Research Article

Nickel–carbon composite plating using a Watts nickel electroplating bath

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Abstract
Metal–carbon composite platings have potential applications in various fields. We previously reported the preparation of nickel–nanocarbon composite platings using a Wood's bath. The maximum carbon content was 1.2 mass%, but the maximum current efficiency of plating was 12%. The present study focuses on improving the current efficiency of the electroplating process used to prepare nickel–carbon black composites in a Watts bath contained carbon black. The microstructure and carbon content in the nickel plating were evaluated. The current efficiency was greater than 90%, but the carbon content of the composite plating layer was approximately 0.6 mass%. The incorporation of carbon black particles into the plating layer was influenced by the adsorption of particles onto the cathode surface, the supply of particles to the surface, and the electrodeposition rate. The carbon content in the plating layer was highest near the cathode surface and decreased with increasing thickness of the plating layer. The grain size of electrodeposits with carbon black was larger than that of deposits without carbon black. The space between grains was increased with increasing grain size. The corrosion resistance was diminished, indicating that the boundary was the originating point of corrosion.

Keywords Carbonous nanomaterials · Composite plating · Wet process · Electroplating

1 Introduction

Nickel is an important element for surface treatment, and it is used to plate accessories, vehicle parts, and building materials. It can also coat resins and other organic materials via the electroless plating method, where it is typically deposited as a nickel–phosphorus alloy or nickel–boron alloy. In the electroplating method, a Watts bath is generally used for various applications and products. Meanwhile, a Wood's bath is usually used when the substrate is stainless steel, nickel alloy, or other metals that form an oxide layer that inhibits the adhesion of materials. Composite plating is a useful technique that can increase the hardness, abrasion resistance, and lubricity through composite formation of a metal coating and fine particles of materials such as silicon carbide [1], alumina [2], boron nitride [3], and polytetrafluoroethylene [4, 5]. Carbon is a stable and highly conductive material. These composites are expected to exhibit both high corrosion resistance and good conduction. Carbon nanotubes, nanodiamond, and carbon black are the major reinforcement materials, and nickel–carbon composites have unique mechanical and electrical properties, especially high hardness, high elasticity, and a low widely adjustable friction coefficient for mechanical properties [6–8]. Applications for such composites have focused on hardness and thermal conductivity of carbon materials. On the other hands, utilization of electrical properties of carbon materials receives interest

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for electrode of battery and electromagnetic shielding materials [9–12].

Several research groups have proposed and verified the co-deposition mechanism. A two-step adsorption process is one of the most widely accepted and useful mechanisms [13]. In the case of nickel–carbon nanotube co-deposition, nickel was reduced on the ends and/or defects of carbon nanotubes and the deposits grew as spherical clusters of electrodeposited nickel [14]. The surface character of the carbon materials was modified by certain processes such as hard treatment, plasma irradiation, mixed-acid cleaning, and dispersant addition [15–18].

In a previous study, we produced a nickel–carbon black composite using a Wood's bath. The carbon content reached 1.2 mass%, but the current efficiency was quite low [19]. In the present study, we investigated the optimum condition and prepared a nickel–carbon black composite using galvanostatic electrolysis with a Watts bath for improving the current efficiency and surface morphology. Adsorption of the particles onto the surface, the supply of particles to the surface, and the reduction rate of metal on the surface are important factors in production of a composite layer during the plating process. The carbon content in the composite plating, surface morphology, and the corrosion resistance were also analyzed.

2 Materials and methods

A Watts-type bath containing 45 g L^{-1} nickel chloride hexahydrate, 240 g L^{-1} nickel sulfate, and 30 g L^{-1} boric acid was used as the electrolyte. The electrolyte pH was adjusted to 4.5 using sodium hydroxide. The carbon black was Vulcan XC 72R produced by CABOT. The carbon black was soaked in 10 vol% sulfuric acid solution to remove impurities. The purified carbon black was collected and rinsed with deionized water. It was ground in a mortar with a pestle after drying in an oven. The purified carbon black was added to the electrolyte, and the resultant mixture was sonicated for 30 min with an ultrasonic generator (VC-505, Sonics & Materials, Inc.) to improve the dispersion of carbon black in the electrolyte.

