PREPARATION OF MICROWAVE ABSORBING NICKEL-BASED ACTIVATED CARBON BY ELECTROLESS PLATING WITH PALLADIUM-FREE ACTIVATION

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Nickel-based activated carbon was prepared from coconut shell activated carbon by electroless plating with palladium-free activation. The materials were characterized by scanning electron microscopy (SEM), X-ray energy dispersion spectroscopy (EDS), vibrating sample magnetometry (VSM), and vector network analyzer, respectively. The results show that the surface of the activated carbon was covered by a Ni-P coating, which was uniform, compact, and continuous and had an obvious metallic sheen. The content of P and Ni was 2.73% and 97.27% in the coating. Compared with the untreated activated carbon, the real permeability μ' and imaginary permeability μ'' of Ni-based activated carbon became greater, whereas the real permittivity ε' and imaginary permittivity ε'' became smaller. Also, the plated activated carbon was magnetic, making it suitable for some special applications. In general, the method reported here might be a feasible procedure to coat activated carbon with other magnetic metals, which may find application in various areas.

Keywords: Electroless nickel plating; Palladium-free; Activation; Activated carbon; Magnetic; Complex permittivity and permeability

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INTRODUCTION

Activated carbon has been widely used because of its interesting properties (Bansal et al. 1988) such as its porosity and high specific surface area, which are interesting characteristics in adsorption and in supported catalysis (Oya et al. 1993; Roskill 1990; Donnet et al. 1990; Wang et al. 1994). However, the electromagnetic properties of untreated activated carbon are poor. It can be expected that if the activated carbon were coated with a layer of metal, wider use would be developed in some fields, such as conducting activated carbon, which has some advantages of good conductivity, high strength, low price, and a good combination of characteristics, as the materials could combine the properties of activated carbon and the metal together. Activation processes for metallization of non-conducting substrates have attracted increasing attention (Seeböck et al. 2001; Toth et al. 1993; Tang et al. 2009; Chen et al. 1995).

Deposition of an electroless nickel alloy coating is considered as the most effective method to alter the chemical and physical properties of some nonmetallic substrates. Electroless nickel plating has found wide uses in many fields. The technique can achieve high permeability, wear resistance (Balaraju and Rajam 2005), nonmagnetostriction, and corrosion resistance (Zhang and Xie 2000). Electroless nickel plating has also been attempted in optical applications (Chen et al. 2003), other metal powders (Motizuki et al. 1999), and polystyrene resin balls (Hagiwara et al. 1997).

In conventional activation processes, the noble metal palladium usually has been employed as the catalyst sites to initiate the electroless plating (Zhang et al. 1996; Omura et al. 2003). The biggest weakness of the conventional activation processes is that Pd compounds are expensive and can significantly increase the cost of the plating process. So, it is necessary to develop Pd-free activation, which is low-cost and can obtain good Ni-P alloy coatings. In order to avoid the use of Pd and to decrease the cost, some other less expensive metals, many attempts have been made to employ Ni activation.

Nowadays, two methods have been widely investigated. In one method, Ni^0 is produced on the substrate from absorbed Ni^{2+} by thermal treatment at higher temperatures (Li and An 2008; Li et al. 2006; Shao et al. 2007); in the other, Ni^{2+} on the surface of the substrate is reduced to Ni^0 by sodium borohydride ($NaBH_4$) in two separate steps (Hu et al. 2006; Lai et al. 2006; Gao and Huang 2007). Seita et al. (1996) developed a chemical process that consists of adsorbing the Cu(II) species onto the sulfonated surface from a cupric aqueous solution and reducing Cu(0) by $NaBH_4$ solution. It would be highly promising if nickel could be successfully used as catalyst sites for nickel deposition in the same way. To our knowledge, direct Ni metallization has been mentioned in the literature (Brocherieux et al. 1995; Charbonnier et al. 2006), but expensive equipment and complex operations have been required.

