BaTiO₃/CARBON CORE-SHELL NANOWIRES USED AS WIDE-BAND AND STRONG ELECTROMAGNETIC WAVE ABSORBERS

Z. Y. HE, J. F. ZHANG, G. Z. WANG, S. H. SHI, G. P. WAN^{*} College of Materials and Chemical Engineering, Hainan University, Haikou 570228, PR China

Comparatively low dielectric properties of barium titanate (BaTiO₃) limits its further application for electromagnetic wave absorption. In this work, we constructed BaTiO₃/carbon core-shell nanowires with the controllable thickness of carbon layer by an acetylene decomposition method to enhance dielectric properties of BaTiO₃. The results indicated that the BaTiO₃ nanowires with a diameter about 30 nm were uniformly coated by carbon shell with a thickness about 6 nm at 500 °C. The measure of microwave absorption performance demonstrated that the BaTiO₃@C-500 composites had the best capability. The best effective bandwidth was 5.9 GHz with a thickness of 2.2 mm, nearly covering all Ku-band (12-18 GHz) and the minimum RL value was -30.1 dB at 17.8 GHz with a thickness of 1.8 mm. With the thickness varying from 1 to 5 mm, the effective absorption bandwidth almost covered all the range of 2 to 18 GHz. The BaTiO₃@C-500 composites are very promising candidate for microwave absorption material.

(Received March 28, 2019; Accepted July 12, 2019)

Keywords: BaTiO₃ nanowires, Carbon-coated composites, Microwave absorption

1. Introduction

The rapid development of electronic technology and the application of more and more electronic products inevitably bring about environment electromagnetic radiation issue, which seriously influences people's healthy and the normal operation of other electron equipment, resulting in unnecessary damage in many situations [1-5]. Electromagnetic wave absorbing materials are a new kind of functional material which by absorbing electromagnetic wave to realize the purpose of eliminating electromagnetic pollution [6-8]. To date, extensive effort has been devoted to developing electromagnetic wave absorbing materials such as ferrite, magnetic metal, metal oxide, carbonaceous material, SiC and conducting polymer [9-13]. However, there were relatively few literatures reported on BaTiO₃ as electromagnetic absorbing materials.

BaTiO₃ is a kind of ferroelectric ceramics with typical perovskite crystal structure, mainly used in capacitor, memory, dielectric amplifier and PTC element fields due to their special piezoelectric, photoelectric and pyroelectric properties, and also occasionally used as electromagnetic absorbing materials owing to its good dielectric properties [14-17]. For example, Yang et al. synthesized ultrathin BaTiO₃ nanowires by one-step hydrothermal treatment and get the unique features of uniform size distribution and ultrahigh aspect ratio [18]. Its excellent absorption performance proved that BaTiO₃ is a kind of promising candidate for electromagnetic wave absorption. Zhu et al reported the fabrication of BaTiO₃ nanotubes via a wet chemical route and BaTiO₃ nanotubes showed the minimum reflection loss reached -21.8 dB at 15 GHz [19]. They considered the decent absorbing properties should be attributed to the special hollow structure and intensive dielectric relaxation. Bi et al prepared La-doped BaTiO₃/multi-walled carbon nanotube nanocomposites by a solvothermal process and found that the electromagnetic wave absorption performance and the absorption frequency can be modulated via changing the concentrations of La³⁺ [20].