The electrodeposition of a nickel–carbon layer was performed in a glass cell with a volume of 200 cm^3. The temperature of the electrolyte was maintained at 40 °C. The electrolyte was agitated with a magnetic stirrer. Control of the electroplating current, data collection, and data analysis were performed with a potentiostat/galvanostat (HZ5000, Hokuto Denko Corp.) connected to a personal computer. The working electrode (cathode) was a nickel plate, and the counter electrode (anode) was a Pt coil. The electrode area of the cathode was adjusted to 4 cm^2 with PTFE tape (No. 903UL, Nitto Denko). The reference electrode was an Ag/AgCl electrode in saturated KCl solution; the electrolysis potential refers to the potential based on an Ag/AgCl electrode.

The carbon content (C_f) of the electrodeposited material was analyzed with a carbon/sulfur analyzer (EMIA-510, Horiba). The C_f (mass%) was calculated from the carbon dioxide content by the following equation:

$$C_f = \frac{M_V \times M_f}{\Delta M},$$

where M_V is carbon content (mass%) in the flaming gas of the carbon/sulfur analyzer, M_f represents the weight of the cathode electrode (g), and ΔM is the weight of electrodeposited material (g). The C_f was calibrated on the basis of the carbon content of the nickel plating electrodeposited under the same electrolysis conditions but without carbon black.

The current efficiency (E) was calculated from the weight change of electrode and carbon content using the following equation:

$$E = \frac{Z_{Ni}\Delta M\left(100 - C_f\right)F}{QW_{Ni}},$$

where Z_{Ni} is the valance of element, F is the Faraday constant (C/mol), W_{Ni} is the molar mass of nickel (mol/g), Q is the quality of electricity (C).

The surface morphology was observed by optical microscopy (OM, BH2-UMA, Olympus) and scanning electron microscopy (SEM, S-4800, Hitachi) equipped with an energy dispersive X-ray analyzer (EDS, X-Max80, HORIBA).

The corrosion resistance of the electroplating layer was determined by anodic polarization measurements in sulfuric acid solution at pH 3. The composite plating served as the working electrode (anode), and a Pt coil was used as the counter electrode (cathode). The scanning rate of the anodic polarization analysis was 2 mV s^{-1} from the rest potential. The corrosion potential was identified by the intersection of the tangent at 0.2 mA cm^{-2} of the anodic polarization curve with the line of 0 mA cm^{-2}. For the anodic polarization measurements, the medium was deoxidized by Ar gas diffusion.

3 Results and discussion

3.1 Effect of carbon black concentration in electrolyte on carbon content in composite plating layer

The effect of carbon black concentration on the carbon content in the plating layer is shown in Fig. 1. In these experiments, the current density, electrical charge, and

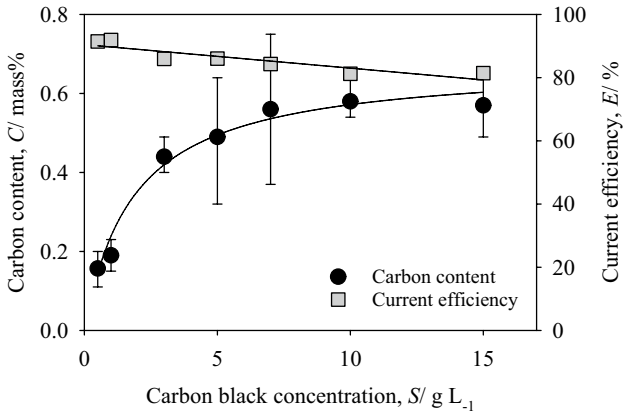

Fig. 1 Effect of carbon black concentration on the carbon content of the plating layer and the current efficiency during the plating process

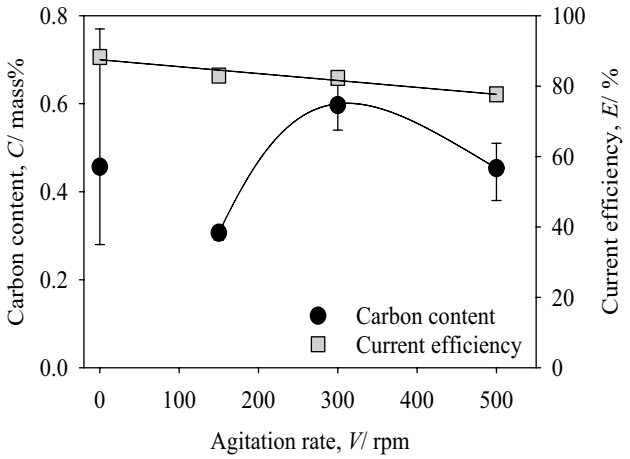

Fig. 2 Effect of the agitation rate on the carbon content of the plating layer and the current efficiency during the plating process

agitation rate were controlled at 30 mA cm^{-2}, 120 C, and 300 rpm, respectively. The carbon content of the plating layer increased with increasing carbon black concentration in the electrolyte until the concentration reached 10 g L^{-1}. The current efficiency decreased with increasing carbon black concentration in the electrolyte. However, the minimum value was greater than 80%.

