

Research Article

Preparation and Microwave Absorbing Properties of an Electroless Ni-Co Coating on Multiwall Carbon Nanotubes Using $[\text{Ag}(\text{NH}_3)_2]^+$ as Activator

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Ni-Co-coated carbon nanotubes (CNTs) composites with different molar ratios of Ni/Co were synthesized using $[\text{Ag}(\text{NH}_3)_2]^+$ as activator and H_2PO_2^- as reductant, thereby replacing the conventional noble metal Pd salt activator and Sn^{2+} reductant. Scanning electron microscopy, X-ray diffraction, and X-ray energy dispersive spectrometry analyses demonstrated that the CNTs were deposited with a dense, uniform Ni-Co coating. The possible mechanism of the electroless method was studied, which indicates that pure Ag^0 acted as a nucleation site for subsequent Ni-Co-P deposition. Network vector analyzer measurements indicated that the composite with only Ni coated had an absorbing value of -12.6 dB and the composite with a Ni/Co ratio of four had the maximum wave absorption (-15.6 dB) and the widest absorption bandwidth (800 MHz, $\text{RL} < -10$ dB), while the saturation magnetization (Ms) was $4.28 \text{ emu}\cdot\text{g}^{-1}$ and the coercive force (Hc) was 31.33 Oe .

1. Introduction

Carbon nanotubes (CNTs), discovered by Iijima [1], have attracted considerable attention due to their perfect structure and outstanding mechanical, electrical properties [2–4]. However, their magnetic properties are not ideal, which limits their extensive application in electromagnetic energy dissipation field, especially in the microwave absorption field. Consequently, it is necessary to improve their magnetic and dielectric properties with electroless magnetic metal plating [5, 6] so as to make CNTs excellent microwave absorbing materials.

Electroless plating is a surface modification method, by which metallic ions were changed into metals under the catalytic activation of the substrate surface and are deposited on the substrate surface without an external current [7]. Considering the good conductivity, chemical stability, and unique one-dimensional structure of CNTs, they were chosen as the substrate of electroless plating. Besides, CNTs composites are light weight and high temperature resistant. In the case of a nonmetallic substrate, such as CNTs, the key to electroless plating lies in activating the substrate and

coating a catalytic metal layer on the substrate surface [8]. Palladium has been employed as an activator for many years [9]. Using SnCl_2 - PdCl_2 as sensitization-activation solution [10], the stannous ions adsorbed by the physical adsorption of the substrate surface reduce the palladium ions to metallic palladium seeds, which can then act as catalytic nuclei for subsequent metal electroless deposition [11]. The palladium activation method is costly [12] and has low efficiency and a risk of contamination.

In this paper, considering that Ag particles have strong oxidability [13, 14] and can also be used as catalysts of an electroless plating reaction [15, 16], we developed a low-cost and low-pollution palladium-free activation process: acidulated multiwalled carbon nanotubes (MWCNTs) were activated with silver ammonia solution and then the adsorbed silver ions were reduced to silver seeds by sodium hypophosphite solution. Silver seeds will catalyze succedent nickel-cobalt alloy deposition on the MWCNTs. The key work lies in the investigation of the effect of the molar ratio of nickel-cobalt on the magnetic properties and microwave absorbing properties of composites. Besides this, the electroless mechanism was studied to some extent.

TABLE 1: Composition of nickel-cobalt plating solution.

Compose	Chemicals	Content (g·L ⁻¹)
Main salt	NiSO ₄ ·6H ₂ O	4.5–18.2
Main salt	CoSO ₄ ·7H ₂ O	8.2–19.4
Reductant	NaH ₂ PO ₂	18.2
Complexing agent	Na ₃ C ₆ H ₅ O ₇ ·H ₂ O	41.3
Buffering agent	(NH ₄) ₂ SO ₄	23.1
Acidity	pH	9

2. Materials and Methods

2.1. Pretreatment of MWCNTs. MWCNTs (Nanoport Co., Ltd., Shenzhen, China) with 10–30 nm diameters, 5–15 μm length, and a purity higher than 98% were roasted in a muffle furnace at 500 °C for 2 h; they were then stirred in a mixed acid solution of concentrated sulfuric and nitric acid (1 : 3 by volume) at 80 °C for 2 h. Afterward, the MWCNTs were rinsed in distilled water several times until the pH value reached neutral and were then dried at 80 °C for further use.