The present work concerns the activation process for immobilizing Ni on the activated carbon substrate as a catalytic site by chitosan for nickel electroless plating. The components on the substrate surface after activating and electroless plating were investigated by Energy Dispersive Spectroscopy (EDS). The appearances of the activated surface on the carbon and the deposited Ni–P layer were characterized by Scanning Electron Microscopy (SEM). The powder is expected to possess advantages common to both activated carbon and metal powder. The electric and magnetic properties of the powder were studied.

EXPERIMENTAL

Materials

The Hainan Xingguang Activated Carbon Company of China supplied the activated carbon. Chitosan (CTS, Deacetyl Degree ~92%) was purchased as industrial grade power from Jinan Haidebei Chemical Agent Ltd. All other chemicals used were of analytical grade purity.

Pretreatment of Activated Carbon

Prior to electroless nickel deposition, activated carbon particles were dispersed in distilled water with ultrasonic vibration (Model KQ-100B, 40 kHz transducers, Bran sonic) for 30 min and then dried in air at 60 °C overnight. A pretreatment step of the activated carbon structures was included to clean and to increase the surface area.

Samples were dispersed in a 2 mol/l sodium hydroxide solution at 40 °C for 3h. The samples were then rinsed with distilled water.

Activating and Electroless Plating

After pretreatment, the samples were dipped into 5% acetic acid solution containing 5 g/L CTS for 5 min at room temperature, and then dried at 60 °C for 30 min. Afterwards, the powders (activated carbon–CTS for short) were immersed in plating solution containing sodium citrate as complexing agent and sodium hypophosphite as reducing agent at room temperature for 10 min (after filtration, the filtrate retained), and then reduced in a solution of $NaBH_4$ (3.0 g/L) at 40 °C for 5 min. Activated carbon–CTS–Ni was obtained. The electroless nickel deposition was achieved catalytically by dipping the pre-nucleated substrates (Activated carbon–CTS–Ni) into the filtrate, which was retained at 70 °C for 1 min. The plating solution used is shown in Table 1. The ammonia solution was used to adjust the pH of the bath.

Table 1. Composition of Nickel-Plating Solution

Chemicals	Content ($g\cdot L^{-1}$)
$NiSO_4\cdot 6H_2O$	7.5
$NaH_2PO_2\cdot H_2O$	7.5
Lactate	3.75
NH_4Cl	6.25
Thiourea	0.0005
pH	8.5

Measurement of Metal Deposition

The composition of deposits was determined with an X-ray energy dispersion spectrometer (EDS) equipped on a Quanta 200 electron microscope. The morphology was observed using scanning electron microscopy (SEM) before and after plating.

Measurement of Electromagnetic Properties

Magnetic properties were measured using a vibrating sample magnetometer (VSM) (Lake Shore 7407). The complex permittivity and permeability of the activated carbon/paraffin wax composites were measured by the coaxial line method at 2 to 18 GHz using an HP8722ES network analyzer, in agreement with the method reported in Liu and Zhao (2006). The content of the activated carbon was 10 wt. %.

RESULTS AND DISCUSSION

Surface Morphology and Phase Structure of the Coating

The SEM photographs of uncoated activated carbon particles are presented in Fig. 1(a) and (b), from which it was shown that the surface had many pores and was otherwise smooth. Typical SEM micrographs of one of the Ni–P coated activated carbon particles at low and high magnifications are presented in Figs. 1(c) and (d), respectively. It can be observed that the surface of plated activated carbon was covered by the coating, which was uniform, compact, and continuous, and it had an obvious metallic sheen. It can be also observed that the coating was composed of small cells. These cells have been deposited together closely. And the pore structure of Ni-based activated carbon can be still seen clearly.

Figure 2 show the distribution of the elements on the Ni-P/activated carbon. It can be seen that Ni and P were the main elements of the coating (the C and O come from activated carbon). After eliminating the disturbance of the carbon, the composition (mass fraction) of the Ni-P layer was calculated as: Ni 97.27% and P 2.73%. The amount of P was lower.