But one-component material is often difficult to satisfy all-round requirement to electromagnetic absorbers including thin thickness, wide absorption bandwidth, strong absorption

^{*} Corresponding author: wangengping001@163.com

and low density. Constructing core-shell structure with carbon materials as coating layer was considered as an effective strategy to solve this problem via produce more interface and multiple reflections to dissipate electromagnetic energy [21]. Du et al prepared core-shell $Fe_3O_4@C$ composites through in situ polymerization following a high-temperature carbonization [22]. They found that the electromagnetic wave absorption performance was greatly enhanced compared with bare Fe_3O_4 and thought the improved characteristic impedance and unique core-shell structure was responsible for the absorption properties. Liang et al synthesized SiC@C nanowires by combining an interfacial in situ polymer encapsulation and carbonization treatment, and the optimal performance reached -50 dB at the frequency of 12 GHz and the effective absorption bandwidth was 8 GHz [23]. Li et al fabricated microporous Co@C nanoparticles by dealloying CoAl@C precursors and discussed the relation between carbon shell thicknesses and microwave absorption performance [24]. The enhanced microwave attenuation was ascribed to the cooperation effect of the core-shell structure and microporous morphology.

Based on the above theory and research, we successfully prepared $BaTiO_3@C$ core-shell structure composites with different carbon shell thickness by changing the heat treatment temperature in this work. In this composite system, the synergistic effect of uniform $BaTiO_3$ nanowires and compact carbon shell effectively enhanced microwave absorption performance. As expected, our results indicate the $BaTiO_3@C$ composites have much advantage such as easy synthesis, wide absorption bandwidth and light weight, and are a promising candidate in microwave absorption field.

2. Experimental

2.1. Preparation of BaTiO₃ nanowires

The preparation of BaTiO₃ nanowires was based on Tang's method [25]. Typically, 0.53 g Ba(OH)₂·H₂O (2.8×10^{-3} mol) and 0.12 g H₂Ti₃O₇ (0.467×10^{-3} mol) were dissolved in 56 ml ultrapure water and stirred for 30 min. Then the suspensions were transferred to an 80 ml Teflon-autoclave and heated at 210 °C for 1.5 h. The obtained precipitate was washed with ultrapure water and ethanol for three times, and vacuum-dried at 60 °C for 6 h.

2.2. Synthesis of BaTiO₃@C composites

The BaTiO₃@C composites was synthesized by an acetylene decomposition method. 0.1 g as-prepared BaTO₃ was put into a porcelain boat and transferred to the centre of tube furnace. Then evacuation and a stream of acetylene (an atmosphere pressure) were introduced. The furnace was respectively heated to 500 °C and 450 °C for 1 h with a heating rate 5 °C min⁻¹ to obtain BaTiO₃@C composites. The obtained samples were denoted as BaTiO₃@C-500, BaTiO₃@C-450, respectively. The process for preparation of the BaTiO₃@C composites is schematically depicted in Fig. 1.



Fig. 1. The preparation process of $BaTiO_3@C$ composites.

2.3. Characterization

The crystalline structure of the samples was characterized by an X-ray diffractometer (Bruker D8 Advance) with Cu K α radiation ($\lambda = 0.154178$ nm). The morphology of the samples

was observed by TEM (JEOL JEM-2100, Japan). The elemental chemical states were carried out on an X-ray photoelectron spectroscopy (AXIS SUPRA) with a monochromatic Al K α source. Thermogravimetric (TG) results were conducted under air atmosphere with a heating rate of 10 °C min-1 by using a thermal analysis system (SDT Q600 TGA). Raman spectroscopy was determined by a Raman spectrometer (Renishaw inVia Reflex) using a 514 nm green laser excitation. The electromagnetic parameters of the complex permeability and permittivity were measured using a network analyzer (Agilent N5230A) at a 2-18 GHz band by the transmission/reflection coaxial line method. The measured composites were prepared by dispersing the sample in paraffin wax uniformly and pressing the mixture into a toroid of 7.00 mm outer diameter and 3.04 mm inner diameter. The reflection loss values were calculated via the obtained complex permeability and permittivity.

3. Results and discussion

Fig. 2 (a) shows the typical XRD patterns of $BaTiO_3$ and $BaTiO_3@C$ samples. All the diffraction peaks can be assigned to the cubic perovskite structure of $BaTiO_3$ (JCPDS, 81-2203). It can be found that all three samples are highly crystalline with very few impurity peaks [26].