2.2. Activation of Pretreated MWCNTs. Silver ammonia solution was first prepared by dropping dilute aqua ammonia into 20 g/L silver nitrate solution until the solution changed from turbidity to clarity. Then, the pretreated MWCNTs were added to the silver ammonia solution, sonicated for 0.5 h, and stirred at 80 °C for 0.5 h after adding 25 g/L sodium hypophosphite solution to the mixture just mentioned. Finally, the activated solution was filtered and the residue was rinsed in distilled water until the pH value reached neutral and was then dried at 70 °C for 8 h for further use.

2.3. Electroless Ni-Co Alloy Deposition on MWCNTs. Figure 1 shows the procedure used for the preparation of Ni-Co plated MWCNTs; Table 1 shows the composition of the nickel-cobalt plating solution. NiSO₄·6H₂O, CoSO₄·7H₂O ($n_{\text{Ni}} : n_{\text{Co}} = 4 : 1, 3 : 2, 1 : 1, 2 : 3$), Na₃C₆H₅O₇·H₂O, and (NH₄)₂SO₄ were dissolved in distilled water of different volumes, respectively, orderly added to a certain quality of activated MWCNTs (the ratio of Ni-Co particles to MWCNTs was 9 : 1), and sonicated for 0.5 h; sodium hypophosphite solution was finally added, and ultrasonic treatment was continued for 20 min. Afterward, the mixture was stirred at a medium speed at 80 °C for 1 h. During the entire reaction, the pH value was adjusted to 9 with aqua ammonia and sodium hypophosphite solution being added until the solution no longer bubbled. Finally, the solution was filtered and the residue was rinsed in distilled water until the pH value reached neutral and was then dried for 8 h at 80 °C; samples were marked as A, B, C, and D. The Ni-MWCNTs composite was prepared in a similar manner and marked as E.

2.4. Characterization. The surface morphology and elemental composition of the coating were determined by scanning electron microscopy (SEM) and an X-ray energy dispersive spectrometer (EDS). The phase structure was analyzed by X-ray diffraction (XRD). The magnetic property was measured

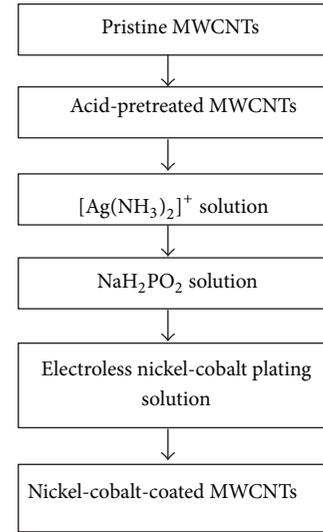


FIGURE 1: Procedure for preparation of nickel-cobalt-coated MWCNTs.

at room temperature using a vibration sample magnetometer (VSM) with a maximum field of 10 kOe. The absorbing property was detected by a Network Vector Analyzer.

3. Results and Discussion

3.1. Morphology Analysis. Figure 2 depicts the SEM micrographs of MWCNTs before and after electroless plating. The pristine MWCNTs are highly entangled (Figure 2(a)); the black dots on the surface of the MWCNTs were expected to be graphite, metallic catalyst particles, and amorphous carbons. After acid treatment, the black dots were completely removed; long MWCNTs were cut off; the caps of MWCNTs were opened and etched off (Figure 2(b)). The surface of the activated MWCNTs appeared to be coated with many uniform and white silver particles (Figure 2(c)), implying that the $\text{Ag}(\text{NH}_3)_2^+$ activator can also form well-distributed active centers. Figure 2(d) was only the Ni-coated composite, which had a netty structure. As observed from the images of the Ni-Co-coated MWCNTs with a different molar ratio of nickel-cobalt, apparently, MWCNTs were completely covered with uniform and continuous alloy particles. Ni-Co grew into sphericity along active centers and formed metal nanofibers, which took carbon nanotubes as the core (Figures 2(e) and 2(f)). In particular, from Figure 2(g), we can see different radial nickel and cobalt atoms clusters getting together and forming a dense coating. Meanwhile, with the increase of Co content, the size of the Ni-Co particles gets bigger from 400 nm (Figure 2(e)) to 1 μm (Figure 2(g)).

