Rare Metal Materials and Engineering
Volume 49, Issue 7, July 2020
Available online at www.rmme.ac.cn

Science Press

Cite this article as: Rare Metal Materials and Engineering, 2020, 49(7): 2250-2255.

ARTICLE

Preparation of MWCNTs/TiO_2 Dioxide Composite Powder and Study on Spatial Absorption Model

Song Xinhua[1], Zhao Tiejun [1,2], Liu Zhenfeng[1], Li Xiaojie[1], Yan Honghao[1]

[1]State Key Laboratory of Structural Analysis for Industrial Equipment, Dalian University of Technology, Dalian 116024, China; [2] Henan University, Kaifeng 475004, China

Abstract: Multi-walled carbon nanotubes (MWCNTs) and TiO_2 were mixed by ball milling to obtain composite powders. The composite powders were characterized by XRD, SEM and network vector analyzer. The absorbing properties of composite powders in space were analyzed by theoretical calculation using numerical models. The results show that the dispersibility of MWCNTs in the MWCNTs/TiO_2 composite powders with anhydrous ethanol wet mixing is better. Wet-mixed MWCNTs/TiO_2 composite powders have better impedance matching characteristics and spatial absorbing ability in 2~18 GHz band, which provides a theoretical reference for the practical application of composite absorbing materials.

Key words: MWCNTs/TiO_2; space absorbing; ball milling; attenuation value

Multi-walled carbon nanotubes (MWCNTs) have excellent electrical properties and large specific surface area. Mixing MWCNTs with TiO_2 can improve the photocatalytic activity of titanium dioxide. Ye et al[1] prepared the titanium dioxide coated multiwalled carbon nanotubes (MWCNTs) composite photocatalysts by the controllable oxidation of titanium carbide coated MWCNTs obtained by the molten salt method using MWCNTs as a reaction template and metal titanium powder as a titanium source. Xu et al[2] prepared a carbon nanotubes (CNT)/TiO_2 nanocomposite photocatalyst by a simple impregnation method, which is used, for the first time, for gas-phase degradation of benzene. It is found that the as-prepared CNT/TiO_2 nanocomposite exhibits an enhanced photocatalytic activity for benzene degradation, as compared with that over commerical titania (Degussa P25). Lee et al[3] reported an efficient and environmentally benign biomimetic mineralization of TiO(2) at the graphitic carbon surface, which successfully created an ideal TiO(2)/carbon hybrid structure without any harsh surface treatment or interfacial adhesive layer. The direct contact of the NCNT surface and TiO(2) nanoshell without any adhesive interlayer introduced a new carbon energy level in the TiO(2) band gap and thereby effectively lowered the band gap energy. Consequently, the created core/shell nanowires showed a greatly enhanced visible light photocatalysis. Zhang et al[4] prepared anatase TiO_2-CNT catalysts with high specific surface areas by depositing TiO_2 particles on the surface of carbon nanotubes (CNTs) by a modified sol-gel technique. The catalytic activity of the anatase TiO_2-CNT catalysts was assessed by examining the degradation of methylene blue (MB) from model aqueous solutions as a probe reaction under visible light and ultrasonic irradiation. Yang et al[5] reported a new method for improving the photocatalytic activity of TiO_2 by dispersing titanium dioxide onto carbon nanotubes (CNTs) modified by acid and polyvinyl alcohol. Wang et al[6] prepared a novel kind of carbon nanotubes/titanium dioxide (CNTs/TiO_2) composite photocatalyst by a modified sol-gel method in which the nanoscale TiO_2 particles were uniformly deposited on the CNTs modified with poly (vinyl pyrrolidone) (PVP). Hu et al[7] prepared TiO_2 sol by sol-gel method and TiO_2 films were coated on industrial diamond surface by impregnation method. Ma et al[8] successfully

Received date: July 25, 2019
Foundation item: National Natural Science Foundation of China (11672068, 11672067)
Corresponding author: Yan Honghao, Ph. D., Professor, State Key Laboratory of Structural Analysis for Industrial Equipment, Dalian University of Technology, Dalian 116024, P. R. China, Tel: 0086-411-84708397, E-mail: yanhh@dlut.edu.cn