During the process of Ni–P plating, the self-catalysis reduction reactions on the surface can be described as follows:

$$4Ni^{2+} + BH_4 \quad + 8OH \quad \rightarrow 5H_2O + H_2BO_3 \quad + 4Ni\downarrow \tag{1}$$

$$Ni^{2+} + H_2PO_2 \quad + H_2O \rightarrow HPO_3^{2} \quad + 3H^{+} + Ni\downarrow \tag{2}$$

$$H_2PO_2 \quad + [H] \rightarrow H_2O + OH \quad + P\downarrow \tag{3}$$

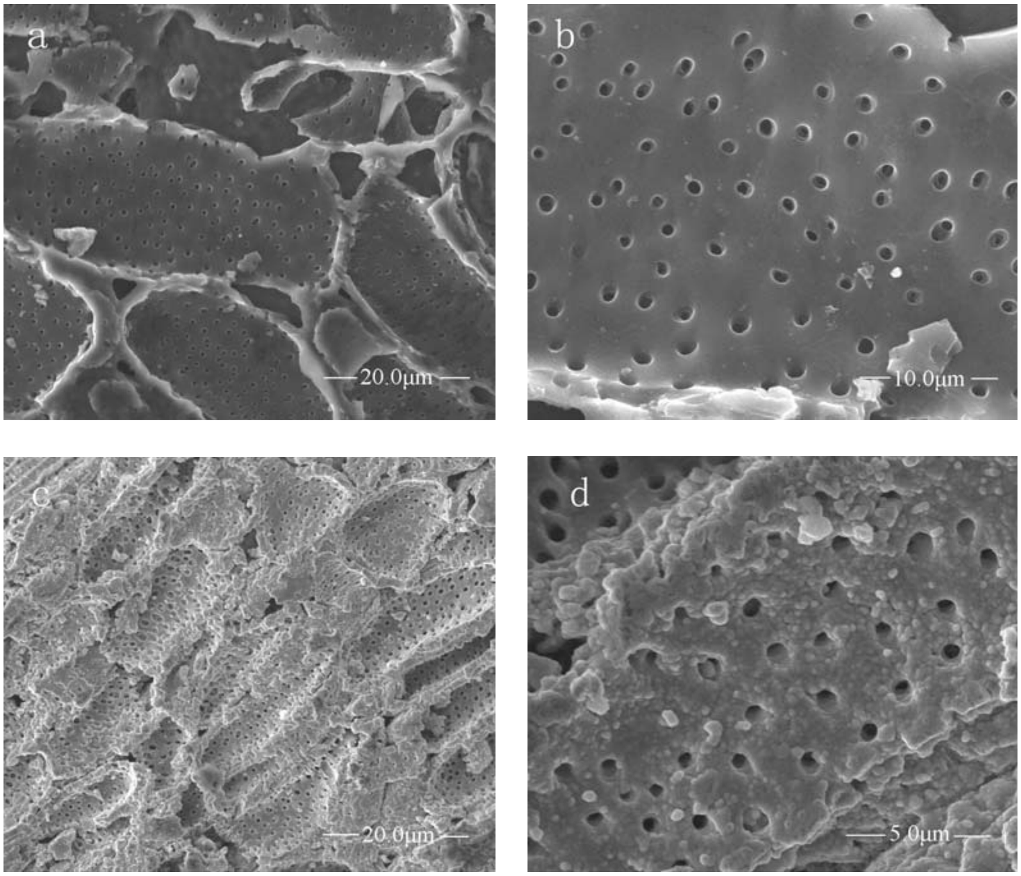

Fig. 1. Surface morphology of activated carbon before and after electroless plating. (a) SEM photograph of uncoated activated carbon particles (low magnifications). (b) SEM photograph of uncoated activated carbon particles (high magnifications). (c) SEM photograph of Ni-P-coated activated carbon particles (low magnifications). (d) SEM photograph of Ni-P-coated activated carbon particles (high magnifications).

