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Rapid synthesis and morphology control of nickel powders via a microwave-assisted chemical reduction method

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Abstract Nickel powders with different morphologies, such as sphere, chain, and thorn-like nickel wire have been successfully synthesized by hydrazine reduction of $NiCl_2$ in the presence of polyvinyl pyrrolidone (PVP) by using microwave-assisted chemical reduction method. The obtained products were characterized by XRD, SEM, TEM, and SAED techniques. Characterization by TEM and SAED showed that as-produced nickel powders were formed by self-assembly and aggregation of nanometer-sized nickel crystallites. PVP served as the structure directing agents and plays a key role for the morphology transformation of the nickel powders. In addition, compared with conventional heating method, microwave irradiation heating was in favor of the formation of nickel wires. The resultant nickel wires showed excellent electrical properties in the nickel wires/epoxy composite.

Introduction

In recent years, synthesis of nickel powders with different morphologies has attracted much attention due to their unique properties and applications in various fields, such as chemical catalysts, electrical conductive polymers, battery materials and nickel–ceramics complex, etc. [1–4]. Their electric and magnetic properties are strongly dependent on the size and shape of the nickel particles. So far, nickel powders with different morphology and shape, such as nano-sphere, hollow sphere, nano-belt, and core-shell structure, have been synthesized by various methods [5–11]. However, compared with noble metallic clusters (Au, Ag, Pd, etc.), morphology control of nickel powders is relatively difficult due to its high chemical activity and magnetic attraction. It is a challenging job to find a simple method to control the morphology of the nickel powders.

Generally, the key for the morphology controlling of metal powders is to direct the nucleation, growth, and aggregation process of metal crystallite. Various techniques have been exploited for the morphology control of metal powders, such as electro-deposition on nano-porous anodic aluminum oxide template, hydrothermal micro-emulsion method, self-assembly of nanoparticle by soft-template technique, magnetic field inducing, etc. [12–16]. Among these methods, the most popularly used approach was self-assembly of nanoparticle by soft-template technique due to its simplicity and efficiency. Surfactant and block co-polymer were usually used as soft template to control the crystal growth and aggregation. For example, chain-like nickel wire formed by self-assembly of small nickel crystallites using triethanolamine (TEA) as coordinative agents has been explored [2]. Chain-like nanostructures consisting of Co hollow mesospheres in a polymer solution have been obtained [17]. However, the mechanism of surfactant and polymer in the morphology control of metal particles is still not well understood.

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Microwave is electromagnetic radiation with frequency range of 0.3–300 GHz and corresponding wavelengths from 1 mm to 1 m. It was well known that microwave could increase the kinetics of metal formation due to its non-thermal effect of microwave, and many reports have proved that reaction rate could be increased by microwave radiation [18–20]. Herein we report a simple and fast microwave-assisted route for preparing nickel powders with controlled morphologies. Effects of polyvinyl pyrrolidone(PVP) concentration and microwave irradiation heating on the morphology of nickel products were mainly investigated. Electrical properties of epoxy composite incorporated with nickel spheres or nickel wires were also compared.

Experimental procedure

The starting material was nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$). Hydrazine hydrate ($N_2H_4 \cdot H_2O$, 50%) was used as a reducing agent. Sodium hydroxide (NaOH) was used as a pH control agent. Polyvinyl pyrrolidone (PVPk30, molecule weight = 40000) served as structure directing agent. Palladium chloride (Tedia, Japan) was chosen as a nucleation accelerator for nickel synthesis. A typical nickel powder preparation experiment is as follows: 0.5 g PVP and 8.85 mg $PtCl_2$ (Tedia, Japan) were added into 100 mL aqueous solution of 0.0625 M $NiCl_2$ under stirring, and 12.5 mL reducing agents hydrazine hydrate ($N_2H_4 \cdot H_2O$, 50%) and 2 g NaOH were dissolved in 12.5 mL deionized water. A purplish red solution was obtained after mixing the above two solutions quickly. A domestic microwave oven (WP700, MS-2030T) was used to heat the reaction system. The solution becomes black quickly as its temperature reaches 55 °C, indicating many nickel nano-crystallites are forming. After the reaction solution reached 80 °C, microwave oven was turned on and off repeatedly to keep the solution around 80 °C. After the completion of the reaction, black products were washed with distilled water and alcohol alternately three times, and dried at 50 °C in a vacuum oven.

