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Facile Synthesis of Novel Heterostructure Based on SnO₂ Nanorods Grown on Submicron Ni Walnut with Tunable Electromagnetic Wave Absorption Capabilities

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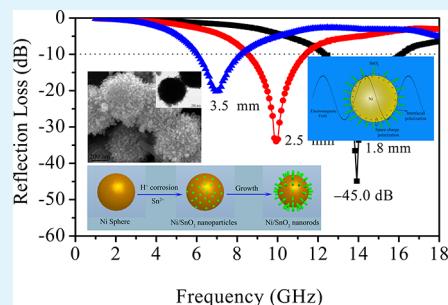
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Supporting Information

ABSTRACT: In this work, the magnetic–dielectric core-shell heterostructure composites with the core of Ni submicron spheres and the shell of SnO₂ nanorods were prepared by a facile two-step route. The crystal structure and morphology were investigated by X-ray diffraction analysis, transmission electron microscopy (TEM), and field emission scanning electron microscopy (FESEM). FESEM and TEM measurements present that SnO₂ nanorods were perpendicularly grown on the surfaces of Ni spheres and the density of the SnO₂ nanorods could be tuned by simply varying the addition amount of Sn²⁺ in this process. The morphology of Ni/SnO₂ composites were also determined by the concentration of hydrochloric acid and a plausible formation mechanism of SnO₂ nanorods-coated Ni spheres was proposed based on hydrochloric acid concentration dependent experiments. Ni/SnO₂ composites exhibit better thermal stability than pristine Ni spheres based on thermalgravimetric analysis (TGA). The measurement on the electromagnetic (EM) parameters indicates that SnO₂ nanorods can improve the impedance matching condition, which is beneficial for the improvement of electromagnetic wave absorption. When the coverage density of SnO₂ nanorod is in an optimum state (diameter of 10 nm and length of about 40–50 nm), the optimal reflection loss (RL) of electromagnetic wave is −45.0 dB at 13.9 GHz and the effective bandwidth (RL below −10 dB) could reach to 3.8 GHz (12.3–16.1 GHz) with the absorber thickness of only 1.8 mm. By changing the loading density of SnO₂ nanorods, the best microwave absorption state could be tuned at 1–18 GHz band. These results pave an efficient way for designing new types of high-performance electromagnetic wave absorbing materials.

KEYWORDS: Ni/SnO₂, core-shell, SnO₂ nanorods, electromagnetic wave absorption, dielectric loss, interfacial polarization



1. INTRODUCTION

Heteronanostructure composites are an important class of materials, which not only derive the properties from their individuals but also probably pave the way to improve the functionality and multifunctional properties due to the interaction between individual constituents.^{1–5} Recently, with the explosive development of electrical and electronic industries in gigahertz frequency, electromagnetic interference (EMI) from the invisible electromagnetic wave used in many fields continues to be a serious issue in society.^{6–9} The unwanted electromagnetic wave cannot only interrupt electronic instruments but also be harmful to human beings.^{10,11} Thus, to settle this invisible and omnipresent pollution, lots of effort has been devoted to exploiting a variety of materials and structures which can be applied as microwave absorbers for stealth or shielding unwanted electromagnetic waves.^{12–15} They can absorb electromagnetic waves effectively and transform electromagnetic energy into heat energy or attenuate electromagnetic waves by interference.¹⁶ There are numerous research papers about microwave absorbing materials in the X-band (8.2–12.4 GHz) with its application in military correspondence satellites, aviation authority, and defense tracking and Ku band (12.5–18

GHz) with its utilization in high-determination imaging radars, broadcast services, and satellite digital data transmission.^{17,18} It is well-known that the electromagnetic wave absorption properties are crucially controlled by the relative complex permittivity ($\epsilon_r = \epsilon' - j\epsilon''$) and permeability ($\mu_r = \mu' - j\mu''$) of absorbing materials.^{19,20} The balance of the permittivity and permeability, called the electromagnetic wave impedance matching, is beneficial for the improvement of microwave attenuation.²¹ According to loss mechanism of microwave energy, microwave absorbing materials could be clarified into two kinds: dielectric loss and magnetic loss.^{12,22} An effective way to reach the impedance matching is to combine magnetic and dielectric materials, which are expected to achieve the excellent microwave absorption because of the cooperative effect on dissipation of electromagnetic wave energy.^{21,23}

In the recent period, there is plentiful research in building composites based on Ni because of high permeability and easy preparation, which show the potential applications in electro-

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magnetic wave absorption application.^{24–36} Tong et al.²⁴ synthesized rambutan-like composites composed of Ni microspheres and oriented multiwall carbon nanotubes (MWCNTS). This heterostructures coated by short MWCNTs exhibited the minimal reflection loss of -37.9 dB occurring at 12.8 GHz. Wang et al.²⁶ prepared flower-like Ni/ZnO through an atomic layer deposition (ALD) method. The ZnO@Ni composite exhibits remarkably enhanced electromagnetic wave absorption properties compared to the pure ZnO. Xu and co-workers²⁷ fabricated the core-shell structured Ni/Polypyrrole composites with enhanced electromagnetic wave absorption. The enhanced electromagnetic absorption of composites is attributed to electromagnetic impedance matching due to the synergistic consequence of Ni cores and polypyrrole shells. In our previous report,²⁸ we designed core-shell composites composed of Ni cores and Al₂O₃ nanoflake shells and investigated electromagnetic wave absorption properties. From these results, it can force us to conclude that the electromagnetic wave absorption properties of Ni-based heterostructure composites can be significantly improved compared with the individual composition, which is assigned to proper impedance originating from combination of dielectric loss and magnetic loss.