3.2. Schematic Procedure of Preparation of Nickel-Cobalt-Coated MWCNTs. Figure 3 depicts the schematic procedure. In the process of electroless, the MWCNTs act as a one-dimensional template for Ni-Co deposition. At the same time, because of its outstanding conductivity, it can also enhance the property of composites. The whole nickel-cobalt

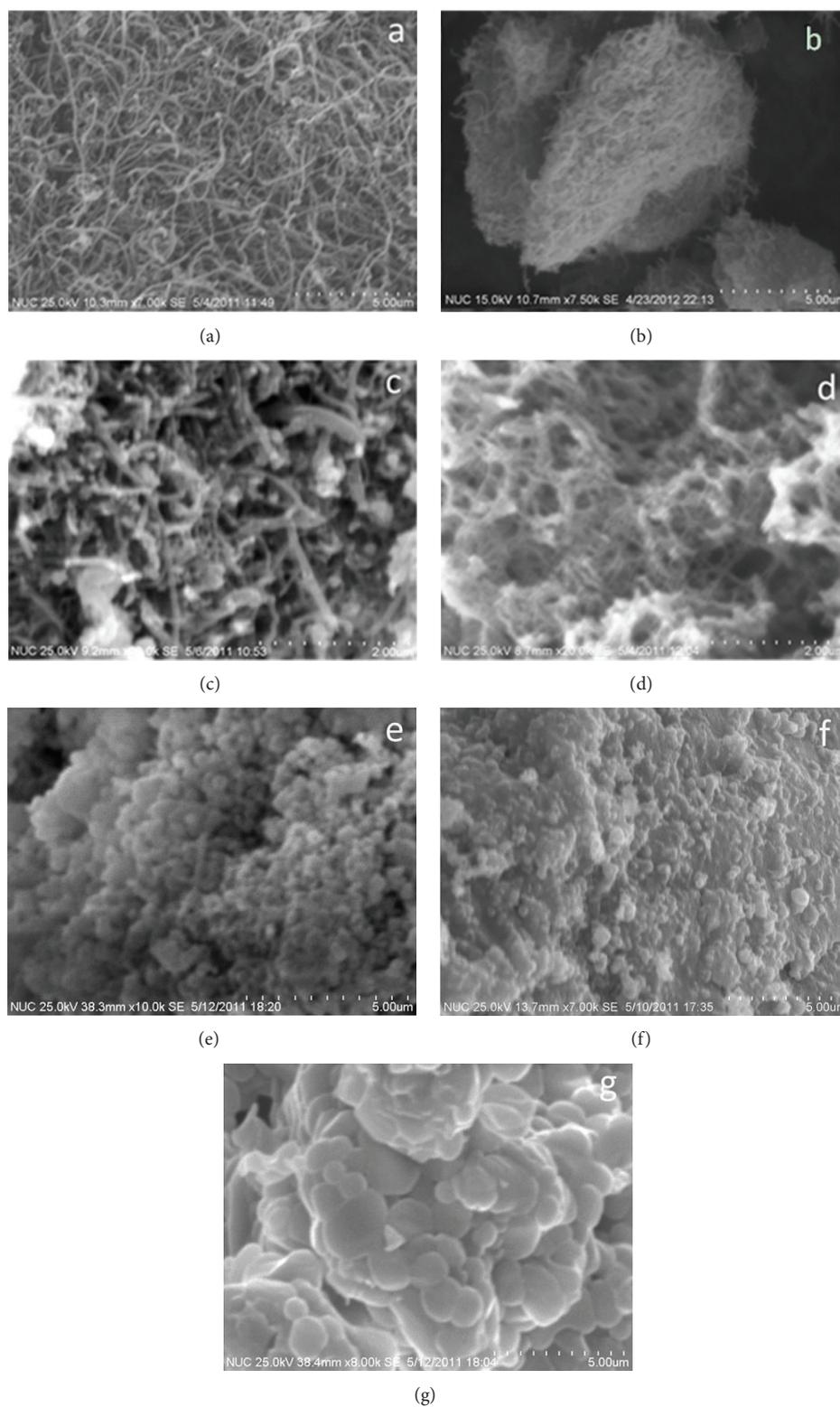


FIGURE 2: SEM micrographs of MWCNTs before and after coated (a) pristine MWCNTs; (b) acid-pretreated MWCNTs; (c) activated MWCNTs; (d) Ni-MWCNTs; (e) Ni_8Co_2 -MWCNTs; (f) Ni_5Co_5 -MWCNTs; (g) Ni_4Co_6 -MWCNTs.