All the nickel powders were examined for the morphology and shape by scanning electron microscopy (JEOL, JSM-6330F), transmission electron morphology (JEOL, JEM-2010HR). The crystal structure was identified using an X-ray diffractometer (D/Max-III, Rigaku, Japan, $\lambda_{\text{Cu-K}\alpha} = 1.5405$ Å) and selected area electron diffraction (SAED). IR analysis of powder was carried out in a Fourier transformation infra-red spectrometer (IR; model EQUINOX 55, Bruker, Germany).

Synthesis of the nickel powder/epoxy composite was as follows: prior to blending, all nickel powders were dried at 60 °C in vacuum for about 8 h. The Ni/epoxy blends were prepared in a Haake RC300P Rheometer (Germany) at 100 °C and 50 rpm for 10 min, followed by the addition of solidified agent triethylenetetramine. The resultant blends were subsequently compression molded in a 0.5 M semi-automatic pressure forming machine (model:YXC-25, Zimmerli Weili, China) at 200 °C with the pressure of 10 MPa to form plaques of 4 mm in thickness. Then, 4 mm plaques were cut into specimens of 90 mm length and 10 mm width according to the sample size of ASTM D 4496. The content of the nickel powders in the nickel powder/epoxy composite was 15, 20, 30, 40, 50, 65, 75%, respectively, and all blend ratios described are related to percentage by weight.

The volume resistivity of the nickel powder/epoxy composite was measured according to ASTM D 4496 with a set of low resistance measurement apparatus, consisting of current electrodes, potential electrodes, a DC power supply, a digital multimeter (DT 97). All samples are tested under a voltage of 1,000 V.

Results and discussion

Figure 1a presents a typical SEM image of the nickel powders prepared with 4 g/L PVP, which shows that all the products were uniform nickel wires. The length of Ni wires was roughly 10 μm and its average diameter was about 0.83 μm. Figure 1b shows the XRD pattern of the nickel wire. All diffraction peaks can be indexed in the face-centered cubic phase of nickel (J CPDS. No 0420860), and no nickel oxides or nickel hydroxides were checked in the nickel powders, which illustrated that all the nickel salts have been reduced by the ample reducing agents $N_2H_4 \cdot H_2O$. From the full width at half maximum of (111) peak, the mean grain size was calculated to be 16.7 nm using Scherrer Formula. The crystallite size of all the nickel powders is much smaller than the diameter of the nickel powders, which suggests that nickel wires were composed of many nanometer-sized nickel crystallites. To our surprise, the surface of these nickel wires was non-smooth, and there were many nano-sized spikes grown on the surface of nickel wires as shown in Fig. 1c. The corresponding SAED pattern of nickel wires (inset in Fig. 1c) indicates that nickel wires were polycrystalline. However, SAED pattern (inset in Fig. 1d) of a single nickel spike demonstrated that nano-sized spikes were single crystalline nickel. Above results clearly showed that nickel wires were formed by self-assembly and aggregation of nanometer-sized nickel crystallites.

