMI shielding materials with high absorption efficiency.
Two-dimensional transition metal disulfides (TMDs) with low density are widely used as EMW absorbing materials due to their large specific surface area and small size effect\[^9\]. As a representative of TMDs, WS\(_2\) can achieve adjustable electronic properties by manufacturing a large number of defects and dislocations on the surface of WS\(_2\), which shows excellent dielectric properties\[^10\]. However, the low conductivity of WS\(_2\) with less secondary reflection limits its application in the field of EMI shielding. Therefore, introducing the second component material into WS\(_2\) is an important way to improve its EMI shielding performance. Zhang et al.\[^11\] prepared a unique WS\(_2\)-rGO architecture of mountain-like wall achieving efficient and green EMI shielding. The synergy of relaxation and conduction, multi-scattering and the equivalent wedge effect play a decisive role in EMI shielding.

In this work, a novel WS\(_2\)-NS/CNTs hybrids were prepared via a one-step hydrothermal method and the EMI shielding performance was investigated. The best EMI shielding performance was explored by adjusting the reaction time and the doping amount of CNTs, further explaining the EMI shielding mechanism by analyzing the dielectric properties. This work provides an effective approach to construct the green high-performance EMi shielding materials.

2. Experimental section

2.1. Materials

Tungsten chloride (WCl\(_6\)) was purchased from Shanghai Aladdin Biochemical Technology Co. Ltd.. Thioacetamide (CH\(_3\)CSNH\(_2\)) was purchased from Tianjin Guangfu Fine Co. Ltd.. CNTs were purchased from Nanjing Xianfeng Nano Material Technology Co. Ltd. Nitric acid (HNO\(_3\)) and sulfuric acid (H\(_2\)SO\(_4\)) were purchased from Tianjin Kemiou Chemical Reagent Co. Ltd. All chemicals were of analytical grade and used without further purification.

2.2. Synthesis of WS\(_2\) Nanosheets

1.0 g WCl\(_6\) and 2.0 g CH\(_3\)CSNH\(_2\) were dissolved in 60 mL of deionized water by vigorously stirring for 1 h. Then the mixed solution was transferred to a hydrothermal reactor (75 mL) and heated to 210 °C for 24 h. At the end of the reaction, the mixture was cooled to room temperature. The black precipitate was obtained by centrifugation and washed with deionized water and ethanol for several times. Finally, the product was dried in a vacuum at 60 °C for 24 h, which were noted as WS\(_2\).

2.3. Synthesis of WS\(_2\)/CNTs hybrids

Firstly, the CNTs were pretreated by acidification. The mixed acid of sulfuric acid (H\(_2\)SO\(_4\)) and nitric acid (HNO\(_3\)) was added to a certain amount of CNTs (V\(_{\text{H}_{2}\text{SO}_{4}}\):V\(_{\text{HNO}_{3}}\) = 3:1). The mixture was transferred to a hydrothermal reactor for 2 h at 80 °C. After the reaction, the reactor was cooled to room temperature. After being cooled to room temperature, the acidified CNTs were washed with deionized water until the pH was neutral. The proportion of CNTs in deionized water was 0.94%. 11.684 g acidified CNTs dispersion (ultrasonication for 30 min) and WS\(_2\) nanosheets prepared in the above steps were added into the hydrothermal reactor and heated at 210 °C for 24 h (WS\(_2\) to CNTs molar ratios is 0.5:1). After the reaction, the reactor was naturally cooled to room temperature, the product obtained by centrifugation was washed several times with deionized water and ethanol and dried in vacuum at 60 °C for 24 h, which was recorded as 5WS\(_2\)/CNTs-24. Under the condition of constant reaction time 24 h, when the amount of acidified CNTs are 5.842 and 1.169 g, the molar ratios of WS\(_2\) to CNTs are 1:1 and 5:1, which were recorded as 10WS\(_2\)/CNTs-24 and 50WS\(_2\)/CNTs-24. Under the condition of no change of other reaction conditions, the samples with reaction time of 25 h were recorded as 5WS\(_2\)/CNTs-25, 10WS\(_2\)/CNTs-25 and 50WS\(_2\)/CNTs-25.