In the process of electroplating, the carbon black particles must be adsorbed onto the cathode surface to be incorporated into the plating layer. In the case of a high concentration of carbon black in the electrolyte, although some adsorbed carbon black particles could be removed from the cathode surface to the electrolyte by agitation force, the concentration of carbon black particles in the electrolyte was sufficient to ensure adsorption onto the empty area of the cathode surface. The carbon content in the plating layer decreased with decreasing carbon black concentration in the electrolyte because the concentration of carbon black was insufficient to cover the cathode surface. Although the frequency of collision between carbon black particles on the cathode surface and particle in the electrolyte increased as the carbon black concentration in the electrolyte was increased, the incorporation of materials into the plating layer was balanced between the adsorption time of carbon black on the cathode surface and the metal electrodeposition rate. The carbon content was highest with small deviation at a carbon black concentration of 10 g L^{-1}. Thus, we selected a carbon black concentration of 10 g L^{-1} for use in subsequent experiments.

3.2 Effect of agitation rate of the electrolyte on carbon content in composite plating layer

The carbon content in the plating layer might be influenced by the adsorption period of carbon black particles onto the cathode surface. The agitation is the important factor governing the supply and removal of carbon black to and from the cathode surface. The effect of the agitation rate on the carbon content is shown in Fig. 2. These experiments were conducted at a current density of 30 mA cm^{-2} and at an electrical charge of 120 C. The carbon content in the plating layer reached 0.6% at 300 rpm. The agitation rate of 300 rpm was the optimum condition for supplying the carbon black particles to be absorbed onto the cathode surface.

The carbon content varied greatly in experiments conducted without agitation. In the absence of agitation, the carbon black particles near the cathode surface were electrodeposited to the plating layer smoothly. However, the carbon black particles weakly interacted with the cathode surface and could be removed from the cathode surface by the force from the reductive reaction. In the case of agitation, the carbon black particles agglutinated with time. The carbon black particles on the cathode surface were agglutinated to a greater extent than the particles in suspension. Agglutinated carbon black incorporated into the plating layer would increase the carbon content, although carbon black aggregates were removed from the cathode surface easily. Therefore, the variation of the carbon content in the absence of agitation was greater than that observed under other conditions.

The aforementioned results suggest that carbon black was concentrated in the plating layer near the surface of the cathode. That is, when carbon black particles were adsorbed onto the cathode surface, some were buried in the plating layer. The carbon content in the plating layer decreased when the agitation rate was 500 rpm, suggesting that strong agitation could remove the carbon black from the cathode surface. On the contrary, at low agitation rates, insufficient carbon black was supplied to the

surface, resulting in a low carbon content. On the basis of the aforementioned results, the agitation rate was fixed at 300 rpm in subsequent experiments.

3.3 Effect of plating thickness on carbon content in the composite plating layer

The results discussed in Sect. 3.2 suggest that carbon black was concentrated in the plating layer near the surface of the cathode. The effect of plating thickness on the carbon content was investigated to check the distribution of the carbon black in the plating layer (Fig. 3). The thickness was calculated on the basis of the weight change and was controlled through variation of the electrical charge. The current density was controlled at 30 mA cm^{-2}.

The carbon content in the plating decreased with increasing plating thickness. At low thickness, the current density was lower and the value varied. In thin plating layers, carbon black particles were not fully incorporated into the plating and were removed by agitation force and hydrogen gas generated on the nickel metal surface. Therefore, the current efficiency was lower and the deviation became large. When the thickness was greater than 6 µm, the current density and carbon content were constant. We found that carbon black particles were buried in the plating layer. Figure 4 shows the cross section of the composite plating. Enriched section of carbon black was not observed by the cross-section SEM image, and carbon contents measured from SEM-EDS in the cross-section and surface of nickel layer similar. And the carbon content of nickel plating surface was only slightly higher than that of cathode. These results support an assumption that carbon black was concentrated near the cathode surface in the plating. Therefore, that the thickness was fixed at approximately 6 µm, because defective plating occurred with thick plating layers.