To determine the factors responsible for the formation of such novel thorn-like nickel wires, a detailed study of the dependence of the amounts of PVP added in the solutions has done. Figure 2 shows the SEM micrographs

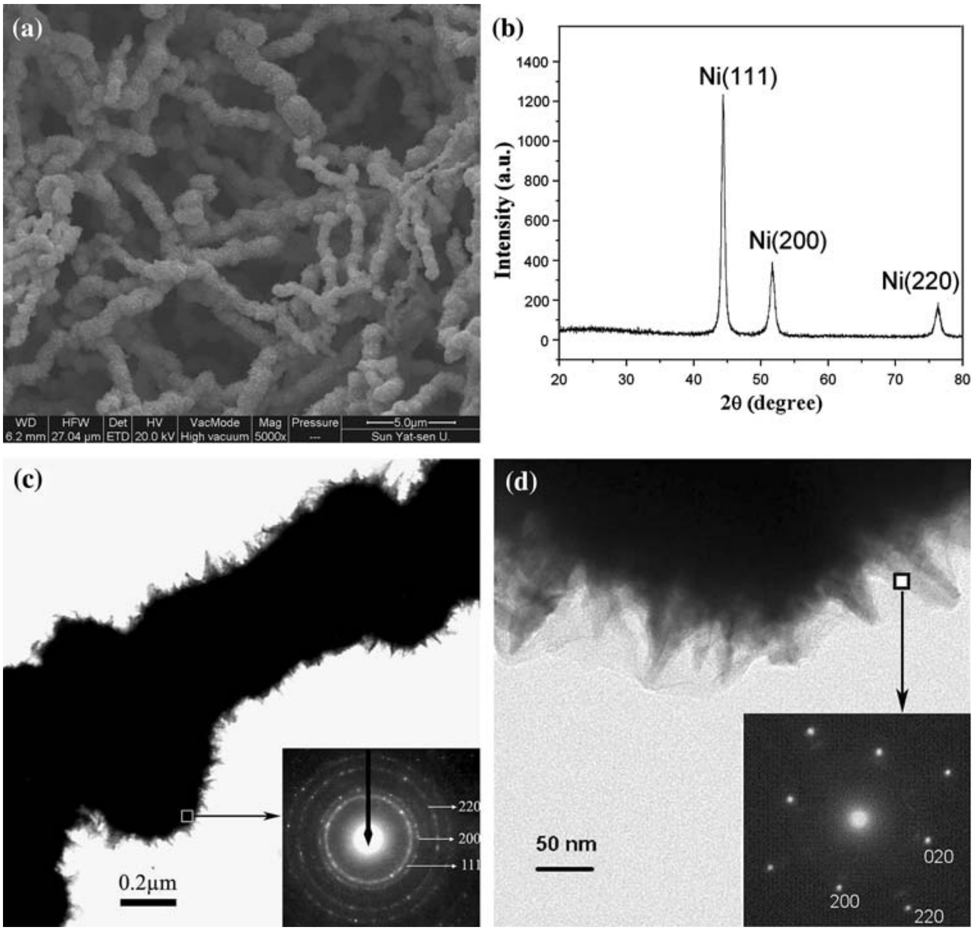

Fig. 1 **a** SEM image shows the uniform nickel wires, **b** XRD patterns of the thorn-like nickel wires, **c** TEM image of a single nickel wire reveals the nano-sized spikes on the surface of nickel wire, **d** TEM image of nickel nano-sized spikes with its corresponding SAED (heating power of microwave oven: 100 W; PVP concentration: 4 g/L)

of nickel powders synthesized by different concentration of PVP. In the absence of PVP, all the obtained products were nickel spheres with diameter of 0.2–1 μm (Fig. 2a). When 1 g/L PVP was added in the solutions, all the products were nickel chains formed by the aggregation of nickel spheres (Fig. 2b). However, the products transfer into some aggregated nickel powders with irregular morphology as PVP concentration increases to 16 g/L (Fig. 2c). Above results indicate that morphology of the nickel powders was critically dependent on the PVP concentration.