Copyright © 2020, Northwest Institute for Nonferrous Metal Research. Published by Science Press. All rights reserved.

prepared CNTs/TiO_2 complexes by the sol gel method without using surfactants, and the photocatalytic activity of CNTs/TiO_2 composite was investigated by UV-Vis spectrophotometer. The effect of CNTs doping amount on the photocatalytic degradation efficiency was studied systematically. Ma et al[9] prepared CNTs/TiO_2 composite photocatalyst by the sol-gel method. X-ray diffraction (XRD), scanning electron microscopy (SEM), nitrogen adsorption and desorption analyzer (BET), differential thermal-gravimetric analyzer (TG-DTA) and infrared absorption spectrometer (FT-IR) were used to characterize the crystal form, thermal stability and morphology of CNTS/TiO_2 composite photocatalyst. Wang et al[10] used sol-gel method, with four butyl titanite as precursor, carboxylate multi-walled carbon nanotubes (oCNTs) as a carrier, ethanol as solvent, glacial acetic acid as an inhibitor, to successfully prepare TiO_2 nanoparticles loaded carbon nanotubes composite photocatalyst (TiO_2/oCNTs).

At present, the research on MWCNTs/TiO_2 mainly focuses on its preparation process and photocatalytic activity. Considering that TiO_2 is a semiconductor material with high dielectric constant, good thermal stability, good dielectric property and chemical corrosion resistance, its conductivity varies with temperature, and can be combined with microwave absorbent to improve the microwave absorbing properties of materials[11-14]. In addition, MWCNTs have many defects but excellent conductivity, excellent microwave absorptivity and lighter mass. They are excellent microwave absorbents and are used in the preparation of stealth materials and electromagnetic shielding materials[15-18]. Considering the excellent absorbing properties of TiO_2 and MWCNTs, the microwave absorbing properties of MWCNTs/TiO_2 were studied by homogeneous mixing dry grinding and wet grinding with ethanol with the rolling ball mill.

1 Experiment

MWCNTs and chemically pure TiO_2 were placed in a polyester tank and uniformly mixed by a rolling ball mill. The ball milling experiment was carried out in two groups. One group is MWCNTs mixed with TiO_2 in a mass ratio of $m(TiO_2):m(\text{MWCNTs})=19:1$, and dry grinding at 300 r/min for 1 h under the protection of argon. The ball to material ratio is $m(\text{ball}):m(\text{sample}) = 10:1$. The steel ball is GCr15 (10 mm). For the other group, about 50 mL of ethanol was added to make the steel beads submerge, and other conditions are the same as the first group.

X-ray diffractometer (D/MAX 2400, Japan Science, Cu target, 40 kV, 30 A) was used for sample element composition analysis. Field emission scanning electron microscopy (SEM) (Nova Nano SEM 450) for material characterization and analysis is at the nanoscale. The network vector analyzer (HP-8722ES) measured electromagnetic parameters.

In this study, the transmission model of TE wave (transverse wave) perpendicularly incident into the random dispersion space of MWCNTs/TiO_2 composite powder particles is shown in Fig.1. Assuming that the particles are uniformly distributed, TE waves propagate along the z-axis, the electric field is parallel to the y-axis and the magnetic field is parallel to the x-axis. The medium is divided into three layers, and the thickness of the absorber is d.

The basic equations of electromagnetic field are Maxwell's equations[19-22]:

$$\nabla \times \boldsymbol{E} = -\mathrm{j}\omega\mu_0\boldsymbol{H}\ ,\ \nabla \times \boldsymbol{H} = -\mathrm{j}\omega\varepsilon\boldsymbol{E}\ ,$$
$$\nabla \cdot \varepsilon\boldsymbol{E} = 0\ ,\ \nabla \cdot \mu_0\boldsymbol{H} = 0 \tag{1}$$

Among them, μ_0 is vacuum permeability, ε is dielectric constant, ω is electromagnetic angular frequency, $\boldsymbol{E}$ is electric field strength, and $\boldsymbol{H}$ is magnetic field strength.