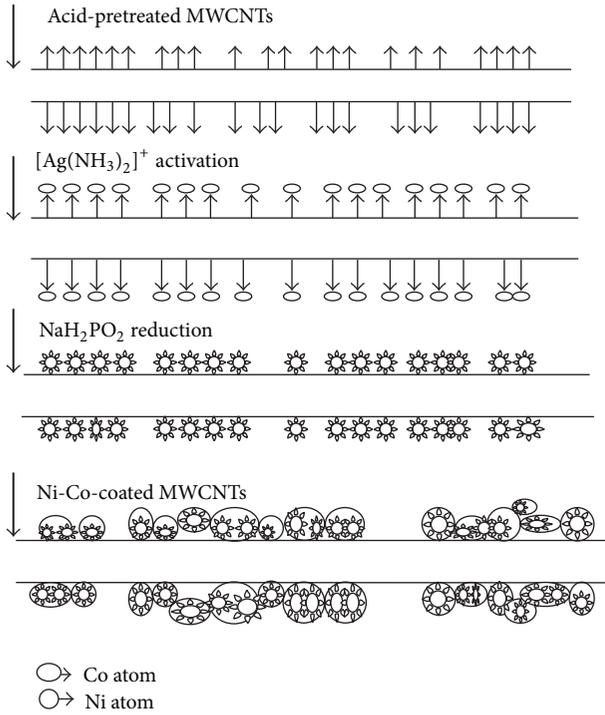
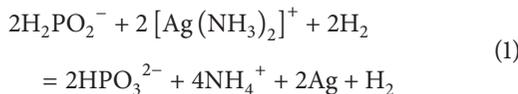


FIGURE 3: Schematic of electroless Ni-Co alloy-coated MWCNTs.

plating process consisted of four steps. After acid treatment, the caps of MWCNTs were etched off and the MWCNTs were activated with more oxidized functional groups, such as carboxylic groups and hydroxyl groups, which can improve the dispersion, water-solubility, and activity of MWCNTs in the electroless solution (step 1).

$\text{Ag}(\text{NH}_3)_2^+$ ions were adsorbed on the MWCNTs surface with considerable OH^- ions forming an $\text{Ag}(\text{NH}_3)_2\text{OH}$ complex by an electrostatic interaction (step 2). Immersing MWCNTs into NaH_2PO_2 solution, H_2PO_2^- will reduce the adsorbed $\text{Ag}(\text{NH}_3)_2^+$ ions into Ag particles as active centers being uniformly distributed on the MWCNTs surface [17]. In alkaline condition, the standard electrode potential of $\text{HPO}_3^{2-}/\text{H}_2\text{PO}_2^-$ couple is -1.57 V , while $\text{Ag}(\text{NH}_3)_2^+/\text{Ag}$ is $+0.373\text{ V}$. The standard battery electromotive force of such electrode couples is positive value [$\Delta E^\circ = +0.373\text{ V} - (-1.57\text{ V}) = 1.943\text{ V}$]; therefore, the reaction is spontaneous, and the equation is as follows (step 3):



Under the catalytic action of Ag, complex Ni^{2+} and Co^{2+} ions in the plating solution are changed into Ni and Co particles and deposited onto the surface by capturing electrons furnished by the reductant (H_2PO_2^-) by the following reactions [18]:

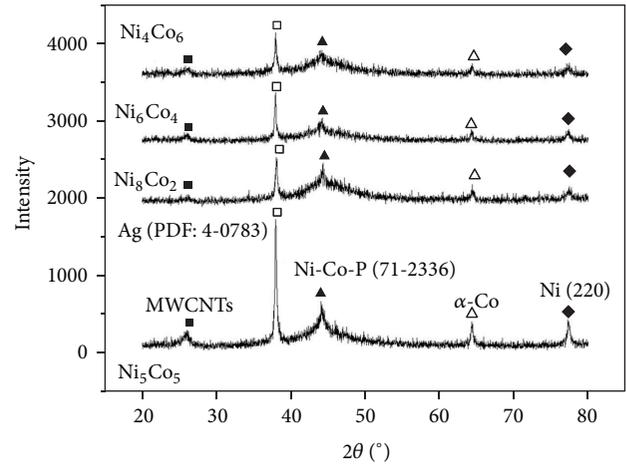
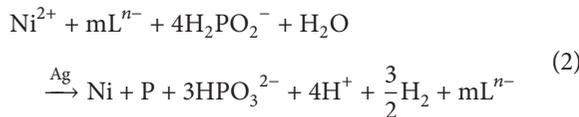
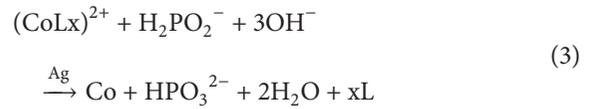
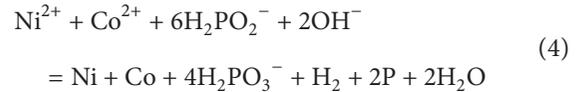


FIGURE 4: XRD patterns of different samples.



L stands for a complexing agent, and the overall reaction can be written as follows:



The deposited Ni and Co atoms then can act as self-catalysts for obtaining a well-developed Ni-Co coating. With the decrease in the Ni^{2+} and Co^{2+} ion concentration, fewer bubbles are released, implying that the reaction is gradually slowing down. In order to obtain a compact and continuous coating, we need to add an electroless solution and adjust the pH value constantly.

3.3. X-Ray Diffraction Analysis and EDS Analysis. Figure 4 depicts the XRD patterns of nickel-cobalt-coated MWCNTs composites without heat treatment. It was found that the molar ratio of nickel-cobalt influenced the intensity of only some peaks. A broad peak at about $2\theta = 45^\circ$ was assigned to the Ni-Co-P amorphous diffraction peak, which indicated that the Ni-Co-P plating was amorphous under the electroless state. The amorphous peak was the most obvious and the sharpest when the molar ratio of nickel-cobalt was 1:1. Diffraction peaks at $2\theta = 77.22^\circ$, 64° , 38.2° were attributed to Ni (220), α -Co, and Ag (111) (PDF: 4-0783) in each pattern. An intense Ag diffraction peak demonstrated the formation of many active centers on the surface of the MWCNTs, which were critical to the later electroless plating. Additionally, for the Ni-Co-MWCNTs composites, a diffraction peak assigned to the (002) plane of the MWCNTs at 26.1° has been less obvious, implying that the MWCNTs were completely coated by the Ni-Co alloy.

Figure 5 displays EDS spectra of the electroless MWCNTs, which mainly showed Ni and Co peaks. The element of Au plating on the surface can strengthen the

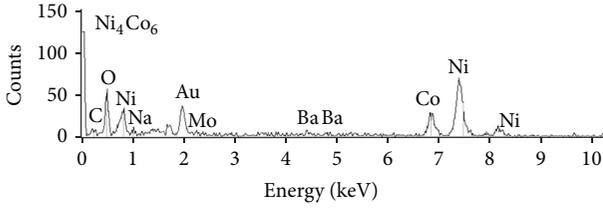


FIGURE 5: EDS spectra of Ni-Co alloy-coated MWCNTs.

reflectivity of the signal in the process of scanning. The contents of Ni and Co were 41.2 and 15.82 wt.%, which demonstrated that the main matter of coating was the Ni-Co alloy. The intense O peak indicated that the surface of the MWCNTs was sufficiently oxidized; the appearance of the weak C peak was attributed to a thin coating.

3.4. Magnetic Property Analysis. Figure 6 shows the hysteresis line of the Ni-Co-coated MWCNTs composites. Table 2 lists the main magnetic properties of different samples. As observed in the table, Ni-Co-coated MWCNTs had more excellent magnetic properties than pristine MWCNTs and Ni-Co alloy without MWCNTs. With an increase of Co content, saturation magnetization (Ms) was gradually enhanced and coercive force (Hc) was typically improved. Co is a densely hexagonal structure and has a great magnetic crystal anisotropic constant K and a magnetostrictive coefficient λ_S , which make the coercive force increase. In addition, the atomic magnetic moment of Co is larger than that of Ni; the increase in Co content is helpful in improving the saturation magnetization (Ms) [19].