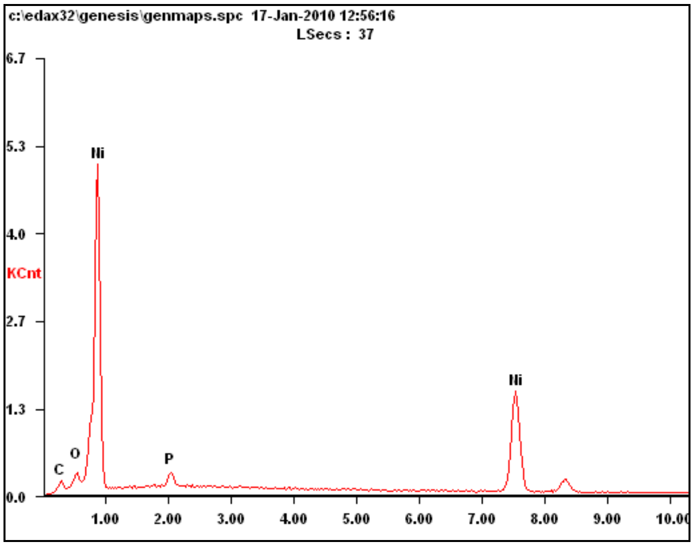

Fig. 2. EDS spectrum of plated activated carbon

VSM Analysis

Figure 3 shows magnetic hysteresis loops of the plated activated carbon at 300 K. As shown in Fig. 3, the saturation magnetization (Ms), the remnant magnetization (Mr), and the coercivity (Hc) of the plated activated carbon were 0.56927 emu/g, 76.140 x 10^{-3} emu/g, and 26.169 G, respectively. The deposit was suitable as a soft magnetic material, because it possessed a high saturation magnetization and low coercivity. The result shows that the plated activated carbon is magnetic, such that it can be used in some special applications. The magnetic Ni-P plating can broaden application range of the plated activated carbon.

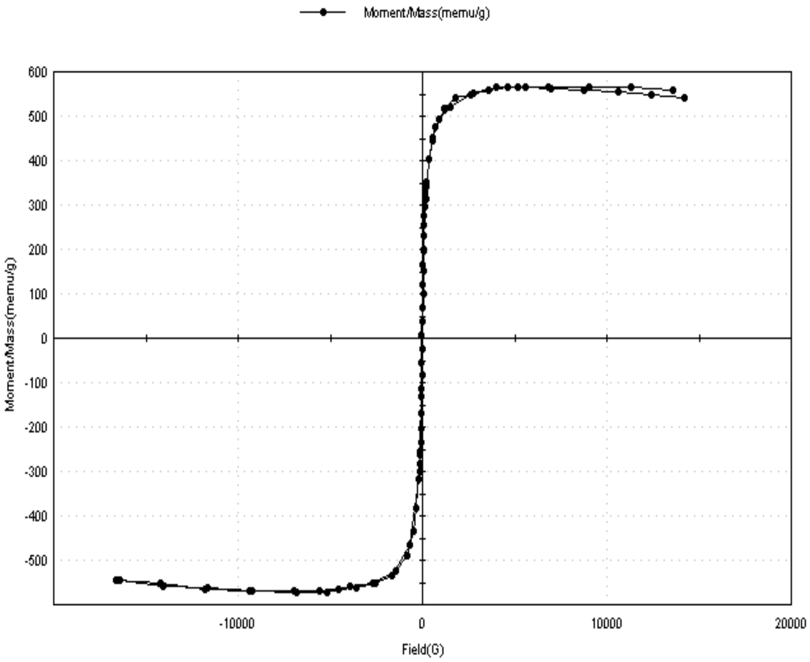

Fig. 3. Hysteresis evaluation results of activated carbon after plating

Vector Network Analysis

In order to investigate the intrinsic reasons for microwave absorption of the Ni-based activated carbon, we measured the complex permittivity of activated carbon/ paraffin wax composites by the coaxial line method at 2-18 GHz. As illustrated in Fig. 4, the real permittivity ε' and imaginary permittivity ε" of Ni-based activated carbon became smaller, the ε" and ε" of the activated carbon/paraffin wax composites were 7.54~8.67 and 0.58~1.12, respectively.