The field in dielectric I is expressed as:

$$\boldsymbol{E}_{0y} = \boldsymbol{E}_0(\mathrm{e}^{-\mathrm{j}k_0 z} + r\mathrm{e}^{\mathrm{j}k_0 z})\ ,$$
$$\boldsymbol{H}_{0x} = \frac{k_0}{\omega\mu_0}\boldsymbol{E}_0(\mathrm{e}^{-\mathrm{j}k_0 z} - r\mathrm{e}^{\mathrm{j}k_0 z}) \tag{2}$$

Among them, $\boldsymbol{E}_0$ is the amplitude of the electric field of the incident wave, r is the reflection coefficient of electromagnetic wave at z=0 interface, and k_0 is the wave number of electromagnetic waves in air.

The field in dielectric II is expressed as:

$$\boldsymbol{E}_{1y} = \boldsymbol{E}_{\mathrm{PT}}\mathrm{e}^{-\mathrm{j}kz} + \boldsymbol{E}_{\mathrm{PR}}\mathrm{e}^{\mathrm{j}kz}\ ,$$
$$\boldsymbol{H}_{1x} = \frac{k}{\omega\mu_0}(\boldsymbol{E}_{\mathrm{PT}}\mathrm{e}^{-jkz} - \boldsymbol{E}_{\mathrm{PR}}\mathrm{e}^{jkz}) \tag{3}$$

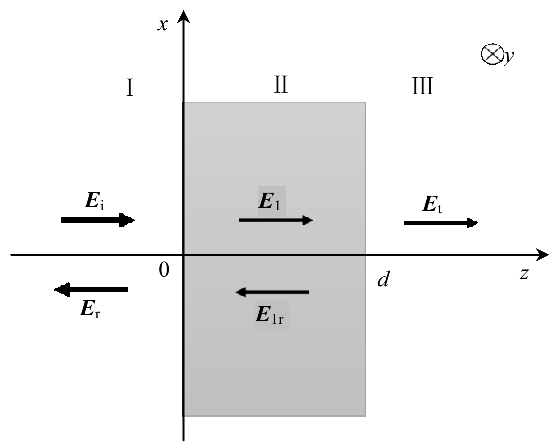

Fig.1 Physical model of electromagnetic wave propagation in absorber with MWCNTs/TiO_2 composite powder particles distribution: I-Air, II-Absorber, III-Air; E_i is the incident wave, E_r is the reflection wave, E_{1i} is the transmission wave entering the absorber, E_{1r} is the reflection wave coming from the absorber, and E_t is the transmission wave

Among them, E_{PT} and E_{PR} are the amplitudes of transmission and reflection electric fields in dielectric II, respectively, and k is the wave number of electromagnetic waves in the absorber.

The field in medium III is expressed as:

$$\boldsymbol{E}_{2y} = \boldsymbol{E}_0 t \mathrm{e}^{-\mathrm{j}k_0 z}, \quad \boldsymbol{H}_{2x} = \frac{k_0}{\omega\mu_0}\boldsymbol{E}_0 t \mathrm{e}^{-\mathrm{j}k_0 z} \tag{4}$$

Where t is the transmission coefficient of electromagnetic wave.

From the continuity boundary conditions of electric field and magnetic field at the interface of z=0 and z=d:

$$\boldsymbol{E}_{0y}\big|_{z=0} = \boldsymbol{E}_{1y}\big|_{z=0}, \quad \boldsymbol{H}_{0x}\big|_{z=0} = \boldsymbol{H}_{1x}\big|_{z=0},$$

$$\boldsymbol{E}_{1y}\big|_{z=d} = \boldsymbol{E}_{2y}\big|_{z=d}, \quad \boldsymbol{H}_{1x}\big|_{z=d} = \boldsymbol{H}_{2x}\big|_{z=d}. \tag{5}$$

The wave impedance of dielectrics I, II and III are Z_0, Z_r and Z_0, respectively [23]:

$$Z_0 = \sqrt{\frac{\mu_0}{\varepsilon_0}}, \quad Z_r = \sqrt{\frac{\mu_0\mu_2}{\varepsilon_0\varepsilon_2}} \tag{6}$$

Among them, the dielectric constant and permeability of the vacuum is ε_0 and μ_0, respectively. The relative dielectric constant and permeability of dielectric II is ε_2 and μ_2, respectively.