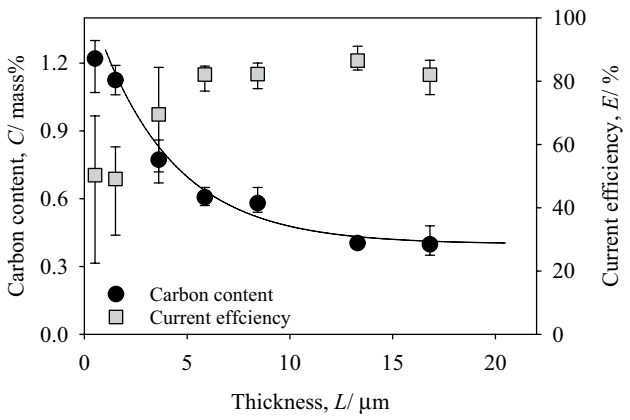

Fig. 3 Effect of plating thickness on the carbon content of the plating layer and the current efficiency during the plating process

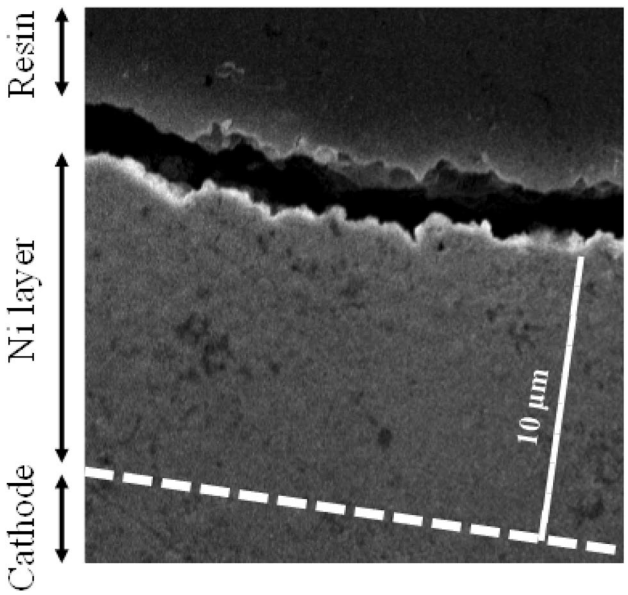

Fig. 4 Cross-section image of the plating layer with carbon black

Figure 5 shows the surface of the composite plating. The black areas were observed on the cathode surface. The size pf each black area was less than 100 μm^2 and the black areas were homogeneously spread on the surface. Carbon content of the black areas were higher than other areas. This implies that carbon black is contained in the black areas. From these observations, it can be said that carbon black was dispersed on the nickel plating surface.

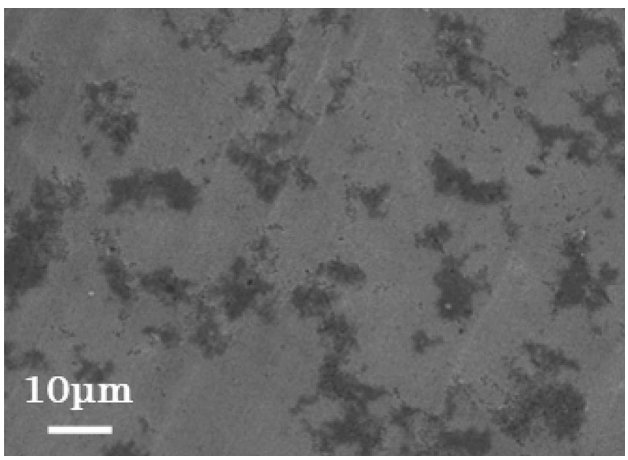

Fig. 5 Surface image of the plating layer with carbon black

3.4 Effect of current density of plating on the carbon content in the composite plating layer

In previous sections, we showed that the adsorption of carbon black particles onto the cathode surface is important for their incorporation into the plating layer. The current density reflects the electrodeposition rate. A high electrodeposition rate is favorable for the incorporation of carbon black particles into the plating layer. The influence of the current density on the carbon content is shown in Fig. 6. At current densities from 30 to 150 mA cm^{-2}, the carbon content of the plating was approximately 0.6 mass%. The current density at 200 mA cm^{-2} was highest among these experiments, although optical microscopic observations of the surface of the plating indicate that it was rough.