2.4. Characterization

The X-ray diffraction (XRD) patterns were recorded using German Bruker-AXS D8 X-ray diffractometer with Cu K\(\alpha\) radiation (\(\lambda=0.1546\) nm). XPS analysis was carried out on X-ray photoelectron spectrometer (ESCALAB250Xi, Thermofisher Co). The morphology and crystal
structure of the as-synthesized products were characterized by scanning electron microscope (SEM, S-4300; Hitachi) with an accelerating voltage of 20 kV and transmission electron microscopy (TEM, Hitachi, H-7650). The microscopic features of the sample were observed using a high-resolution transmission electron microscope (Tecnai G2F30, FEI, USA). The electromagnetic properties of the samples were determined by the coaxial method with a vector network analyzer (VNA, MS-200644A Anritsu) in the frequency range of 2-18 GHz. The samples containing 60 wt. % paraffin wax were prepared.

3. Results and Discussion
The schematic illustration of the synthesis process of WS2/CNTs hybrids is shown in Figure 1. WCl6 and CH3CSNH2 provide W and S source for WS2, respectively. The W4+ and S2- are combined by the covalent bond to form the base material for EMI shielding materials[12]. As the basic framework of the shielding system, the acidification pretreatment of CNTs makes the surface of CNTs carry a large number of oxygen-containing functional groups and defects, which is conducive to the combination of WS2 and CNTs, and also provides relaxation loss for the WS2/CNTs hybrids. The WS2/CNTs hybrids take advantage of the good dielectric properties of WS2 nanosheets and the high conductivity of CNTs to construct a EMI shielding system with good performance.

![Figure 1. Schematic illustration of the synthesis process of WS2/CNTs hybrids](image)

The XRD of WS2, CNTs and 5WS2/CNTs-25 are presented to investigate the structure of the samples, as shown in Figure 2. The XRD pattern of the 5WS2/CNTs-25 is basically the same as that of the original WS2, which has three peaks at 14.3°, 32.0°, 56.9°, corresponding to the (002), (101) and (110) planes of WS2 (JCPDS No. 08-0237)[13]. Due to the low concentration of CNTs dispersion, the amount of CNTs introduced into the system is too small, and the (002) characteristic peak of CNTs located at 26.1° is not displayed in the 5WS2/CNTs-25 phase[14]. It will be demonstrated in the subsequent high-resolution transmission electron microscopy (HRTEM) characterization, which proves the successful combination of WS2 and CNTs. Besides, the peak appearing in 43.2° can justify the (100) plane of CNTs (PDF#41-1487).

![Figure 2. XRD pattern of WS2, CNTs, and 5WS2/CNTs-25](image)

To further demonstrate the structure of WS2/CNTs heterostructure, each elements (W, S, C, O) of the 5WS2/CNTs-25 are analyzed by using XPS in Figure 3(a). In Figure 3(b), the C 1s spectrum in the acidified CNTs consist of C=C and C=O, which are located at 284.2 and 285.2 eV respectively, indicating that acidified CNTs provide a large number of oxygen-containing functional groups for EMI shielding system, which is conducive to EM attenuation[15]. In Figure 3(c), except the W 4f7/2 and W 4f5/2 located at 32.4 and 34.5 eV, which corresponding to the WS2, the WS3 and WO3 located at 35.9 and 38.3 eV.
eV show the other electronic valence states of the element W. In Figure 3(d), the S 2p spectrum exhibits $S_{2p_{3/2}}$ and $S_{2p_{1/2}}$, which located at 161.9 and 163.1 eV. The above results fully demonstrate the successful combination of WS$_2$ and CNTs.