Fig. 2. a) XRD patterns and b) Raman spectra of BaTiO₃, BaTiO₃@C-450 and BaTiO₃@C-500.

No evident differences are observed between pristine $BaTiO_3$ nanowires and $BaTiO_3@C$ composites, proving that the $BaTiO_3$ crystal structure was hardly influenced during the carboncoated process in temperature range from 450 °C to 500 °C. It should be noted that characteristic peaks related to carbon layer cannot be identified in two $BaTiO_3@C$ composites, indicating the amorphous feature and low content of carbon.

The Raman spectra are used to further discover the crystal state of carbon shell and are given in the Fig. 2 (b). Two cognizable carbon peaks can be found in the range of 800-2000 cm⁻¹. The D band located at 1329 cm⁻¹ is associated with disordered structures resulting from vacancies and defects of carbon shell, while the G band at 1604 cm⁻¹ is generally taken as characteristic feature of graphitic carbon [27]. The values of I_D/I_G represent graphitization degree of carbon. The nearly equal intensity ratios of the D band to the G band mean the same carbon layer crystallinity of the two composites. The higher value (0.75) of I_D/I_G indicates much disorder structure of carbon layer, which would introduce more defects and help to enhance microwave absorption performance.



Fig. 3. TG curves of BaTiO₃, BaTiO₃@C-450 and BaTiO₃@C-500.



Fig. 4. (a, b) TEM images of pristine BaTiO₃ nanowires. c) TEM and d) HRTEM images of BaTiO₃@C-450.e) TEM and f) HRTEM images of BaTiO₃@C-500.

Thermogravimetric (TG) analysis can effectively acquire the carbon content of different composites. From the thermogravimetric curves in Fig. 3, we can see the weight loss of BaTiO₃ nanowires steadily increases during the whole process due to the evaporation of adsorbed water before 200 °C and the decomposition of impurities such as $H_2Ti_3O_7$ after 200 °C. For BaTiO₃@C composites, the weight loss is mainly ascribed to the combustion of carbon components at 400-500 °C [28]. Obviously, the weight loss of BaTiO₃@C-500 is much higher than BaTiO₃@C-450, which confirms the carbon content of BaTiO₃@C-500 is more than BaTiO₃@C-450. And this results also manifest that the present method is appropriate to control content of carbon in composites by changing heating temperature.

The morphology and inner structure of the samples are further studied by TEM. As shown in Fig. 4 (a) and (b), the pristine BaTiO₃ nanowires have a uniform distribution and the average diameter is about 30-50 nm. Fig. 4 (c) and (e) shows the BaTiO₃ nanowires were wrapped with a clear carbon shell after acetylene treatment, and the thickness of carbon shell obviously increase with the rise of heat temperature. The HRTEM images of BaTiO₃@C-450 and BaTiO₃@C-500 are shown in Figure 4 (d) and (f), respectively. It can be seen that the well-crystallized BaTiO₃ nanowires were coated an amorphous carbon shell, the interplanar spacing of 0.39 nm can be indexed as (100) crystal plane. It is worth noting that the thickness of carbon shell is about 2 nm for BaTiO₃@C-450 and the BaTiO₃@C-500 reached 6 nm, which further proves the carbon shell can be controlled through the change of temperature.



Fig. 5. a) XPS survey spectral. High-resolution spectra of BaTiO₃ a)C-500: b) Ba 3d, c) Ti 2p, d) C 1s.