The expressions of reflection coefficient r and transmission coefficient t of electromagnetic wave can be obtained from the Eq.(7):

$$r = \frac{\chi^2 - 1}{1 + \chi^2 + 2\chi\coth(\mathrm{j}kd)},$$

$$t = \frac{2\chi \mathrm{e}^{\mathrm{j}k_0 d}}{(1+\chi^2)\sinh(\mathrm{j}kd) + 2\chi\cosh(\mathrm{j}kd)} \tag{7}$$

Among them, $\chi = \sqrt{\mu_2/\varepsilon_2}$.

From the above, the reflectivity R, transmittance T and an attenuation value A_{tt} of electromagnetic wave can be obtained as follows:

$$R = |r|^2, \quad T = |t|^2, \quad A_{tt} = -10\log_{10} T \tag{8}$$

2 Results and Discussions

2.1 XRD analysis

Dry mixed MWCNTs/TiO_2 and wet mixed MWCNTs/TiO_2 were characterized by XRD. The results of the characterization are shown in Fig.2. Diffraction peaks (224) of dry mixed MWCNTs/TiO_2 (JCPDS file No. 21-1272) showed the weakest peak intensity at 2θ=82.698°. Diffraction peaks (116) of wet mixed MWCNTs/TiO_2 (JCPDS file No.71-1168) appeared to have the weakest peak intensity at 2θ = 68.466 °. The peaks are 25.040°, 37.483°, 47.722°, 53.718°, 54.919°, 62.422°, 68.657°, 70.137°, 74.980°, 82.698° (marked with black prisms) as dry mixed MWCNTs/TiO_2 diffraction peaks. The peaks are 25.039°, 37.420°, 47.641°, 53.679°, 54.799°, 62.444°, 68.466°, 70.102°, 74.720°, 82.699° (marked with inverted triangles) as wet mixed MWCNTs/TiO_2 diffraction peaks. The peak intensity of dry mixed MWCNTs/TiO_2 and the peak intensity of wet mixed MWCNTs/TiO_2 are nearly identical.

In summary, the peak value of TiO_2 of the mixed powders of MWCNTs/TiO_2 by dry and wet milling is basically the same by XRD characterization, which indicates that the phase of MWCNTs/TiO_2 by dry milling and that of MWCNTs/TiO_2 by wet milling is unchanged, and the peak strength reaches the maximum when 2θ reaches about 25°. It is further found that the peak value of MWCNTs/ TiO_2 in wet milling is gentler than that in wet milling, which indicates that wet milling has better dispersion effect.

2.2 SEM analysis results

Fig.3a and 3b are SEM images of dry mixed MWCNTs/TiO_2 and wet mixed MWCNTs/TiO_2, respectively. It can be seen from the figure that the MWCNTs are long and thin graphite cylinders, and the nanometer TiO_2 is spherical. Fig.3a shows the MWCNTs/TiO_2 mixed by direct ball milling, and the fusion dispersion effect of MWCNTs and TiO_2 is relatively poor, and the agglomeration phenomenon occurs in MWCNTs. Fig.3b shows the MWCNTs/TiO_2 mixed by ethanol ball milling, and the fusion dispersion effect of MWCNTs and TiO_2 is better, and there is no agglomeration in MWCNTs.

2.3 Network vector analytical test result

The dry ground MWCNTs/TiO_2 and the wet ground MWCNTs/ TiO_2 with alcohol powder samples are mixed with paraffin with a 7:3 mass radio, respectivety, The sample thickness is 2 mm. The network vector analyzer HP-8722ES