The microstructure and lattice phase of WS$_2$ and 5WS$_2$/CNTs-25 were demonstrated by TEM and HRTEM in Figure 4. As shown in Figure 4(a), the ultra-thin WS$_2$ with large specific surface area prepared by one-step hydrothermal method is wrinkled, which has uniform distribution and stable
morphology. With the intervention of CNTs, WS$_2$ nanosheets are tightly coated on the surface of CNTs, which further disperse CNTs and construct the 3D carbon conducting network in Figure 4(b). In order to prove the formation of effective heterostructure between WS$_2$ and CNTs, the lattice phase of the 5WS$_2$/CNTs-25 was characterized by HRTEM in Figure 4(c). It can be clearly seen that there is an obvious interface between WS$_2$ nanosheets and CNTs. The interlayer spacing of 0.275 and 0.342 nm correspond to the (100) crystal plane of WS$_2$ and the (002) crystal plane of CNTs, respectively. It is proved that WS$_2$ and CNTs coexist in the system and form the heterostructure which is beneficial to the EMI shielding.

In general, the EMI shielding performance is investigated by EM parameters which are represented by $S_{11}$ and $S_{21}$ measured by vector network analyzer. The coefficients of absorption (A), reflection (R), and transmission (T) calculated by $S_{11}$ and $S_{21}$ are the important factors to determine the EMI shielding performance, they can be expressed by the following formulas\cite{16}:

$$R = |S_{11}|^2$$  \hspace{1cm} (1)
$$T = |S_{21}|^2$$  \hspace{1cm} (2)
$$A = 1 - R - T$$  \hspace{1cm} (3)

Based on A, R and T, we calculate the SE of all samples, including the SE of absorption (SE$_A$), reflection (SE$_R$) and total SE (SE$_T$), which are obtained according to the following formulas\cite{17}:

![Figure 4. (a) TEM images of WS$_2$; (b) TEM and (c) HRTEM images of 5WS$_2$/CNTs-25](image-url)
\[ SE_R = 10\log\left(\frac{1}{1-R}\right) = 10\log\left(\frac{1}{1-|S_{11}|^2}\right) \] (4)

\[ SE_A = 10\log\left(\frac{1-R}{T}\right) = 10\log\left(\frac{1-|S_{11}|^2}{|S_{21}|}\right) \] (5)

\[ SE_T = SE_R + SE_A = 10\log\left(\frac{1}{|S_{21}|}\right) \] (6)

The EMI shielding performances of all samples in the frequency range of 2-18 GHz are shown in Figure 5. At the same reaction time 24h, which is the same time as the original WS$_2$, the maximum $SE_T$ ($SE_{T\text{max}}$) of 5WS$_2$/CNTs-24, 10WS$_2$/CNTs-24, 50WS$_2$/CNTs-24 increasing from 16.0 dB to 20.7 dB with the increase of the CNTs content in the system. As far as maximum $SE_A$ ($SE_{A\text{max}}$) is concerned, it has the same upward trend as $SE_T$ (11.6 to 17.8). This fully demonstrates that the $SE_T$ and $SE_A$ can be effectively adjusted by controlling the doping amount of the CNTs, further improving the EMI shielding performance of WS$_2$/CNTs hybrids. In order to form more effective heterostructures between WS$_2$ and CNTs, the reaction time was increased to 25 h. Interestingly, with the increase of CNTs doping amount, the $SE_T$ and $SE_A$ have the same upward trend, which confirm the above view. As shown in Figure 5(d), the excellent EMI shielding performance of 5WS$_2$/CNTs-25 can reach up to 27.8 dB. In addition, the increase of reaction time can also have a positive effect on the EMI shielding performance, which shows that the appropriate increase of reaction time and CNTS doping amount can greatly improve the EMI shielding performance. The excellent EMI shielding performance is attributed to the high conductivity of CNTs, which leads to a part of EMW reflect back to the free space through reflection due to the impedance mismatch\cite{18}. The dielectric loss of WS$_2$/CNTs heterostructure is beneficial to the effective absorption of EMW entering the EMI shielding material. Finally, only a small part of EMW can pass through the EMI shielding material, which has achieved effective EMI shielding of EMW. However, for WS$_2$/CNTs hybrids, $SE_A$ is the main way to achieve high EMI shielding performance.
The dielectric properties of the all samples in the frequency range of 2.0-18.0 GHz have been further investigated for effective absorption of EMW within the EMI shielding material. The complex permittivity (εᵣ) is usually used to indicate the EM properties of EMI shielding material. The real part (ɛ') of the complex permittivity expresses the storage capacity of electric energy, and the imaginary part (ɛ'') of the complex permittivity represents the loss capacity of electric energy[19]. Moreover, the dielectric loss tangent tanδₑ (tanδₑ=ɛ''/ɛ') shows the degree of dielectric loss[20]. In generally, the εᵣ is calculated by the Debye theory[21]:

\[ \varepsilon_\infty = \varepsilon_\infty - \frac{\varepsilon_s - \varepsilon_\infty}{1 + j2\pi f \tau} \]  (7)

\[ \varepsilon' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2 \tau^2} \]  (8)

\[ \varepsilon'' = -\frac{\varepsilon_\infty - \varepsilon_s}{1 + \omega^2 \tau^2} \frac{\omega \tau + \sigma}{\omega \varepsilon_0} \]  (9)

where, εᵣ is the relative dielectric constant at infinite frequency, εₛ is the static permittivity, ω is the angular frequency, τ is the polarization relaxation time, σ is the electrical conductivity, and ε₀ is the vacuum dielectric constant.

It is clear that ε' and ε'' is increasing with the increase of CNTs content, indicating that CNTs contribute to dielectric loss. When the reaction time and CNTs content increase simultaneously, ε' of 5WS₂/CNTs-25 reaches the maximum value, which represents a strong storage capacity of the electric energy. The ε'' is determined by relaxation loss and conductivity[22]. The high ε'' is attributed to the higher conductivity of CNTs and the dipole polarization and interface polarization at the WS₂/CNTs heterostructure. However, the tanδₑ value of 5WS₂/CNTs-25 with strong dielectric loss ability is lower. The higher tanδₑ values are not better for SEA, too high tanδₑ value will cause most of the EMW to be reflected back to the free space. Through the analysis of the EMI shielding performance, we can see that the SEA is the main factor to improve the EMI shielding performance, rather than the SER. The suitable conductivity and strong dielectric loss of the 5WS₂/CNTs-25 can ensure the effective absorption of the EMW and make the redundant EMW reflect back to the free space concurrently, preventing the EMW from passing through the EMI shielding material and optimizing the EMI shielding performance of the WS₂/CNTs hybrids.

The EMI shielding mechanism of WS₂/CNTs hybrids is shown in Figure 7. Firstly, dipole polarization occurs at the acidified CNTs with a large number of functional groups and defects, and interfacial polarization located at the WS₂/CNTs heterostructure, resulting in the enhancement of dielectric loss of the WS₂/CNTs hybrids. Secondly, the conductive network formed by a large number of CNTs is conducive to the multiple reflection and scattering of EMW, which promotes the absorption of EMW. It is worth noting that the ultra-high conductivity of CNTs makes all the unabsorbed EMW...
reflected back into free space. The synergistic effect of various factors promotes the EMI shielding performance.

4. Conclusions
In conclusion, the WS₂/CNTs hybrids were successfully prepared via a simple hydrothermal method. The EMI shielding performance can be optimized by adjusting the CNTs doping amount and reaction time. The excellent EMI shielding performance of 5WS₂/CNTs-25 can reach up to 27.8 dB at 18.0 GHz, which is attributed to the regulation of high conductivity of CNTs on SEₐ and SEᵣ. The effective WS₂/CNTs heterostructure is used to increase the dielectric loss, and the conductive network of CNTs is used to increase the multiple reflections, which is beneficial to improve the SEₐ. The unique conductive loss ability of CNTs promotes the improvement of SEᵣ. The excellent EMI shielding materials were constructed by introducing conductive materials into dielectric materials.