Microwave irradiation heating also has a great influence on the morphology of the obtained nickel powders. Figure 3 presents the SEM images of nickel powders prepared with 4 g/L PVP with conventional heating method and high heating power of microwave oven. As shown in Fig. 3a, using conventional heating method to heat, all products were nickel chains formed by magnetic attraction of small nickel particles. Nickel chains transformed into thorn-like nickel wires as the reaction solutions were heated by microwave oven with 100 W (Fig. 1a) or 400 W (Fig. 3b), indicating that microwave irradiation heating was in favor of the formation of such thorn-like nickel wires. Figure 4 presents the effect of heating power of microwave oven on the formation time of nickel powders. It can be seen that formation time of nickel powders decreases with the increase of heating power of microwave oven. This suggests that nucleation, growth, and aggregation process of nickel crystallites can be promoted with the increase of heating power of microwave oven.

In general, PVP molecule containing nitrogen (N) and (O) could easy coordinate with metal ions to form PVP–metal complex, which was proved by the infrared or ultraviolet spectrum in the earlier research works [21–23]. We confirmed this finding by IR spectra of nickel wires prepared with 4 g/L PVP and pure PVP. As shown in Fig. 5, absorption peak of C=O bond at 1666 cm^{-1} for pure PVP was shifted to 1633 cm^{-1} for prepared nickel wires. This decrease of wavenumber for C=O absorption may result from bond weakening via partial donation of oxygen loan pair electrons of PVP to the vacant orbits of the nickel wire. The change of the spectrum indicated that the coordination between O of PVP and nickel was formed, that is to say, Ni–PVP complex was formed during the formation process of the nickel powders. On the other hand, physical absorption would inevitably exist due to the

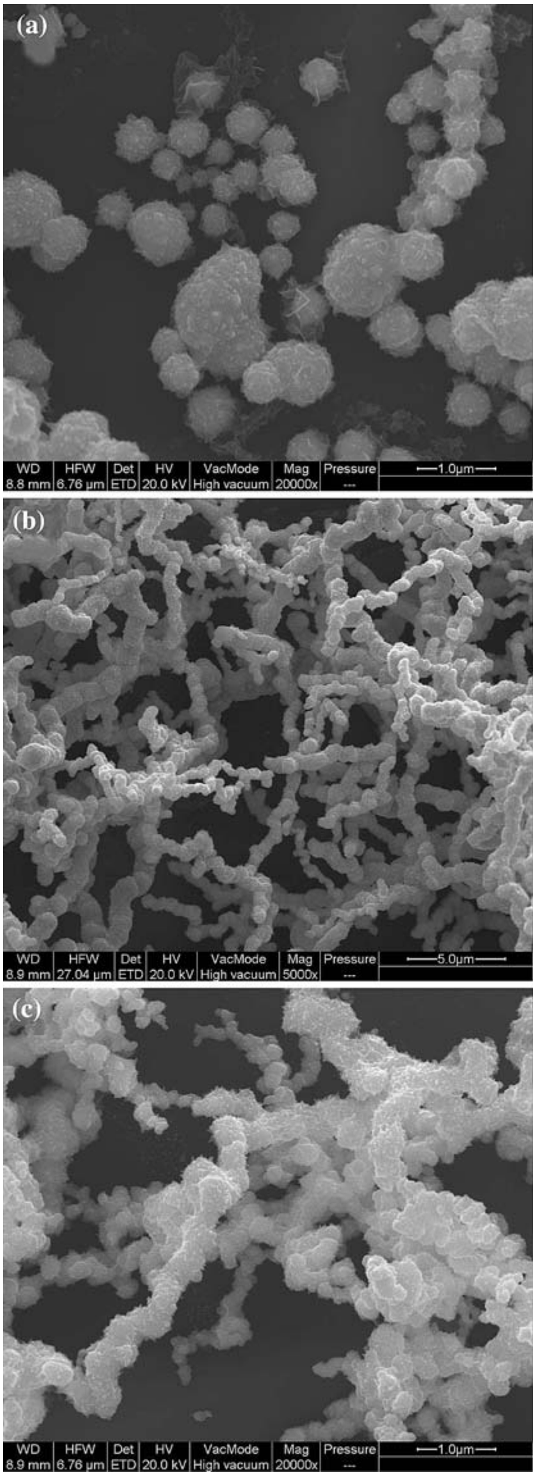

Fig. 2 SEM micrographs of nickel powders synthesized at different concentrations of PVP: **a** 0 g/L, **b** 1 g/L, **c** 16 g/L (heating power of microwave oven: 100 W)

static attractive force between nickel crystal and PVP molecule.