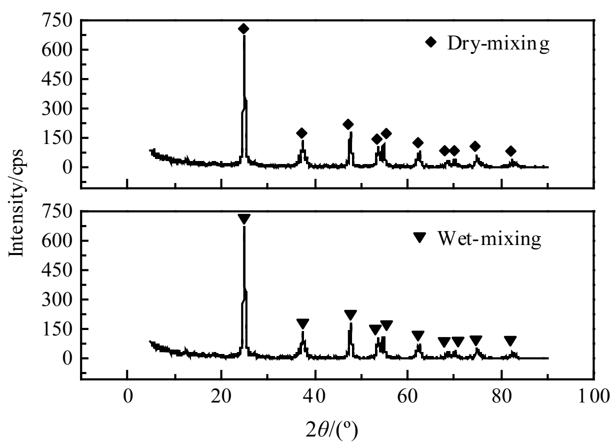

Fig.2 XRD patterns of the MWCNTs /TiO_2 samples

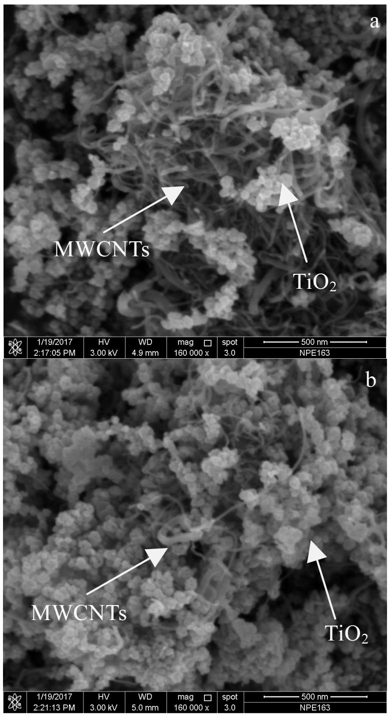

Fig.3 SEM images of dry-mixed (a) and wet-mixed (b) MWCNTs/TiO_2 samples

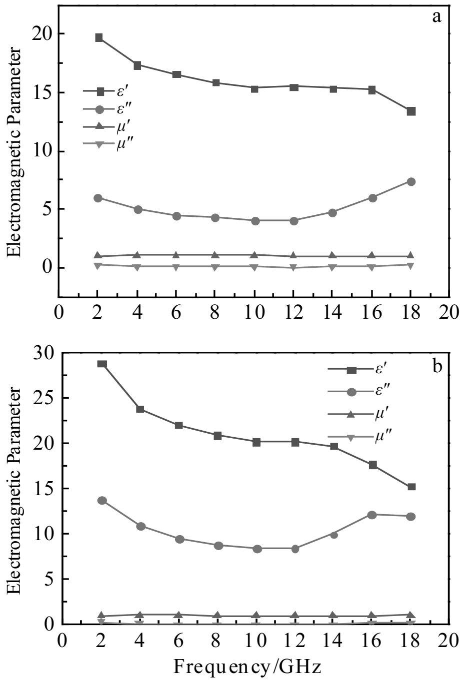

Fig.4 Electromagnetic parameters of dry mixed MWCNTs/TiO_2 (a) and wet mixed MWCNTs/TiO_2 (b)

was used to measure the electromagnetic parameters in the frequency range of 2 GHz to 18 GHz, as shown in Fig.4.

It can be seen from the electromagnetic parameters in Fig.4 that the real part of the relative dielectric constant of the dry mixed MWCNTs/TiO_2 is 13.46~19.77, and the imaginary part is 4.02~7.40. The real part of the relative magnetic permeability is 0.94~1.03, and the imaginary part is 0.01~0.21. The real part of the relative dielectric constant of wet mixed MWCNTs/TiO_2 is 15.29~28.91, and the imaginary part is 8.35~13.74.The real part of the relative magnetic permeability is 0.94~1.02, and the imaginary part is 0.02~0.25. The above indicates that the electromagnetic parameters of MWCNTs/TiO_2 powder added to ethanol wet milling are larger than those of dry milled MWCNTs/TiO_2.

The high SE results of these composites are related to the formation of a MWCNT micro-current network in the composites[24-26]. It can be seen in Fig.3 that MWCNTs and TiO_2 cross each other to form a network. The hopping and migrating electronic transport, which occur in the MWCNT network on the conductivity, dielectric properties and microwave attenuation performances.

2.4 Analysis of numerical simulation results

Substituting the electromagnetic parameters ε and μ in Fig.4 into the Eq.(8), and the reflectance R, the transmittance T, and the attenuation value A_{tt} of the electromagnetic wave through the dry mixed MWCNTs/TiO_2 and the wet mixed MWCNTs/TiO_2 are calculated, as shown in Fig.5.