As far as we know, there are few reports about the electromagnetic properties of Ni/SnO₂ heterostructure composites.^{29,37} In the earlier literature,³⁷ SnO₂ nanoparticles coated Ni microspheres were successfully synthesized and their microwave properties were also investigated. However, the size of Ni particles is too large, which is close to the skin depth of metal Ni ($\sim 1.0 \mu\text{m}$), and the core-shell structure is ambiguously observed, which is harmful for interfacial polarization. In this work, the novel heterostructure of SnO₂ nanorods grown on a Ni submicron sphere was synthesized by a simple two-step method. The diameter and length of SnO₂ nanorods can be effectively controlled by tuning the amounts of Sn resource, which is critical for determining their microwave absorption properties.

2. EXPERIMENTAL SECTION

2.1. Materials. All chemicals used in this process are commercially available without further purification. Nickel chloride hexahydrate (NiCl₂·6H₂O), glycerol, trisodium citrate dehydrate, and sodium acetate were supplied by Xilong Chemical Reagent Co. Ltd. (Guangdong, China). NaH₂PO₂·H₂O was supplied by Kemiou Chemical Reagent Co. Ltd. (Tianjin, China). Anhydrous ethanol, hydrochloric acid, and SnCl₂·2H₂O were provided from Guangfu Chemical Reagent Technologies Co. Ltd. (Tianjin, China).

2.2. Synthesis of Walnut-Like Ni Particles. The Ni walnut spheres were synthesized according to our earlier literature.³⁴ In brief, NiCl₂·6H₂O (1.2 g), sodium acetate (3.0 g), and trisodium citrate dihydrate (0.2 g) were dissolved in the mixture solution containing glycerol (30 mL) and distilled water (30 mL). Subsequently, 1.6 g of NaOH and sodium hypophosphite (NaH₂PO₂·H₂O, 3.2 g) were in turn introduced into the above mixture. The solution was transferred into an autoclave. The autoclave was heated to 140 °C and kept for 15 h. The final products were collected from the solution.

2.3. Preparation of SnO₂ Nanorods Grown on Ni Particles. The resultant walnut-like Ni spheres were dispersed in the mixture of 40 mL of distilled water and 20 mL of anhydrous ethanol. Then SnCl₂·2H₂O (1 mmol) and hydrochloric acid (4 mL, 0.1 M) were added into the above solution. Then the mixture was shifted into an autoclave and heated to 200 °C for 15 h. The final product was filtered out and rinsed with anhydrous ethanol and distilled water three times. To investigate the influences of the concentration of hydrochloric acid and SnCl₂·2H₂O on the morphologies of Ni/SnO₂ hybrids, a series of comparison experiments were performed. For convenience, the Ni/

SnO₂ composites were prepared at 0.5, 1.0, 1.5, and 2.0 mmol of SnCl₂·2H₂O were denoted as S-1, S-2, S-3, and S-4, respectively.

2.4. Characterization. The X-ray powder diffraction (XRD) pattern of the as-obtained samples was recorded on XD-3 (Beijing Purkinje General Instrument Co. Ltd.). The morphology and microstructures were analyzed by transmission electron microscope (TEM, JEOL JEM-2010) and field emission scanning electron microscopy (FESEM, JEOL JSM-7001F) equipped with energy dispersive X-ray spectroscopy (EDS, Oxford Instruments). The thermal stability of the Ni particles and Ni@SnO₂ is analyzed by thermogravimetric analysis (TGA, STA 409, Netzsch, Germany). TGA is performed on these samples from 25 to 800 °C with a heating rate of 10 °C/min in air flow. The specimen for microwave measurement was prepared by uniformly blending the Ni/SnO₂ absorbents with paraffin-wax in a mass fraction of 50 wt % and then being pressed into a ring-like compact structure (with a 3.04 mm inner diameter, 7.00 mm outer diameter). The relative complex permeability and permittivity of the Ni@SnO₂–paraffin composites were measured by a vector network analyzer (Agilent, N5244A) using the transmission/reflection method.

3. RESULTS AND DISCUSSION

The composition and phase of as-received products were characterized by X-ray diffraction (XRD). Figure 1a shows the

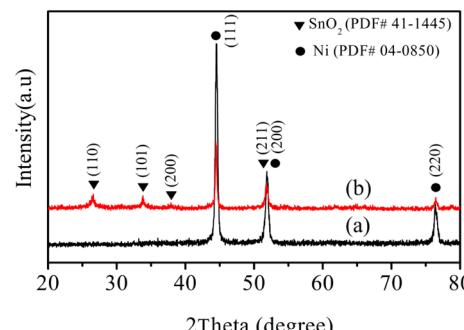


Figure 1. XRD patterns of (a) walnut-like Ni particles and (b) core-shell Ni/SnO₂ composite.

XRD profile of walnut-like Ni powders. The whole diffraction peaks could be well attributed to the face-centered cubic Ni (JCPDS card no. 04-0850). After adding HCl solution (0.1 M) and SnCl₂·2H₂O (1 mmol) into hydrothermal system, the XRD pattern of final products was exhibited in Figure 1b. Besides the peaks associated with the Ni phase, the other peaks could match well with the tetragonal rutile SnO₂ (JCPDs no. 41-1445), which suggests that the composites are composed of Ni and SnO₂ (Figure 1b).