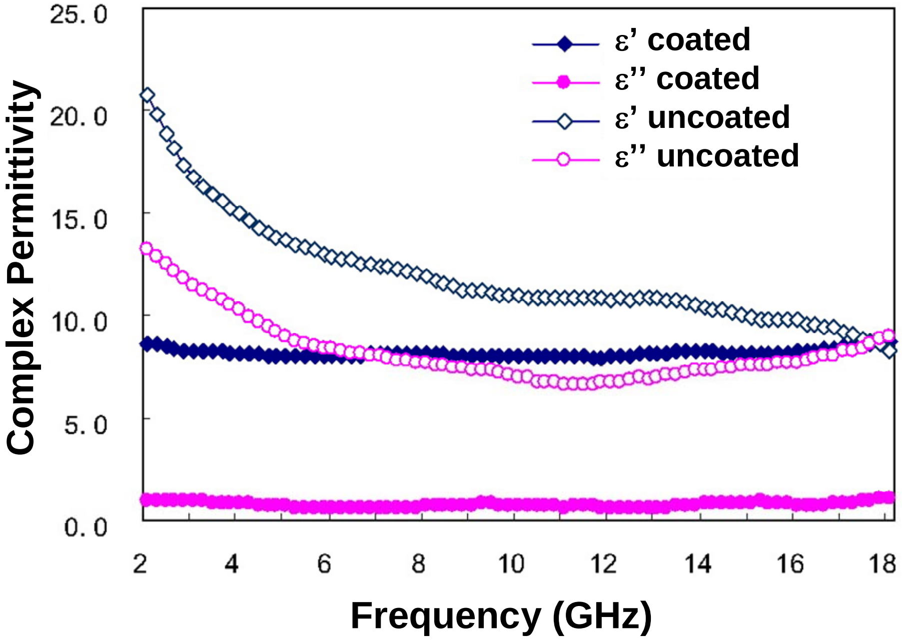

Fig. 4. Complex permittivity of activated carbon before and after plating

The films exhibited low relative permittivity due to micro-pores formed in the film. Therefore, the conduction loss was observed to be small. However, as illustrated in Fig. 5. The Ni-based activated carbon particles exhibited higher magnetic properties compared to the uncoated activated carbon. In particular, an increase in the magnetic loss (μ") is evident. The values of μ' and μ" were constant at 0.91~0.98 and -0.08~-0.02 in the range of 2 to 18 GHz, respectively. This behavior stems from the Ni fillers embedded in the coatings.

According to the tangent values of dielectric loss (tan δε=εr″/εr′) and magnetic loss angle (tan δμ=μr″/μr′) shown in Fig. 6, obvious dielectric loss was larger than magnetic loss. The microwave absorption of the Ni-based activated carbon resulted mainly from dielectric loss rather than magnetic loss.