The current efficiency was approximately 60%, and a large amount of hydrogen gas was generated. Hydrogen gas generation can influence the generation of micropores in the plating, and the corrosion originates on the micropores of nickel plating. At low current density (< 10 mA cm^{-2}), electrodeposited nickel did not bury the carbon black particles, and carbon black particles on the cathode surface were pushed into the electrolyte. The carbon black particles pushed from the cathode surface had electrodeposited nickel. Therefore, the current efficiency under the low-current-density condition was lower than that under other current-density conditions. A current density of 50 mA cm^{-2} was the optimum condition with respect to both the carbon content in the plating layer and the current efficiency.

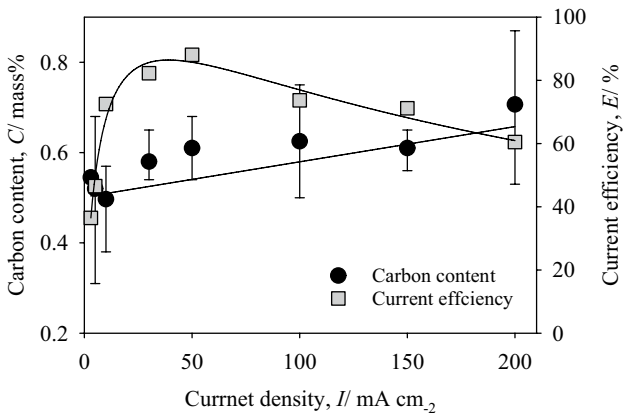

Fig. 6 Effect of current density on the carbon content of the plating layer and the current efficiency during the plating process

3.5 Effect of carbon black on corrosion resistance and surface morphology

The surface morphology was influenced by carbon incorporated into the plating. SEM micrographs of these plating specimens are shown in Fig. 7. The surface morphology differed between platings with and without carbon black. The grain size was larger in specimens with carbon black. The corrosion potential of the nickel plating was – 0.20 V, and that of the nickel–carbon black plating decreased to – 0.32 V.

Carbon black does not influence the corrosion potential directly because it is a stable material under aqueous conditions. The coarsened grain increased the space between grains. The nickel–carbon plating was corroded from the space between grains; therefore, the corrosion potential of the nickel–carbon black plating was lower than that of the nickel plating without carbon black. At the beginning of electrodeposition, the cathode surface was covered by carbon black particles and the crystal cores of nickel metal were not produced in the interspaces among carbon black particles. The growth of grains was not inhibited by other grains in the nickel–carbon black plating. The grain size increased with increasing electroplating time until the grains contacted other grains. Therefore, the grain size of the nickel–carbon black plating was larger than that of the nickel plating without carbon black.

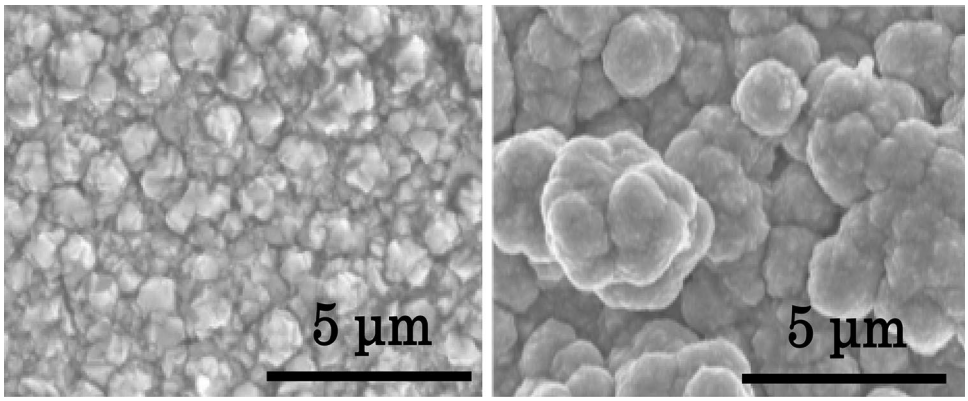

Fig. 7 SEM micrograph of surface of nickel platings with (left: 0.58 mass%) and without (right: 0 mass%) 0.58 mass% carbon black

4 Conclusion

We prepared nickel–carbon black composite films using galvanostatic electrolysis with a Watts bath to study the factors that influence electroplating. The current efficiency was greater than 90% when using a Watts bath. However, the carbon content of the composite plating layer was approximately 0.6 mass%. The uptake of carbon black particles into the plating layer was influenced by the supply and adsorption of particles onto the cathode surface and by the electrodeposition rate. The carbon black was concentrated in the plating layer near the cathode surface. The corrosion resistance of the composite film decreased compared with that of a nickel plating layer without carbon black. The adsorption of carbon black particles onto the cathode surface resulted in larger electrodeposit grains and increased the space between grains, which was the originating point of corrosion.