To further analysis the elemental composition and chemical state of the BaTiO₃ nanowires and BaTiO₃@C, XPS measurement was employed. The fully scanned spectra of composites are shown in Fig. 5 (a), displaying that Ba, O and Ti exist in the BaTiO₃ samples. Compared to the pristine BaTiO₃ nanowires, the obviously sharp C peak of the BaTiO₃@C composites indicate the BaTiO₃ nanowires have been compactly surrounded by carbon shell, due to the high sensitivity of XPS to the surface of sample. Fig. 5 (b) shows the high-resolution Ba 3d spectrum of the BaTiO₃@C-500. Two obvious peaks at 779.4 eV and 794.7 eV can be assigned to the Ba 3d_{5/2} and Ba $3d_{3/2}$, which is consistent with the previous literature [29]. The peaks located at 458.9 eV and 464.9 eV corresponds to the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ in Fig. 5 (c) [30]. The high-resolution C 1s spectrum with the evident peak value at 284.7 eV determines the exist of C (Fig. 5 (d)). As discussed above, the XPS results further verify that the composites of carbon coated BaTiO₃ nanowires have been successfully synthesized.



Fig. 6. Three-dimensional representations of reflection loss values versus frequency and thickness: a) BaTiO₃, c) BaTiO₃@C-450, e) BaTiO₃@C-500; b), d) and f) corresponding values with different thickness.

To reveal the microwave absorption properties of these composites, the relative complex permittivity and permeability were measured by mixing 60 wt% of the samples with paraffin at the frequency range of 2-18 GHz. According to the transmit line theory, the reflection loss (RL) coefficients of these composites were derived by the following equations [31]:

$$Z_{in} = Z_0 (\mu_r / \varepsilon_r)^{1/2} \tanh[j(2\pi f d/c)(\mu_r \varepsilon_r)^{1/2}]$$
(1)

$$RL = 20\log|(Z_{in} - Z_0)/(Z_{in} + Z_0)|$$
⁽²⁾

where Z_{in} is the input impedance of the absorber, Z_0 is the impedance of free space, f is the frequency of microwaves, d is the thickness of the absorber, c is the velocity of light in free space, μ_r and ε_r are the relative complex permeability and permittivity, respectively. It is generally considered that RL values of -10 dB is comparable to 90% microwave absorption, and the effective absorption bandwidth is the relevant frequency range with the RL values less than -10 dB.



Fig. 7. The frequency dependence of a) real permittivity, b) imaginary permittivity, c) real permeability, d) imaginary permeability, e) dielectric loss tangents and f) magnetic loss tangents of BaTiO₃, BaTiO₃@C-450 and BaTiO₃@C-500.

The reflection loss curves in the frequency range of 2-18 GHz for these composites with different thicknesses are shown in Fig. 6. It can be seen obviously that the absorption ability of bare $BaTiO_3$ is relatively poor, while the $BaTiO_3@C$ composites display the much stronger absorption ability. With the increase of carbon-coated temperature, the absorption ability is

improved greatly, and at 500 °C reaches the best RL value. Fig. 6 (a) and (b) shows the RL curves of BaTiO₃ nanowires. The minimum value is -7.64 dB and no RL values is less than -10 dB over the whole frequency range. Fig. 6 (d) indicates that BaTiO₃@C-450 has the best RL value of -22.5 dB at 4.5 GHz with a thickness of 5 mm and an effective bandwidth of 2.2 GHz in the range of 11.6-13.8 GHz with a thickness of 2 mm. It is interesting that with the increase of thickness, the RL curves show two RL peak values from Fig. 6 (c). The RL curves of BaTiO₃@C-500 in Fig. 6 (f) reveal a better microwave absorption ability. The minimum RL value is -30.1 dB at 17.8 GHz with the thickness of 1.8 mm. The best effective bandwidth is 5.9 GHz in the range of 11.7-17.6 GHz with a thickness of 2.2 mm, almost covering all the Ku-band (12-18 GHz). The effective bandwidth can reach to 3.8 GHz with the thickness of 3 mm in the range of 8.2-12 GHz, nearly covering all the X-band (8-12 GHz). From Fig. 6 (e) we can see that, the RL values below -10 dB cover all the frequency in the thickness range of 1-5 mm. Moreover, along with the increase of thickness, the effective bandwidth turns to lower frequency, and covers the whole C, X, Ku wave bands, so it is easy to control microwave absorption frequency only to change the thickness of absorber. The above-mentioned results prove BaTiO₃@C composites can be used as an effective wide frequency microwave absorber.