Figure 2a shows the morphology of as-obtained Ni submicron particles. It can be clearly observed that the as-synthesized Ni samples were comprised of monodispersed walnut-like spheres with a mean diameter of 500 nm. The overview morphology of Ni/SnO₂ composite is shown in Figure 2b. Obviously, the Ni particles were coated by a large number of nanoparticles to form a core-shell structured composite and the surface becomes rougher in comparison with raw Ni walnut spheres. Further observation from high magnification photographs of Ni/SnO₂ (Figure 2c,d), one can note that SnO₂ nanorods with the length of 30–50 nm and diameter of 10–20 nm were perpendicularly grown on the surface of nickel spheres and the average size of Ni/SnO₂ composite is about 600 nm. From FESEM images of nickel spheres and Ni/SnO₂ composites, it can draw the conclusion that a novel core–shell heterostructure (SnO₂ nanorods grown

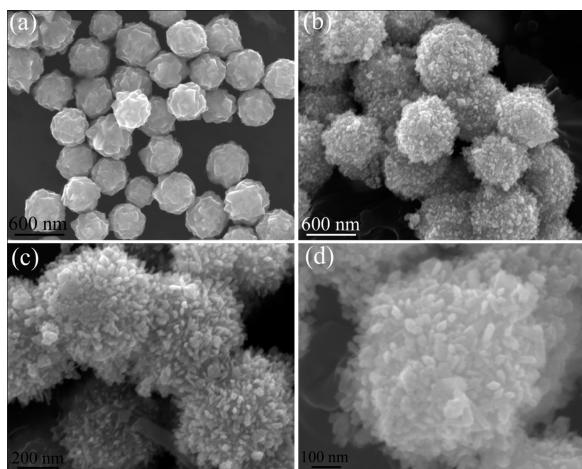


Figure 2. FESEM images of (a) Ni walnut spheres and (b–d) core-shell Ni/SnO₂ composites.

on Ni) was generated when HCl solution (0.1 M) and SnCl₂·2H₂O (1 mmol) were introduced into this reaction system.

To further uncover the composition of heterostructure, the EDS and elemental mappings were performed and the results were shown in Figure 3. From the EDS pattern (Figure 3b) of Ni/SnO₂ composite (mark in Figure 3a), it can be concluded the core-shell composites were made up of Ni, Sn, and O elements. The carbon element is also observed in the EDS profile. The C element is due to the rubberized fabric, which is utilized for pasting the sample. Pt peaks are also observed in the EDS profile because the SEM sample was prepared by sputtering of platinum onto the sample. The element mappings of Ni, Sn, and O are presented in Figure 3c–e, respectively. The elemental distribution is relatively uniform, which illustrates that the SnO₂ nanorods were uniformly grown on Ni particles.

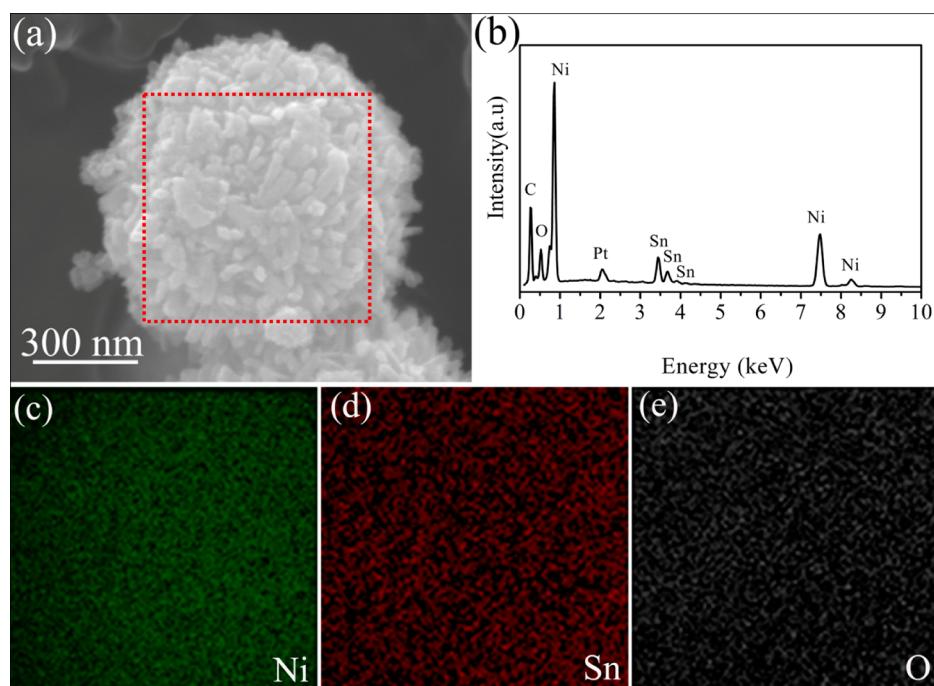


Figure 3. (a) FESEM image of an individual Ni/SnO₂ heterostructure, (b) EDS profile of Ni/SnO₂ composite and (c–e) corresponding elemental mappings of Ni, Sn, and O.