We will now discuss the influence of PVP on the nucleation, growth, and aggregation of the nickel crystalline which may help to understand the effect of PVP concentration on the morphology transformation of nickel powders. According to the Gibbs-Thomson formula of classical nucleation theory:

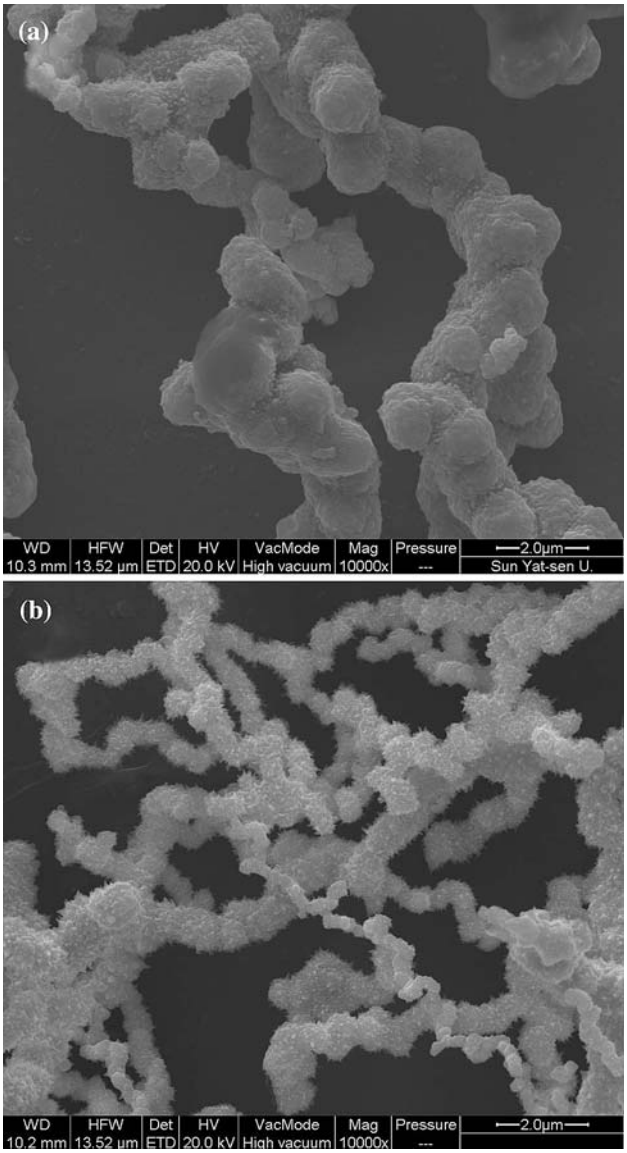

Fig. 3 SEM images of nickel wires prepared with conventional heating method or microwave heating with different powers **a** 80 °C water, **b** 100 W, **c** 400 W (PVP: 4 g/L)

$$J = A\exp\left[-B(\ln S)^{-2}\right] \quad (1)$$

where J and S are nucleation rate and super-saturation, A and B are constants, respectively. It is clear that reduction rate of stable Ni–PVP complex was lower than that of $NiCl_2$ or $Ni(OH)_2$, which inevitably increases the time for nickel atoms reaching super-saturation. Therefore, it was believed that the nucleation rate of nickel crystallite decreased with increasing PVP concentration. As for the