It is generally agreed that the microwave absorption properties of the composites are closely related with their relative complex permittivity ($\varepsilon_r = \varepsilon' - j\varepsilon''$) and relative complex permeability ($\mu_r = \mu' - j\mu''$), where the real parts of complex permittivity and permeability stand for the storage ability of electric and magnetic energy, the imaginary parts of complex permittivity and permeability symbolize the loss capability of electric and magnetic energy [32]. The electromagnetic parameters of composites are shown in Fig. 7. The real (μ') and imaginary parts (μ ") of the relative complex permeability are approximately 1 and 0, respectively. It is ascribed to the absence of magnetic materials. As shown in Fig. 7 (a), the real part ε' of pristine BaTiO₃ nanowires have a slightly fluctuation from 8.9 to 8.3, and a lower imaginary part ε " from 0.1 to 1. After coating with carbon layer, both real part ε' and imaginary part ε'' show holistic declining tendency, presenting significant frequency dispersion behavior, which is positive for enhancing microwave absorption performance [33]. The real part ε' of BaTiO₃@C-450 decreases from 13.7 to 9.7 and BaTiO₃@C-500 shows a decline from 13.4 to 5.9. While the imaginary part ε " is obviously higher than bare BaTiO₃ nanowires. The imaginary part ε " of BaTiO₃@C-450 decreases from 4.8 to 2.5 and BaTiO₃@C-500 declines from 11.6 to 3.3 as shown in Figure 7b. It can be proved that the introduction of carbon promotes the dielectric loss, and with the increase of carbon content, the loss capabilities of composites get notable improvement [34]. The dielectric loss tangent ($tan\delta_{\epsilon} = \epsilon''/\epsilon'$) is also an important assessment index to estimate the energy lost versus the energy storage in composites, and higher tangent value represents more energy consumption [35]. From Fig. 7 \in , the tan δ_{ϵ} values of the pristine BaTiO₃ nanowires have a slow rise in a relative lower range from 0.01 to 0.12, indicating poor loss capabilities for electric energy. The BaTiO₃@C-450 has preferable loss capabilities and the tan δ_{ϵ} value fluctuate slightly in the range of 0.35 to 0.25, indicating a mild dielectric relaxation process. And the tan δ_{ϵ} values of the BaTiO₃@C-500 show remarkable improvement compared with the former. The tan δ_{ϵ} values are almost a constant with several slight fluctuations, which should be ascribed to multiple dielectric loss mechanism in the measured frequency [36]. Moreover, the rate of acetylene decomposition substantially accelerates in 500 °C. A more dense and uniform carbon layer of was formed on the surface of BaTiO₃ nanowires after heat treatment. Their bonding with the BaTiO₃ nanowires can provide suitable conductive network. The migrate and hop of electrons can consume a certain amount of electromagnetic energy, and increase the ability of microwave attenuation, as described by Cao's Electron-Hopping model and Conductive-Network equation [37]. This is an important factor that the microwave absorption ability of BaTiO₃@C-500 is apparently improved. The magnetic loss tangent values of composites are about 0 owing to no magnetic materials component (Fig. 7 (f)).

The Debye theory is a powerful tool to explain the dielectric relaxation process of the composites. According to the Debye theory [38]. ε' and ε'' can be expressed by the following equation:

555

$$\varepsilon_{r} = \varepsilon' - j\varepsilon'' = \varepsilon_{\infty} + \frac{\varepsilon_{s} - \varepsilon_{\infty}}{1 + j2\pi f\tau}$$
(3)

where ε_s is the static permittivity, ε_{∞} is the relative permittivity at the high-frequency limit, f is the frequency and τ is the polarization relaxation time. Thus, the ε' and ε'' can be written as

$$\varepsilon' = \varepsilon_{\infty} + \frac{\varepsilon_s + \varepsilon_{\infty}}{1 + (2\pi f)^2 \tau^2}$$
(4)

$$\varepsilon'' = \frac{2\pi f \tau (\varepsilon_s - \varepsilon_{\infty})}{1 + (2\pi f)^2 \tau^2}$$
(5)