3.5. Microwave Absorbing Analysis. The Ni-Co-P-coated MWCNTs composite is a kind of microwave absorbing material which has both hysteresis losses and electric loss. The reflection loss can be defined by the loss tangent ($\tan \delta$), which includes dielectric loss tangent and magnetic loss tangent [20]. Their relationship can be explained by the following formulas:

$$\begin{aligned} \tan \delta \epsilon_\gamma &= \frac{\epsilon_\gamma''}{\epsilon_\gamma'}, \\ \tan \delta \mu_\gamma &= \frac{\mu_\gamma''}{\mu_\gamma'}, \\ \tan \delta &= \tan \delta \epsilon_\gamma + \tan \delta \mu_\gamma = \frac{\epsilon_\gamma''}{\epsilon_\gamma'} + \frac{\mu_\gamma''}{\mu_\gamma'}. \end{aligned} \quad (5)$$

Here, ϵ_γ and μ_γ are the complex relative permittivity and complex relative permeability, respectively. Electromagnetic parameters (ϵ_γ' , ϵ_γ'' , μ_γ' , and μ_γ'') are the real part and imaginary part of relative permittivity and relative permeability, respectively. In this work, both the loss tangent and reflection loss are measured by the Network Vector Analyzer. The composite was mixed with paraffin in the mass ratio of 7 : 3; meanwhile, the absorbing layer thickness was 3 mm. As observed from

TABLE 2: The magnetic properties of different samples.

Sample	Hc/Oe	Ms/emu·g ⁻¹	Mr/emu·g ⁻¹
Ni-Co alloy without MWCNTs	11.09	3.21	0.27
Pristine MWCNTs	32.21	0.56	0.06
Ni ₈ Co ₂	31.33	4.28	0.56
Ni ₆ Co ₄	48.56	8.99	0.81
Ni ₅ Co ₅	66.74	12.74	1.06
Ni ₄ Co ₆	85.21	15.89	1.15

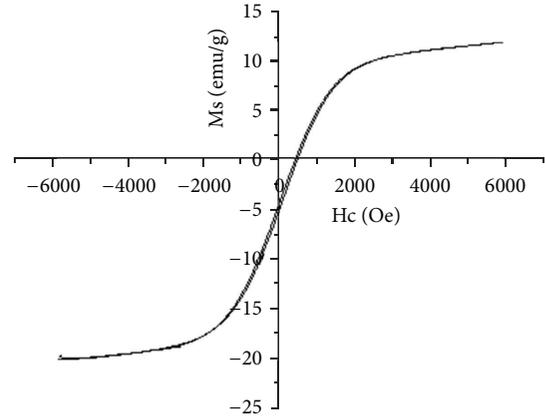


FIGURE 6: Hysteresis line of the composites.

Figures 7 and 8, the order of the dielectric loss tangent was $A > C > E > D > B$, while the magnetic loss tangent was $B > A > D > C > E$. As depicted in Figure 9, the reflection loss of sample A was the largest (-15.6 db); next was that of the ordinal samples E (-12.6 db), C (-9.8 db), B (-9.6 db), and D (-6 db). The frequency range of the attenuation peak was 3000 MHz–5500 MHz; the bandwidth (RL < -5 db) of sample E was the largest (1.8 GHz), with B (1.7 GHz), A (1.5 GHz), C (1.2 GHz), and D (0.8 GHz) successively; the bandwidth (RL < -10 db) of samples A and E was 800 MHz and 400 MHz, respectively. Ni-Co-coated MWCNTs composites displayed stronger wideband microwave absorbing properties, and the possible reason was as follows: the surface of the MWCNTs consisted of coated metal nanoparticles, which possessed magnetism and microwave absorbing abilities of general nanoparticles. Coupling between the microwave field and internal magnetic field of the nanoparticles caused magnetic resonance absorption; magnetic particles were magnetized in an alternating magnetic field and produced a certain magnetic flux density, whose change produced magnetic induced electromotive force and eddy current, thus resulting in an eddy current loss. In addition, the magnetic lag effect also caused a part of electromagnetic energy loss.