Acknowledgments
This work was supported by the National Natural Science Foundation of China (51772160 and 51977009).

References
[1] Yun T, Kim H, Iqbal A, Cho Y S, Lee G S, Kim M-K, Kim S J, Kim D, Gogotsi Y, Kim S O and Koo C M 2020 Adv. Mater 32 2070064
[2] Yun T, Kim H, Iqbal A, Cho Y S, Lee G S, Kim M-K, Kim S J, Kim D, Gogotsi Y, Kim S O and Koo C M 2020 Adv. Mater. 32 1906769
[3] Iqbal A, Sambyal P and Koo C M 2020 Adv. Funct. Mater. 30 2070307
[4] Wang C, Murugadoss V, Kong J, He Z, Mai X, Shao Q, Chen Y, Guo L, Liu C, Angaiah S and Guo Z 2018 Carbon 140 696-733
[5] Gupta S and Tai N-H 2019 Carbon 152 159-87
[6] Hong X and Chung D D L 2017 Carbon 111 529-37
[7] Zhan Y, Oliviero M, Wang J, Sorrentino A, Buonocore G G, Sorrentino L, Lavorgna M, Xia H and Iannace S 2019 Nanoscale 11 1011-20
[8] Liu S, Qin S, Jiang Y, Song P and Wang H 2021 Compos. Part A. Appl. S 145 106376
[9] Liu L, Zhang S, Yan F, Li C, Zhu C, Zhang X and Chen Y 2018 ACS. Appl. Mater. Inter 10 14108-15
[10] Zhang D, Wang H, Cheng J, Han C, Yang X, Xu J, Shan G, Zheng G and Cao M 2020 Appl. Surf. Sci 528 147052
[11] Zhang D, Liu T, Shu J, Liang S, Wang X, Cheng J, Wang H and Cao M 2019 ACS. Appl. Mater. Inter 11 26807-16
[12] Xu W, Kozawa D, Zhou Y, Wang Y, Sheng Y, Jiang T, Strano M and Warner J 2020 Small 16 1905985
[13] Zhang D, Liu T, Cheng J, Cao Q, Zheng G, Liang S, Wang H, Cao M 2019 Nano-Micro. Lett 11 38
[14] Dong S, Zhang W, Zhang X, Hu P and Han J 2018 Chem. Eng. J 354 767-76
[15] Song C, Yin X, Han M, Li X, Hou Z, Zhang L and Cheng L 2017 Carbon 116 50-8
[16] Qu M, Yang X, Peng L, Liu L, Yang C, Zhao Z, Liu X, Zhang T and He J 2021 Carbon 174 110-22
[17] Liang L, Han G, Li Y, Zhao B, Zhou B, Feng Y, Ma J, Wang Y, Zhang R and Liu C 2019 ACS. Appl. Mater. Inter 11 25399-409
[18] Jiang D, Murugadoss V, Wang Y, Lin J, Ding T, Wang Z, Shao Q, Wang C, Liu H, Lu N, Wei R, Subramania A and Guo Z 2019 Polym. Rev 59 280-337
[19] Dai X, Du Y, Yang J, Wang D, Gu J, Li Y, Wang S, Xu B and Kong J 2019 Compos. Sci. Technol 174 27-32
[20] Xu J, Xia L, Luo J, Lu S, Huang X, Zhong B, Zhang T, Wen G, Wu X, Xiong L and Wang G 2020 ACS. Appl. Mater. Inter 12 20775-84
[21] Qu B, Zhu C, Li C, Zhang X and Chen Y 2016 ACS. Appl. Mater. Inter 8 3730-5
[22] Lu Y, Zhang S, He M, Wei L, Chen Y and Liu R 2021 Carbon 178 413-35