Further detailed structural analysis of core–shell composites was analyzed by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). The TEM image in Figure 4a exhibits that the core–shell

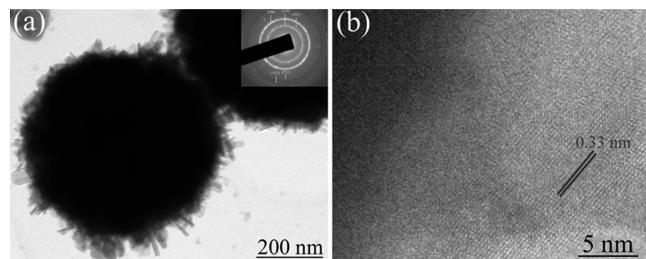


Figure 4. (a) TEM images of the as-prepared core–shell Ni/SnO₂ composites, selected area electron diffraction (SAED) pattern in rim region (inset) and (b) HRTEM of the nanorod in part a.

structured composite could be clearly observed from the obvious different contrast between Ni and SnO₂. Furthermore, close observation from Figure 4a, the core–shell heterostructures were composed of plentiful SnO₂ nanorods grown on the surface of Ni spheres, which coincided with FESEM observations. The corresponding selected-area electron diffraction (SAED) photograph (Figure 4a, inset) signifies that the SnO₂ nanorods are polycrystalline and the diffraction rings from inside to outside are in agreement with (110), (101), (200), (211), and (112) planes of rutile SnO₂, respectively. The lattice fringe spacing in HRTEM pattern was observed to be 0.33 nm (Figure 4b), which fitted well with the (110) planes of a tetragonal rutile structure of SnO₂.

The morphologies of Ni/SnO₂ composites were closely associated with the concentration of HCl in this reaction system. For the sake of investigating the relationship between morphology and concentration of HCl as well as mechanism

formation of SnO_2 nanorods grown on the Ni composite, a series of experiments with different concentrations of HCl (0.05 M, 0.1 M, 0.4 M, 1.0 M) were carried out and the results were shown in Figure 5. From Figure 5a, it can be clearly

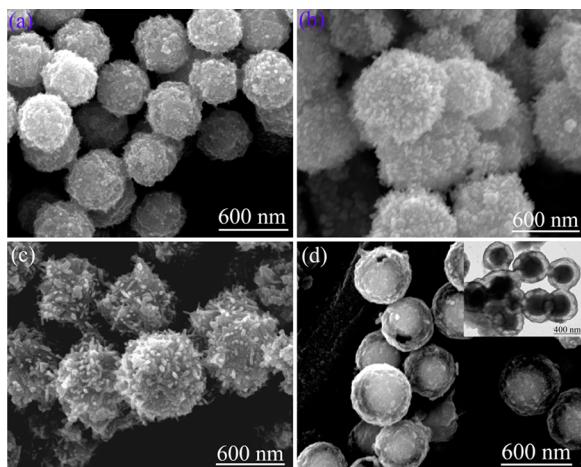


Figure 5. FESEM images of Ni/SnO_2 prepared at different concentrations of HCl: (a) 0.05 M, (b) 0.1 M, (c) 0.4 M, and (d) 1.0 M while other preparation concentrations remained constant. Inset of part d is the TEM image of Ni/SnO_2 prepared at 1.0 M HCl.

observed that the walnut-like Ni spheres were coated by dense plentiful SnO_2 nanoparticles at low concentration of HCl (0.05 M). The unique heterostructures of SnO_2 nanorods grown on Ni were obtained when the concentration of HCl is 0.1 M (Figure 5b), which is in accordance with the above observation (Figure 2). With increasing the concentration of HCl to 0.4 M, notably, the urchin-like Ni/SnO_2 were observed in Figure 5c. The thorn-like SnO_2 nanoparticles were grown on the Ni particles. Interestingly, further increasing the concentration of HCl to 1.0 M, combining Figure 5d and the inset, the novel core–void–shell structured Ni/SnO_2 can be obviously seen. The mechanism of such a structure is not clear and the related works are underway. In this protocol, HCl plays dual roles in forming SnO_2 nanorods grown on the Ni composite. On the one hand, the surfaces of the Ni walnut spheres were corroded by hydrochloric acid, which is beneficial for subsequent nucleation of SnO_2 nanoparticles. On the other hand, the SnO_2 nanoparticles were easily grown to SnO_2 nanorods with the assistance of an acid solution.^{38,39} Too low of a concentration of hydrochloric acid, the SnO_2 nanoparticles are produced on the surface of Ni particles instead of the nanorods. Too high a concentration of HCl induces suppression of the growth of SnO_2 nanoparticles, which also induce high corrosion of Ni. Finally, the voids between Ni and SnO_2 were generated. These

results push us to draw a conclusion that the unique composite of SnO_2 nanorods grown on Ni particles can be obtained in the hydrochloric acid concentration range of 0.1–0.4 M. A plausible formation mechanism of core–shell SnO_2 nanorods/Ni sphere heterostructure was proposed based on hydrochloric acid concentration dependent experiments. As shown in Figure 6, first, the walnut-like Ni spheres were corroded by hydrochloric acid and SnO_2 nanoparticles were deposited on the corrosive Ni spheres.⁴⁰ Second, because of the acid conditions, the deposited SnO_2 nanoparticles are prone to growing into nanorods.³⁹

Figure 7 shows the FESEM images of Ni/SnO_2 composites synthesized at various $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ contents (0.5, 1.0, 1.5, and

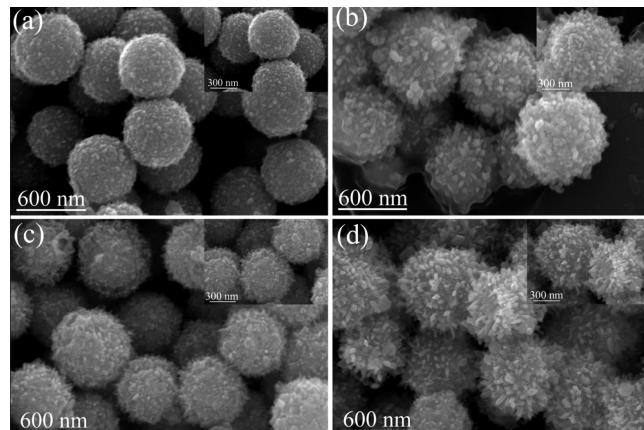


Figure 7. FESEM images of Ni/SnO_2 synthesized at various $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ contents: (a) 0.5 mmol, (b) 1.0 mmol, (c) 1.5 mmol, and (d) 2.0 mmol while other synthesis parameters were kept constant. Insets are the corresponding high-magnification FESEM images.