Combining eqs (4) and (5), the association between ε' and ε'' can be described as

$$\left(\mathcal{E}' - \frac{\mathcal{E}_s + \mathcal{E}_{\infty}}{2}\right) + \left(\mathcal{E}''\right)^2 = \left(\frac{\mathcal{E}_s - \mathcal{E}_{\infty}}{2}\right) \tag{6}$$

On the basis of eq. (6), it can be inferred that the plot of ε' versus ε'' should be a semicircle, generally are denoted as the Cole-Cole semicircle. Each semicircle is assigned to a Debye relaxation process.

The ε '- ε " curve of BaTiO₃@C-500 in the frequency range of 2-18 GHz is displayed in Fig. 8. It can be observed two distinguishable Cole-Cole semicircles at 10 GHz and 15 GHz, indicating that there are probable multiple dielectric relaxation processes, which should be ascribed to dipolar polarization and interfacial polarization. The introduction of carbon shell and some defects in the composites will be conducive to generate electric dipole under the effect of external electromagnetic field. The motion of dipole will keep pace with the change of applied electromagnetic field frequency, which leads to dipole relaxation polarization. It takes great part in Debye dielectric polarization.



Fig. 8. Cole-Cole semicircles of BaTiO₃@C-500.

Besides, interfacial polarization exists widely in multiple composite materials [39]. The structure of BaTiO₃@C composites provides numerous interfaces, such as BaTiO₃ nanowires and carbon shell, carbon shell and carbon shell, carbon and paraffin, which should contribute to the accumulation of bound charges at the interface and result in the interfacial polarization. These polarization effects consume a portion of electromagnetic energy and enhance microwave absorption performance effectively.

Electromagnetic wave attenuation is other important factor for assess microwave absorption ability. On the basis of transmission line theory, the attenuation constant α can be expressed as follows:

$$\alpha = \frac{\sqrt{2\pi f}}{c} \times \sqrt{\left(\mu''\varepsilon'' - \mu'\varepsilon'\right) + \sqrt{\left(\mu''\varepsilon'' - \mu'\varepsilon'\right)^2 + \left(\mu'\varepsilon'' + \mu''\varepsilon'\right)^2}} \tag{7}$$

Fig. 9 shows a comparation of α values for the BaTiO₃ nanowires, BaTiO₃@C-450 and BaTiO₃@C-500 in the frequency range of 2-18 GHz. The α values of BaTiO₃@C-500 are obviously higher than others. It increases from 63 to 232 with the raise of frequency, suggesting the excellent electromagnetic wave attenuation ability.



Fig. 9. Attenuation constant of BaTiO₃, BaTiO₃@C-450 and BaTiO₃@C-500.

In summary, the excellent microwave absorption performances of $BaTiO_3@C-500$ composites can be attributed to the following factors: First, the introduction of carbon shells greatly improve dielectric properties of the composites and thus notably enhance dielectric loss. Second, the combination of carbon shells and $BaTiO_3$ nanowires form the conductive network. Electrons to migrate and hop will dissipate part of the energy [40]. Third, the special construction of $BaTiO_3@C$ brings about many interfaces, leading to more interfacial polarization.

4. Conclusions

In this work, $BaTiO_3@C$ composites have been successfully prepared through an acetylene decomposition process. The pristine $BaTiO_3$ nanowires have the minimum RL value - 7.64 dB. After being coated carbon, the minimum RL value reaches -30.1 dB and the effective absorption bandwidth is 5.9 GHz. The excellent microwave absorption performance is ascribed to unique structure and multiple scatterings. The thin coating thickness, wide absorption bandwidth and strong absorption performance prove $BaTiO_3@-500$ may be a potential microwave absorption material.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21706046, 11564011, 51362010), the Natural Science Foundation of Hainan Province (514207, 514212) and the Graduate Student Innovation Research Project of Hainan Province (Hys2018-80, Hys2018-81, Hys2018-82, Hys2018-83, Hys2018-84).