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Compliance of ethical standards

Conflict of interest The authors declares that they have no conflict of interests.

References

1. Zhang SS, Han KJ, Cheng L (2007) The effect of SiC particles added in electroless Ni–P plating solution on the properties of composite coatings. Surf Coat Technol 202:2807–2812
2. Pompei E, Magagnin L, Lecis N, Cavallotti PL (2009) Electrodeposition of nickel–BN composite coatings. Electrochim Acta 54:2571–2574
3. Du LZ, Xu BS, Dong SY, Yang H, Wu YX (2004) Preparation, microstructure and tribological properties of nano-Al_2O_3/Ni brush plated composite coatings. Surf Coat Technol 192:311–316
4. Kunugi Y, Nonaka T, Chong YB, Watanabe N (1992) Electroorganic reactions on organic electrodes—part 15: electrolysis using composite-plated electrodes—part IV. Polarization study on a hydrophobic Ni/PTFE composite-plated nickel electrode. Electrochim Acta 37:353–355
5. Mohammadi M, Ghorbani M (2011) Wear and corrosion properties of electroless nickel composite coatings with PTFE and/or MoS_2 particles. J Coat Technol Res 8:527–533
6. Yang S, Teer DG (2000) Investigation of sputtered carbon and carbon/chromium multi-layered coatings. Surf Coat Technol 131:412–416
7. Laidani N, Miotello A, Perrière J (1996) Chemical, mechanical and electrical properties of CN_x-films produced by reactive sputtering and N^+-implantation in carbon films. J Appl Surf Sci 99:273–284
8. Patscheider J (2003) Nanocomposite hard coatings for wear protection. MRS Bull 28:180–183
9. Tan J, Yu T, Xu B, Yao Q (2006) Microstructure and wear resistance of nickel–carbon nanotube composite coating from brush plating technique. Tribol Lett 21:107–111
10. Goto Y, Kamebuchi Y, Hagio T, Kamimoto Y, Ichin R, Bessho T (2018) Electrodeposition of copper/carbonous nanomaterial composite coatings for heat-dissipation materials. Coatings 8:5
11. Suzuki Y, Arai S, Endo M (2010) Ni–P alloy–carbon black composite films fabricated by electrodeposition. Appl Surf Sci 256:6914–6917
12. do Amaral MA, Marcuzzo J, Pinheiro BD, Lopes BHK, de Oliveira APS, Matsushima JT, Baldan MR (2019) Study of reflection process for nickel coated activated carbon fiber felt applied with electromagnetic interference shielding. J Mater Sci Technol 8:4040–4047
13. Guglielmi N (1972) Kinetics of the deposition of inert particles from electrolytic baths. J Electrochem Soc 119:1009–1012
14. Arai S, Endo M, Kaneko N (2004) Ni-deposited multi-walled carbon nanotubes by electrodeposition. Carbon 42:641–644
15. Chen Q, Dai L, Gao M, Huang S, Mau A (2001) Plasma activation of carbon nanotubes for chemical modification. J Phys Chem B 105:105618
16. Jiang L, Gao L (2003) Modified carbon nanotubes: an effective way to selective attachment of gold nanoparticles. Carbon 41:2923–2929
17. Stevens JL, Huang AY, Peng H, Chiang LW, Khabashesku VN, Margrave J (2003) Sidewall amino-functionalization of single-walled carbon nanotubes through fluorination and subsequent reactions with terminal diamines. Nano Lett 3:331–336
18. Jiang L, Gao L, Sun J (2003) Production of aqueous colloidal dispersions of carbon nanotubes. J Colloid Interface Sci 260:89–94
19. Kamimoto Y, Ohkura S, Tanaka H, Hara H, Hagio T, Deevanhxa P, Ichino R (2018) Development of metal–carbon black composite plating with Wood's bath. Nanosci Nanotechnol Lett 10:805–808