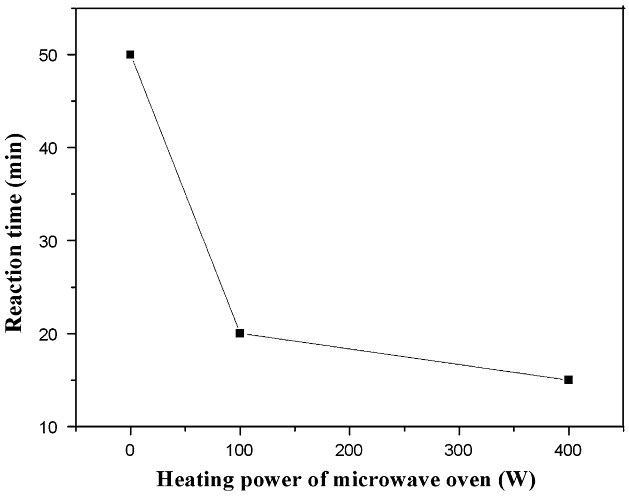

Fig. 4 Effects of heating power of microwave oven on the formation time of nickel powders. **a** 0 W, **b** 100 W, **c** 400 W (PVP: 4 g/L)

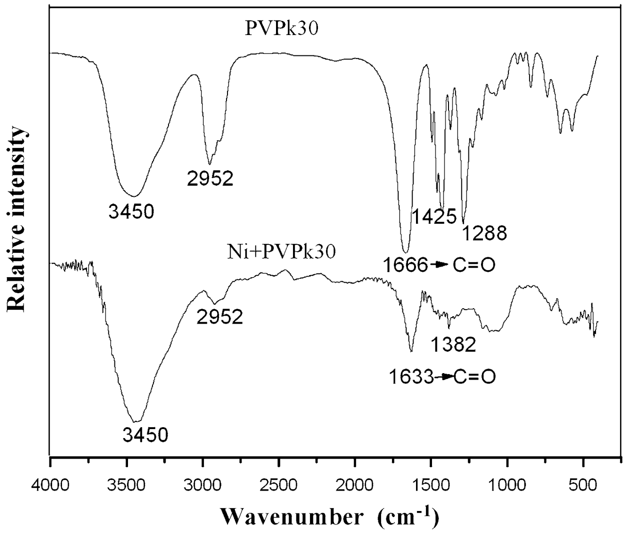

Fig. 5 Infrared spectra of nickel wires prepared with 4 g/L PVP and pure PVP

effect of PVP on the growth process of the nickel crystalline, anisotropic growth of nickel crystal will take place due to the lower growth rate of some nickel crystal faces absorbed by PVP molecules, because growth rate of the crystal faces physically absorbed by polymer was usually reduced [24].

Morphology of the nickel nanoparticles was critically dependent on the PVP concentration. The reason was that different PVP concentrations have different effects on the nucleation, growth, and aggregation of the nickel crystalline. In the absence of PVP, there was no PVP molecule to alter the growth rate of the nickel crystallite in different directions, and growth rate of nickel crystallite in all the directions is the same. Therefore, nickel crystallite will grow up to a spherical crystallite, followed by the aggregation of the crystallites to form nickel spheres. When the PVP concentration is low (1 g/L), it was believed that all PVP molecules coordinated with the Ni to form Ni–PVP complex. During the growth of the nickel crystal, there was no superfluous PVP absorbed on the faces of the nickel crystalline to alter the shape of the nickel crystal, and nickel crystals grow into spheres. Then, Ni–PVP complex may serve as "structure directing agent", which directed the aggregation of nickel crystals and the further assembling of the nickel crystals into nickel sphere chains. When the PVP concentration is proper (4 g/L), in addition to the PVP molecules coordinating with the Ni to form Ni–PVP complex, there are some superfluous PVP adsorbing on some faces of the nickel crystals, which lead to anisotropic growth of nickel crystal and formation of rod crystallite, followed by the aggregation and assembling of the nickel crystals into nickel wires. However, the products change into some aggregated nickel powders with irregular morphology as PVP concentration was too high (16 g/L), which was caused by the connection and winding of the too much superfluous PVP molecules.