The absorbing properties of dry mixed MWCNTs/TiO_2 and wet mixed MWCNTs/TiO_2 were analyzed based on the wave impedance matching characteristics and attenuation characteristics of the electromagnetic wave absorbed by the material. It can be seen from the reflectance curve R in Fig.5, in most of the frequency bands, that the reflectance of the wet mixed MWCNTs/TiO_2 is smaller than that of the dry mixed MWCNTs/TiO_2. Fig.5 shows that the wave impedance matching characteristics of wet mixed MWCNTs/TiO_2 are better than those of dry mixed MWCNTs/TiO_2. The transmittance curve T in Fig.5 shows that the transmittance of the wet mixed MWCNTs/TiO_2 is smaller than that of the dry mixed MWCNTs/TiO_2. It is shown that the electromagnetic loss of wet mixed MWCNTs/TiO_2 in space is greater than that of dry mixed MWCNTs/TiO_2. The attenuation curve A_{tt} in Fig.5 shows that the wetted MWCNTs/TiO_2 has a larger attenuation value in space than in that of the dry mixed MWCNTs/TiO_2. It also shows that the wet-mixed MWCNTs/TiO_2 has better absorbing effect in space in the 2~18 GHz band.

MWCNTs/TiO_2 not only has photocatalytic activity, but also can be used to prepare stealth materials and electromagnetic shielding materials. In this study, the macroscopic spatial wave absorption of MWCNTS/TiO_2 was studied,

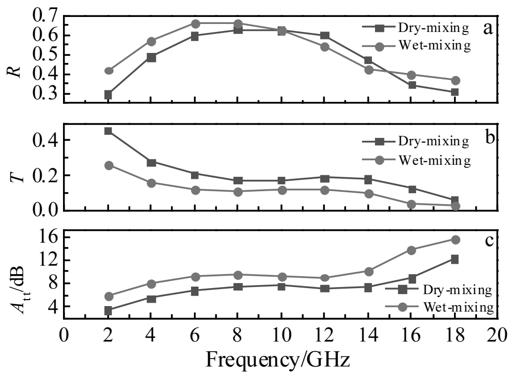

Fig.5 Absorbing characteristics of MWCNTs/TiO_2: (a) *R*-reflectance curves, (b) *T*-transmittance curves, and (c) A_{tt}-attenuation curves

while the microscopic wave absorption of MWCNTS/TiO_2, including relaxation, charge transport, magnetic resonance and eddy current, as well as magnetic-dielectric synergistic effects[27-29], needs to be further studied.

3 Conclusions

1) The dry-milled MWCNTs/TiO_2 fusion dispersion effect is relatively poor, and the MWCNTs are prone to agglomeration. However, the MWCNTs/TiO_2 blended with anhydrous ethanol is better dispersed, and there is no agglomeration in MWCNTs.

2) The wave impedance matching characteristics of wet mixed MWCNTs/TiO_2 in the frequency range of 2~10 GHz and 15~18 GHz are better than those of dry mixed MWCNTs/TiO_2. In the frequency range of 2~18 GHz, the electromagnetic loss of wet mixed MWCNTs/TiO_2 in space is greater than that of dry mixed MWCNTs/TiO_2. In the 2~18 GHz band, the wet MWCNTs/TiO_2 has better absorbing effect in space.