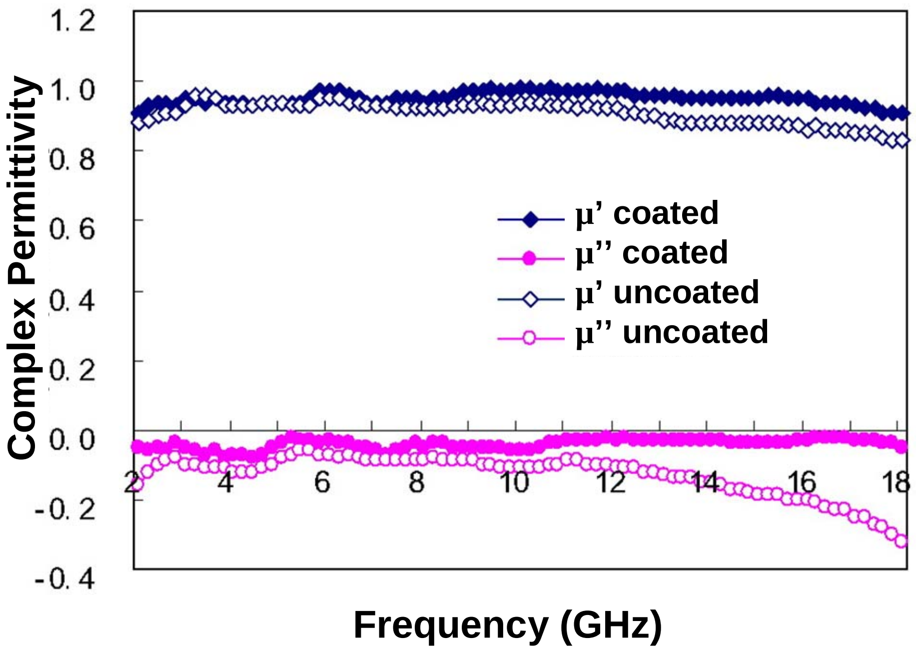

Fig. 5. Complex permeability of activated carbon before and after plating

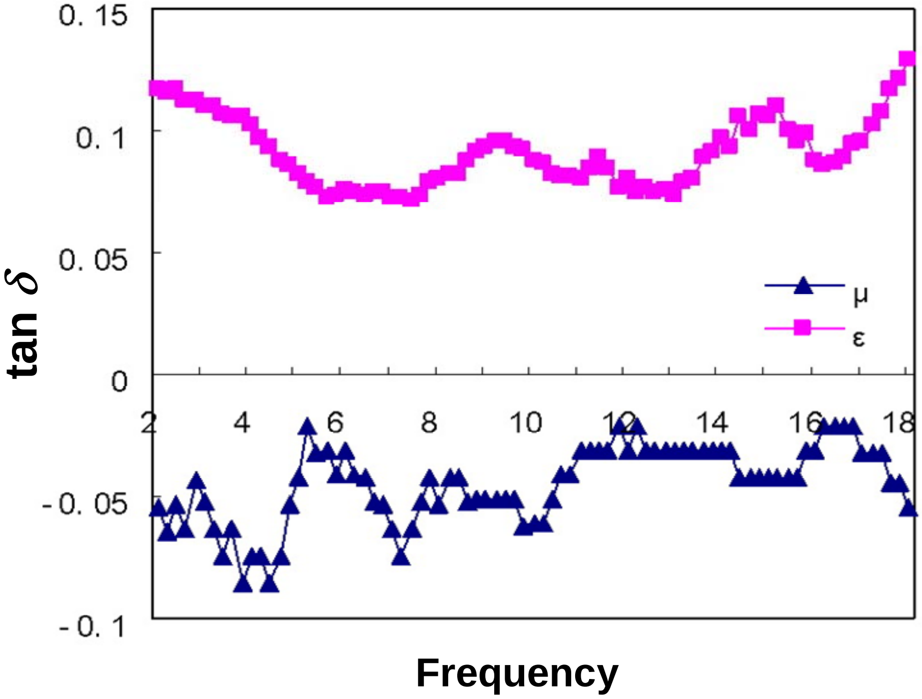

Fig. 6. Tangent values of dielectric loss and magnetic loss of Ni-based activated carbon

CONCLUSIONS

1. Ni-based activated carbon was successfully prepared by electroless plating with palladium-free activation. It was confirmed that the formed Ni was effective as a catalyst for nickel electroless plating.
2. SEM and EDS analysis showed that the surface of the Ni-based activated carbon was entirely covered with a layer of uniform and continuous Ni-P alloy, which made the activated carbon more like metal, while the pore structure of Ni-based activated carbon could be still seen clearly. The composition of the Ni-P layer was 97.27% of Ni and 2.73% of P. The coatings met the definition of low-phosphorus deposition.
3. A preliminary study of magnetic and microwave absorbing properties showed that the complex permittivity and the complex permeability of the Ni-based activated carbon exhibited small variations. The ε′ was in the range of 7.54~8.67, while the ε″ was in the range of 0.58~1.12. The μ′ was in the range of 0.91~0.98, while the μ″ was in the range of -0.08~-0.02. The value of the saturation magnetization, the remnant magnetization and the coercivity indicated that the Ni-based activated carbon was magnetic and could be described as a soft magnetic material.

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