2.0 mmol) while the other synthesis parameters are kept constant. At low $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ contents (0.5 mmol), the final products (S-1) were composed of uniform dispersed composite spheres, in which the Ni spheres were densely covered by SnO_2 nanoparticles (Figure 7a). When the $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ contents is 1.0 mmol (Figure 7b), the samples (S-2) exhibit the similar morphology with Figures 2–4. When the $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ amounts are increased to 1.5 mmol, it is easily understand that the as-obtained products (S-3) show more dense and rodlike SnO_2 -coated Ni particles (Figure 7c). With further increasing the $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ contents to 2.0 mmol (S-4, Figure 7d), the diameter and length of SnO_2 nanorods grown on the surfaces of Ni spheres were bigger than those of products in Figure 7b. From the above analysis, the morphologies of SnO_2 nanorods, which are grown on the surfaces of Ni spheres, were crucially determined by the $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ content.

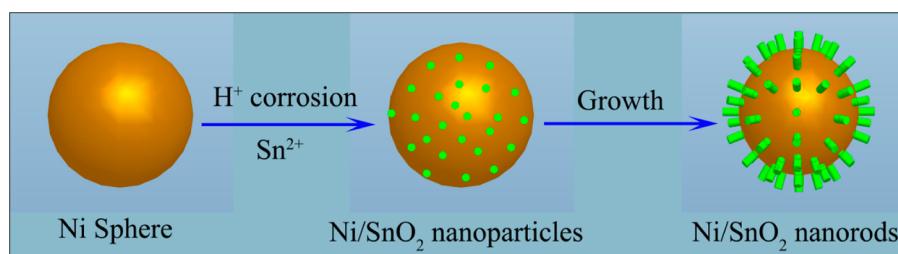


Figure 6. Plausible formation mechanism of core–shell Ni/SnO_2 composites with SnO_2 nanorods grown on Ni spheres.

The Ni/SnO₂ composites prepared at different SnCl₂·2H₂O contents were further analyzed by the TEM instrument, and the results were shown in Figure 8 and Figure S1. From Figure 8

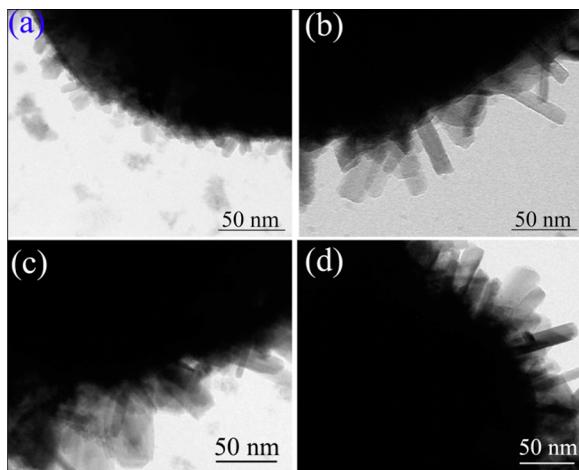


Figure 8. TEM images of Ni/SnO₂ composites prepared at different SnCl₂·2H₂O contents: (a) 0.5 mmol, (b) 1.0 mmol, (c) 1.5 mmol, and (d) 2.0 mmol while the other preparation parameters remained constant.

and Figure S1, notably, all the products obtained at different SnCl₂·2H₂O contents possess the core-shell structure through the different contrast between SnO₂ and Ni. The S-1 sample exhibits that the Ni cores are nearly coated by many SnO₂ nanoparticles with a mean diameter of 10 nm (Figure 8a). Figure 8b exhibits the morphology of products (S-2) obtained at 1.0 mmol of SnCl₂·2H₂O. It can be noted that sparse SnO₂ nanorods with the length and size of about 40–50 and 10 nm were grown on the surfaces of Ni spheres. When 1.5 mmol of

SnCl₂·2H₂O was introduced into this reaction system, the corroded Ni were covered by dense and bigger SnO₂ nanorods with a length and diameter of about 60 nm and 15–20 nm, respectively (Figure 8c). Furthermore, compared with Figure 8b, more dense and uniform SnO₂ nanorods grown on the corrosive Ni spheres can be observed as 2.0 mmol of SnCl₂·2H₂O was added into this reaction process. The length and diameter size of SnO₂ nanorods were about 70 and 20 nm (Figure 8d), respectively.