References

 T. Xia, Y. H. Cao, N.A. Oyler, J. Murowchick, L. Liu, X. B. Chen, ACS Appl. Mater. Interfaces 7(19), 10407 (2015).

- [2] K. Wang, G. P. Wan, G. L. Wang, Z. Y. He, S. H. Shi, L. H. Wu, G. Z. Wang, J. Colloid Interface Sci. 511, 307 (2018).
- [3] X. F. Zhang, Y. Rao, J. J Guo, G. W. Qin, Carbon 96, 972 (2016).
- [4] N. D. Wu, X. G. Liu, C. Y. Zhao, C. Y. Cui, J. J. Guo, J. Alloys Compd. 685, 50(2016).
- [5] P. J. Liu, Z. J. Yao, J. T. Zhou, Z. H. Yang, L. B. Kong, J. Mater Chem. C 4(41), 9738 (2016).
- [6] G. Z. Wang, X. E. Peng, L. Yu, G. P. Wan, S. W. Lin, Y. Qin, J. Mater. Chem. A 3(6), 2735 (2015).
- [7] L. N. Huang, X. F. Liu, D. Chuai, Y. X. Chen, R. H. Yu, Sci. Rep. 6, 35377 (2016).
- [8] X. S. Qi, J. L. Xu, W. Zhong, Y. W. Du, Mater. Res. Bull. 67, 162 (2015).
- [9] H. B. Zhao, Z. B. Fu, H. B. Chen, M. L. Zhong, C. Y. Wang, ACS Appl. Mater. Interfaces 8(2), 1468 (2016).
- [10] G. P. Wan, G. Z. Wang, X. Q. Huang, H. N. Zhao, X. Y. Li, K. Wang, L. Yu, X. E. Peng, Y. Qin, Dalton T. 44(43), 18804 (2015).
- [11] H. X. Pan, X. W. Yin, J. M. Xue, L. F. Cheng, L. F. Zhang, Carbon 107, 36 (2016).
- [12] G. Z. Wang, G. Ran, G. P. Wan, P. Yang, Z. Gao, S. W. Lin, C. Fu, Y. Qin, ACS Nano 8, 5330 (2014).
- [13] B. Wen, M. S. Cao, M. M. Lu, W. Q. Cao, H. L. Shi, J. Liu, X. X. Wang, H. B. Jin, X. Y. Fang, W. Z. Wang, J. Yuan, Adv. Mater. 26(21), 3484 (2014).
- [14] K. J. Choi, M. Biegalski, Y. L. Li, A. Sharan, J. Schubert, R. Uecker, P. Reiche, Y. B. Chen, X. Q. Pan, V. Gopalan, L. Q. Chen, D. G. Schlom, C. B. Eom, Science **306**(5698), 1005 (2004).
- [15] Y. F. Zhu, Q. Q. Ni, Y. Q. Fu, RSC Adv. 5, 3748 (2015).
- [16] L. Jin, X. M. Zhao, J. F. Xu, Y. Luo, D. Q. Chen, G. H. Chen, RSC Adv. 8(4), 2065 (2018).
- [17] H. N. Lee, H. M. Christen, M. F. Chisholm, C. M. Rouleau, D. H. Lowndes, Nature 433, 395 (2005).
- [18] J. Yang, J. Zhang, C. Y. Liang, M. Wang, P. F. Zhao, M. M. Liu, J. W. Liu, R. C. Che, ACS Appl. Mater. Interfaces 5(15), 7146 (2013).
- [19] Y. F. Zhu, L. Zhang, T. Natsuki, Y. Q. Fu, Q. Q. Ni, ACS Appl. Mater. Interfaces 4(4), 2101 (2012).
- [20] C. Bi, M. F. Zhu, Q. H. Zhang, Y. G. Li, H. Z. Wang, Mater. Chem. and Phys. 126(3), 596 (2011).