Reference

1 Ye C, Yun Q, Xuanke L I *et al*. *Acta Physico-Chimica Sinica*[J], 2011, 27(6): 1509
2 Xu Y J, Zhuang Y, Fu X. *The Journal of Physical Chemistry C*[J], 2010, 114(6): 2669
3 Lee W J, Lee J M, Kochuveedu S T *et al. ACS Nano*[J], 2012, 6(1): 935
4 Zhang K, Zhang F J, Chen M L *et al*. *Ultrasonics Sonochemistry*[J], 2011, 18(3): 765
5 Yang Hanpei, Shi Zemin, Dai Kaijing *et al. Acta Chimica Sinica*[J], 2011, 69(5): 536
6 Wang Huanying, Li Wenjun, Chang Zhidong *et al. Spectroscopy & Spectral Analysis*[J], 2011, 31(9): 2529
7 Hu Weida, Wan Long, Liu Xiaopan *et al*. *Journal of Hunan University (Natural Science)*[J], 2008, 35(8): 55 (in Chinese)
8 Ma Baolv, Zhang Yue. *Journal of Inorganic Materials*[J], 2015, 30(9): 937 (in Chinese)
9 Ma Jinyong, Yi Huiyang. *Journal of Hubei Normal University(Natural Science)*[J], 2016, 36(4): 58 (in Chinese)
10 Wang Wenyi, Wang Enxia, Huo Tengbo *et al. Journal of Tianjin Polytechnic University*[J], 2016, 35 (6): 50 (in Chinese)
11 Negishi N, Takeuchi K. *Materials Letters*[J], 1999, 38(2): 153
12 Wang R, Hashimoto K, Fujishima A *et al*. *Nature*[J], 1997, 388(6641): 431
13 Hoffmann M R, Martin S T, Choi W *et al. Chemical Reviews*[J], 1995, 95(1): 69
14 Mills G , Hoffmann M R. *Environmental Science & Technology*[J], 1993, 27(8): 1681
15 Chen H, Huang Z, Huang Y *et al*. *Carbon*[J], 2017, 124: 506
16 Cao Maosheng, Shu Jincheng, Wang Xixi *et al*. *Ann Phys*[J], 2019, 531: 1 800 390
17 Cao Maosheng, Shu Jincheng, Wang Xixi *et al*. *Adv Funct Mater*[J], 2019, 29: 1 807 398
18 Cao Maosheng, Cai Yongzhu, He Peng *et al*. *Chemical Engineering Journal*[J], 2019, 359: 1265
19 Yuan C, Zhou Z, Xiang X *et al*. *Physics of Plasmas*[J], 2010, 17(11): 113 304
20 Jamison S P, Shen J, Jones D R *et al. Journal of Applied Physics*[J], 2003, 93(7): 4334
21 Ling Z. *Acta Physica Sinica*[J], 2012, 61(24): 514
22 Dong Qunfeng, Xiang Jingjing, Li Junjie *et al*. *Equipment Environmental Engineering*[J], 2019, 16(1): 118
23 Jin Xin. *Coal Geology & Exploration*[J], 2018, 46(2): 159
24 Cao M S, Song W L, Hou Z L *et al*. *Carbon*[J], 2010, 48(3): 788
25 Wen B, Cao M S, Hou Z L *et al. Carbon*[J], 2013, 65: 124
26 Cao M S, Yang J, Song W L *et al*. *ACS Applied Materials & Interfaces*[J], 2012, 4(12): 6949
27 Cao M, Wang X, Cao W *et al*. *Small*[J], 2018, 14: 1 800 987
28 Cao M S, Chen H, Wang X X *et al. Journal of Materials Chemistry C*[J], 2018, 10: 1039
29 Wen B, Cao M S, Lu M *et al*. *Advanced Materials*[J], 2014, 26(21): 3484

MWCNTs/TiO_2复合粉体的制备及空间吸波模型研究

宋鑫华[1]，赵铁军[1,2]，刘振锋[1]，李晓杰[1]，闫鸿浩[1]

(1. 大连理工大学 工业装备结构分析国家重点实验室，辽宁 大连 116024)

(2. 河南大学，河南 开封 475004)

摘　要：通过球磨法将 MWCNTs 和 TiO_2 进行混合得出复合粉体，并用 XRD、SEM、网络矢量分析仪对复合粉体进行表征，利用数值模型进行理论计算分析其空间吸波特性。结果表明，加入无水乙醇湿混合的 MWCNTs/TiO_2 复合粉体中的 MWCNTs 分散性较好；湿混合的 MWCNTs/TiO_2 复合粉体在 2～18 GHz 频段的波阻抗匹配特性和空间吸波能力更佳，为复合吸波材料的实际应用提供了理论参考。

关键词：MWCNTs/TiO_2；空间吸波；球磨法；衰减值

作者简介：宋鑫华，男，1989 年生，博士生，大连理工大学工业装备结构分析国家重点实验室，辽宁 大连 116024, E-mail: 984017992@mail.dlut.edu.cn