The electromagnetic wave absorption properties of a material are correlated with their relative complex permeability ($\mu_r = \mu' - j\mu''$) and permittivity ($\epsilon_r = \epsilon' - j\epsilon''$).^{41–43} The frequency dependence of complex permeability and permittivity of four core-shell Ni/SnO₂ composites are measured using a network analyzer. The real permittivity (ϵ') and real permeability (μ') symbolize the storage ability of microwave energy, while the imaginary permittivity (ϵ'') and imaginary permeability (μ'') represent dissipation ability of microwave energy.^{1,16,44} Figure 9 shows the relative complex permeability and permittivity of the core-shell Ni/SnO₂ composites. It was noted that in the whole measured frequency range, ϵ' values are nearly constant with little fluctuation (Figure 9a). Noticeably, the ϵ' values of the S-2 sample are the highest among four core-shell Ni/SnO₂ samples, which suggests the more energy storage and polarization. Figure 9b presents the imaginary parts (ϵ'') of four core-shell Ni/SnO₂ composites. Notably, one can observe that the S-2 sample shows the largest ϵ'' values in the four samples, which indicates the superior dielectric loss. Interestingly, the four samples present the similar trend and multiple peaks on the ϵ'' values, indicating multiple resonances behavior. This resonance behavior is usually correlated with highly conductivity and skin effects,⁴⁵ electronic spin and charge polarizations owing to point effects, and polarized centers.⁴⁶ These phenomena are also clearly observed in our previous reports.^{34,47–49} It mostly comes from the synergistic influence of walnut-like Ni spheres,

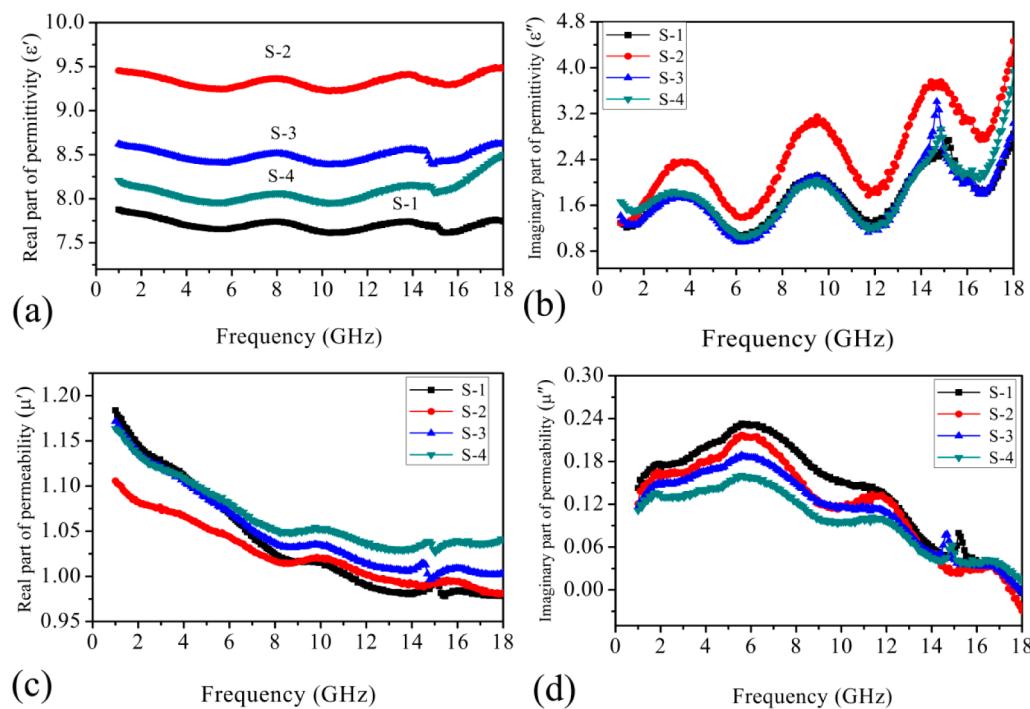


Figure 9. Frequency dependence of (a) the real part (ϵ') and (b) imaginary part (ϵ'') of the complex permittivity, (c) the real part (μ') and (d) imaginary part (μ'') of the complex permeability of four Ni/SnO₂ samples synthesized at different SnCl₂·2H₂O contents.

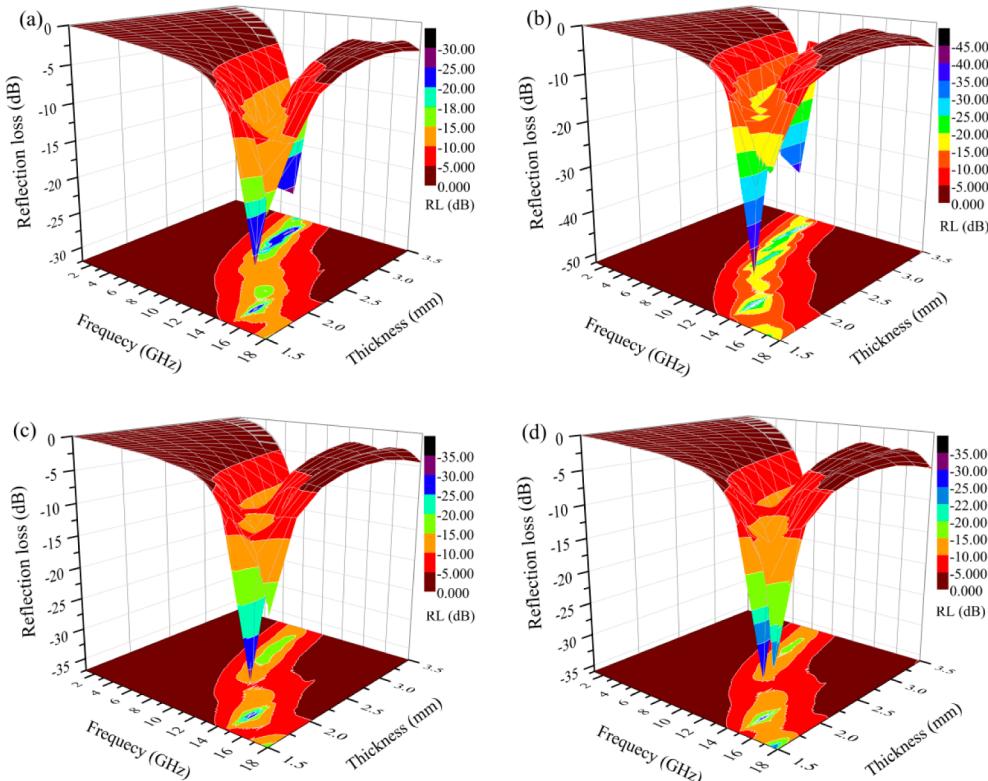


Figure 10. Frequency dependence of simulated reflection loss values of (a) S-1, (b) S-2, (c) S-3, and (d) S-4 samples with various thicknesses.