The microwave irradiation was also responsible for the formation of nickel wires. Above results have shown that using convention heating method, only nickel chains were obtained, That is to say, magnetic interaction and electrostatic attraction of the nickel crystals was not enough to impel the nickel crystal to grow and aggregate into nickel wires. Microwave irradiation heating must play a unique role in the growth and aggregation of nickel crystals. It was believed that Ni–PVP complex with high permanent dipole momentum and magnetic nickel crystals could align itself with the alternating electric field of the microwave reactor, which was in favor of nickel crystalline to aggregate and assemble in certain direction and form of the nickel wires. Furthermore, nickel crystalline on the surface of the nickel wires would grow rapidly to form nickel spikes due to the microwave irradiation heating. As a result, such novel thorn-like nickel wires were synthesized rapidly.

Typical nickel wires (Fig. 1a) and spherical nickel particles (Fig. 2a) were selected for the electrical properties measurement. Figure 6 depicts the volume resistivity of the epoxy incorporated with spherical nickel particles and nickel wires. Volume resistivity of the two composites was decreased with the increase of fraction of nickel powders, and both the two kinds of composites exhibit typical characteristics of percolation. When the fraction of nickel wires reaches 30%, volume resistivity of composite could not greatly reduce with the additional increase of nickel wires, which indicate that the percolation was reached and continuous conducting paths and network was formed by the connection of nickel wires, which allow the electron to transfer through the composite, whereas the percolation

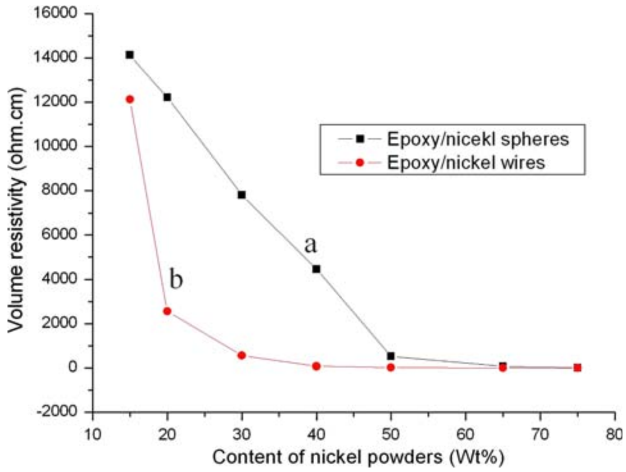

Fig. 6 Effects of **a** nickel spheres and **b** nickel wires content on the electrical properties of nickel powders/epoxy composites

threshold of epoxy/spherical nickel particles composite is about 50%, indicating that nickel wires shows better electrical conductive property in the composite than that of spherical nickel particles. Obviously, nickel wires with high aspect ratio were much easier to contact each other to form conductive channels for the electron than that of spherical nickel particles. Moreover, we suspected that spherical nickel particles were relatively easy to disperse in the nickel/epoxy composite than nickel wires. As a result, it needs much more spherical nickel particles in the nickel/epoxy composite to form conductive channels than that of nickel wires.

Conclusions

In summary, we have successfully synthesized nickel powders with novel structures by hydrazine reduction of $NiCl_2$ in the presence of poly(*N*-vinyl-2-pyrrolidone) by using microwave-assisted chemical reduction method. Nickel spheres gradually transformed into nickel wires with the increase of PVP concentration. Microwave radiation heating was in favor of the formation of nickel wires and nanometer-sized spikes. Compared with nickel spheres, the resultant nickel wires showed excellent electrical properties in the nickel wire/epoxy composite, which may lend a promising application in conductive paste.

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