4. Conclusions

The surface of acid-treated MWCNTs was coated with a dense and uniform Ni-Co plating by utilizing $\text{Ag}(\text{NH}_3)_2^+$ as an activator replacing a conventional, costly, and polluttional Pd (II) activator. Results implied that coercive force (Hc)

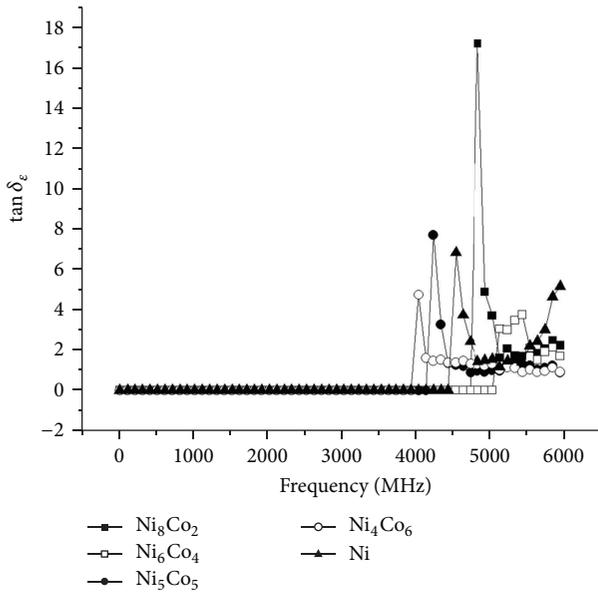


FIGURE 7: Dielectric loss tangent of different samples.

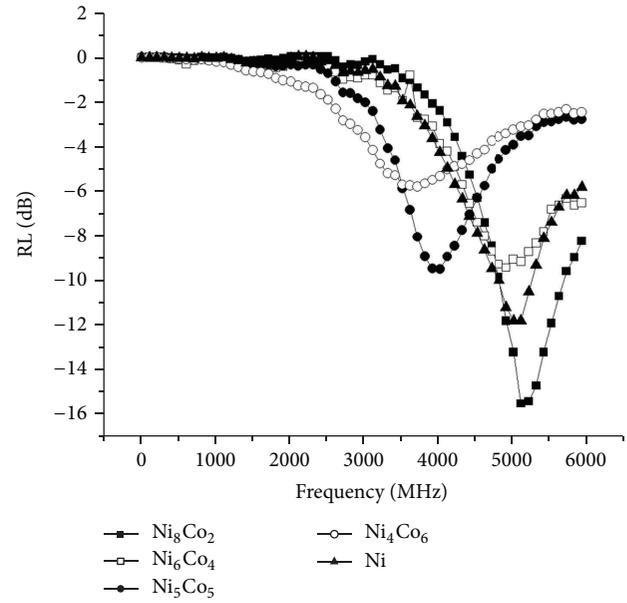


FIGURE 9: Reflection loss of different samples.

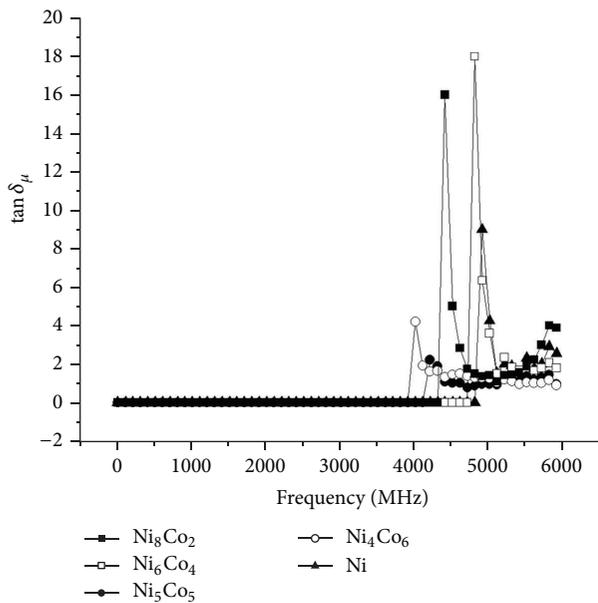


FIGURE 8: Magnetic loss tangent of different samples.

and saturation magnetization (M_s) were gradually enhanced with the increase of Co content; the molar ratio of nickel-cobalt influenced the intensity of only some peaks. The Ni_8Co_2 composite possessed the best microwave absorption (-15.6 dB) in the lower frequency range (0–6000 MHz) owing to its better dielectric loss tangent and magnetic loss tangent and the frequency bandwidth ($RL < -10$ db) was also the largest (800 MHz). The electroless mechanism was studied to some extent, indicating that pure Ag^0 acted as a nucleation site for subsequent Ni-Co-P deposition.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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