SnO_2 nanorods, and the interfaces between Ni and dielectric SnO_2 materials. The interfaces can induce additional interfacial polarizations,^{50–53} which is beneficial for the dissipation of electromagnetic wave energy. Moreover, based on the free electron theory,^{27,54} $\epsilon'' \approx 1/\pi\epsilon_0\rho f$, where ρ is the resistivity. The conductivity of the S-2 samples is higher than those of other core-shell Ni/ SnO_2 composite samples. For the S-2 sample, the sparse SnO_2 nanorods grown on Ni spheres can link with each other, and thus a discontinuous microcurrent gradually generates, which will induce high conductivity and cause conduction and electric loss.⁵⁵

The real part (μ') and imaginary part (μ'') values of core-shell Ni/ SnO_2 are shown in Figure 9c,d. Four Ni/ SnO_2 samples exhibit a similar decreased tendency with increasing the measured frequency (Figure 9c). While the μ'' values first increase and then decrease with increasing frequency, it is noteworthy that the complex permeability of four Ni/ SnO_2 composites shows the same trend (Figure 9d). The μ'' presents the broad resonance peaks at 5–7 GHz, which is assigned to the natural resonance of nickel.³² The other existence of resonance peaks are believed to be exchange resonances.^{56–58} This novel heterostructures composed of SnO_2 nanorods grown on Ni spheres combining dielectric loss of SnO_2 , magnetic loss of Ni, and interfacial polarization can possess enhanced electromagnetic wave absorption properties.

In general, the electromagnetic wave absorption properties of absorbers were evaluated by reflection loss (RL value of -10 dB means 90% of microwave absorption). The RL values of an absorbing material can be simulated based on the measured complex permittivity and permeability with a given absorber thickness using the transmit line theory by the following equation:^{21,33,59,60}

$$\text{RL} = 20 \log_{10} |(Z_{\text{in}} - Z_0)/(Z_{\text{in}} + Z_0)| \quad (1)$$

$$Z_{\text{in}} = Z_0 \sqrt{\frac{\mu_r}{\epsilon_r}} \tanh\left(j \frac{2\pi f d \sqrt{\mu_r \epsilon_r}}{c}\right) \quad (2)$$

in which Z_0 is the impedance of free space, Z_{in} is the input characteristic impedance, ϵ_r is the complex permittivity, μ_r is the complex permeability, f is the frequency, c is the velocity of light, and d is the thickness of the Ni/ SnO_2 composites. The calculated reflection loss (RL) curves of the four Ni/ SnO_2 composites with various thicknesses are shown in Figure 10. In the investigated region, the S-2 sample exhibits significantly enhanced electromagnetic wave absorption compared with the other three Ni/ SnO_2 samples. The electromagnetic wave attenuation properties of the Ni/ SnO_2 composites were dependent on the diameter and length of the SnO_2 nanorods. Too dense (Figure 8c,d) and small diameter (Figure 8a) of SnO_2 nanorods were harmful to microwave absorption, which is due to a poor impedance match caused by an unbalance of complex permittivity and permeability. The minimal RL of the S-2 sample is -45.0 dB at 13.9 GHz with the absorber thickness of only 1.8 mm (Figure 10b). The bandwidth (less than -10 dB) can be adjusted in the frequency of 6.0–18.0 GHz by adjusting the thickness to 1.5–3.5 mm. Compared with our earlier publications,^{29,37} there are at least three advantages in this work. First, it is well-known that the microwave absorption properties were closely correlated with the microstructure of absorbers. By decreasing the size of metal Ni that would suppress the eddy current effect is favorable to the enhancement of microwave absorption properties. Moreover, the effect of the special rodlike SnO_2 shell on microwave absorption was also analyzed. Second, to evaluate the microwave absorption, it is not only based on the minimal

reflection loss but some other factors, such as thickness and bandwidth should be also considered. In comparison with a SnO₂-coated Ni microsphere,³⁷ the SnO₂ nanorods grown on Ni composite shows the minimal reflection loss of -45.0 dB at 13.9 GHz with a thickness of only 1.8 mm, whereas the composite exhibits the minimal reflection loss of -42.8 dB at 9.8 GHz with a thickness of 3.0 mm. Furthermore, the bandwidth (RL less than -10 dB) of SnO₂ nanorods grown on Ni composite can reach 3.8 GHz (12.3–16.1 GHz) with an absorber thickness of 1.8 mm, which is superior to SnO₂-coated Ni microsphere composite with a bandwidth of 3.4 GHz (8.3–11.7 GHz) with a thickness of 3.0 mm. From these views, the SnO₂ nanorods grown on show the enhanced microwave absorption properties with the features of high efficiency absorption, thin thickness, and wide-band. Third, the unique one-dimensional SnO₂ rods can bring about an additional loss mechanism. The SnO₂ nanorods are supposed to be considered as an antenna receiver to allow more microwaves to enter the interior of the absorber. The discontinued microcurrent, which was caused when the SnO₂ nanorods were placed under the radiation of electromagnetic wave, can dissipate electromagnetic energy effectively. Notably, the reflection loss peaks gradually shifted to higher frequencies with decreasing absorber thickness, which could be well addressed by the geometrical effect.^{24,61,62} As for the geometrical effect, it takes place when the reflected and incident waves in the absorbers are out of phase 180°, which is closely related to the thickness (*d*) of the absorbers. The relationship between *d*_m and *f*_m is given by the following equation $d_m = (nc/(4f_m(\mu_r\epsilon_r)^{1/2}))$ (*n* = 1, 3, 5,...). It can also deduce that the location of minimal peaks is inversely proportion to the absorber thickness.