- [21] G. P. Wan, L. Yu, X. E. Peng, G. Z. Wang, X. Q. Huang, H. N. Zhao, Y. Qin, RSC Adv. 5(94), 77443 (2015).
- [22] Y. C. Du, W. W. Liu, R. Qiang, Y. Wang, X. J. Han, J. Ma, P. Xu, ACS Appl. Mater. Interfaces 6(15), 12997 (2014).
- [23] C. Y. Liang, Z. J. Wang, ACS Appl. Mater. Interfaces 9(46), 40690 (2017).
- [24] D. Li, H. Y. Liao, H. Kikuchi, T. Liu, ACS Appl. Mater. Interfaces 9(51), 44704 (2017).
- [25] H. X. Tang, Z. Zhou, H. A. Sodano, ACS Appl. Mater. Interfaces 6(8), 5450 (2014).
- [26] K. Hongo, S. Kurata, A. Jomphoak, M. Inada, K. Hayashi, R. Maezono, Inorg. Chem. 57(9), 5413 (2018).
- [27] G. P. Wan, L. Yang, S. H. Shi, Y. L. Tang, X. F. Xu, G. Z. Wang, Chem. Commun. 55(4), 517 (2019).
- [28] G. P. Wan, K. Wang, Y. M. Luo, L. H. Wu, S. H. Shi, Z. Y. He, G. Z. Wang, Fullerenes, Nanotubes and Carbon Nanostructures 26(6), 398 (2018).
- [29] Ö. Kucuk, S. Teber, I. Cihan Kaya, H. Akyildiz, V. Kalem, J. Alloys Compd. 765, 82 (2018).
- [30] J. Q. Qin, Z. L. Zhang, W. J. Shi, Y. F. Liu, H. P. Gao, Y. L. Mao, ACS Appl. Mater. Interfaces 10(42), 36067 (2018).
- [31] G. Z. Wang, Z. Gao, S. W. Tang, C. Q. Chen, F. F. Duan, S. C. Zhao, S. W. Lin, Y. H. Feng, L. Zhou, Y. Qin, ACS Nano 6, 11009 (2012).
- [32] R. C. Che, L. M. Peng, X. F. Duan, Q. Chen, X. L. Liang, Adv. Mater. 16(5), 401 (2004).
- [33] P. Wang, L. F. Cheng, Y. N. Zhang, L. T. Zhang, ACS Appl. Mater. Interfaces 9(34), 28844 (2017).
- [34] G. P. Wan, Y. M. Luo, L. H. Wu, G. Z. Wang, Nanoscale Res. Lett. 13(1), 68 (2018).
- [35] H. Sun, R. C. Che, X. You, Y. S. Jiang, Z. B. Yang, J. Deng, L. Qiu, H. S. Peng, Adv. Mater. 26(48), 8120 (2014).

- [36] J. de Los S. Guerra, M.H. Lente, J.A. Eiras, Appl. Phys. Lett. 88(10), 102905 (2006).
- [37] M. S. Cao, W. L. Song, Z. L. Hou, B. Wen, J. Yuan, Carbon 48(3), 788 (2010).
- [38] G. Z. Wang, Z. Gao, G. P. Wan, S. W. Lin, P. Yang, Y. Qin, Nano Res. 7(5), 704 (2014).
- [39] Q. H. Liu, Q. Cao, H. Bi, C. Y. Liang, K. P. Yuan, W. She, Y. J. Yang, R. C. Che, Adv. Mater. 28(3), 486 (2016).
- [40] B. Wen, M. S. Cao, Z. L. Hou, W. L. Song, L. Zhang, M. M. Lu, H. B. Jin, X. Y. Fang, W. Z. Wang, J. Yuan, Carbon 65, 124 (2013).