In this heterostructure of SnO₂ nanorods grown on the surface of Ni spheres, SnO₂ nanorods play at least three roles in ameliorating electromagnetic wave absorption properties. First, introducing SnO₂ into this system can tune the complex permittivity of Ni/SnO₂ composites to improve the impedance match. Second, the core-shell structure between nickel and SnO₂ can cause additional space charge polarization and interfacial polarization, as shown in Figure 11, which is beneficial for enhancing microwave absorption. Third, the SnO₂ nanorods are supposed to be considered as an antenna receiver to allow more microwaves to enter the interior of the absorber.^{55,63} The discontinues microcurrent, which was caused

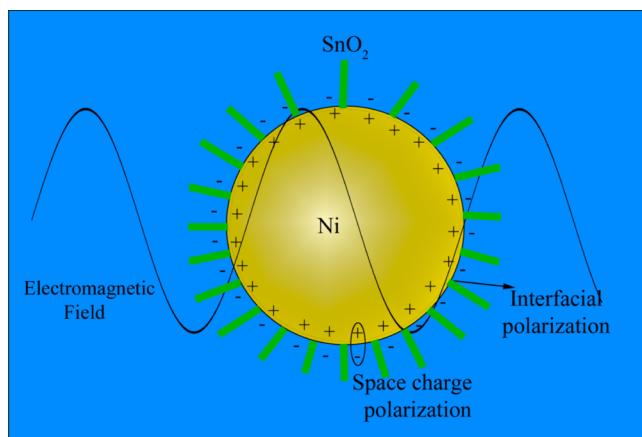


Figure 11. Schematic illustration of the interaction of electromagnetic waves with a core-shell dielectric-magnetic Ni sphere@SnO₂ nanorods composite.

when SnO₂ nanorods were placed under the radiation of electromagnetic wave, can dissipate electromagnetic energy effectively.^{51,64,65}

To apply the electromagnetic wave absorbing materials in harsh conditions (such as high temperature), one important property of thermal stability should be considered.⁶⁶ Figure 12

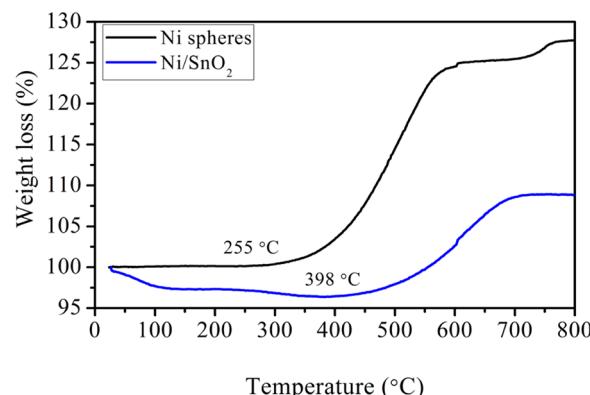


Figure 12. TGA curves of Ni spheres and core-shell structured Ni/SnO₂ (S-2) samples.

shows the thermal stability of Ni spheres and a core-shell composite (S-2) of SnO₂ nanorods grown on the Ni sphere. From Figure 12, both Ni spheres and Ni/SnO₂ composite exhibit a clear weight gain in the final stage because of the oxidation in air at increasing temperature. Notably, the weight of the Ni spheres starts to increase at ~255 °C. After corrosion and growth of SnO₂ nanorods, the Ni spheres are protected and the oxidation temperature reaches to ~398 °C. These results indicate the thermal stability of Ni/SnO₂ is superior to that of Ni spheres due to the presence of a protective SnO₂ nanorod shell.

4. CONCLUSION

In summary, SnO₂ nanorods grown on Ni novel core-shell composites were obtained via a facile two-step method. The morphology and microstructure of Ni/SnO₂ composites are crucially determined by the concentration of hydrochloric acid. Otherwise, on the basis of the hydrochloric acid concentration dependent experiments, a reasonable formation mechanism of such SnO₂ nanorods grown on Ni composites were proposed. The diameter and length of SnO₂ nanorods can be tailored by control of SnCl₂·2H₂O. The electromagnetic absorption properties of the core-shell structured Ni/SnO₂ sample (S-2, SnO₂ nanorods with the diameter of 10 nm and length of about 40–50 nm) prepared with 1.0 mmol of SnCl₂·2H₂O exhibits excellent electromagnetic absorption. The optimal reflection loss (RL) is -45.0 dB at 13.9 GHz and RL less than -10 dB is 3.8 GHz (12.3–16.1 GHz) with only a thickness of 1.8 mm. This novel core-shell structured Ni-SnO₂ nanorods can be used as a promising electromagnetic wave absorber with the features of thin-thickness, high efficient absorption, and a wide-band.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b05482.

TEM images of Ni/SnO₂ composites (PDF)

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Notes

The authors declare no competing financial interest.

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