Scalable Synthesis of Mono-dispersed Nickel Nanoparticles and Their Application as Thermal Conductive Fillers

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Abstract*—With the rapid development of the electronic industry, it is critical for electronic packaging industry to develop superior materials with high thermal conductivity and lower cost, so as to dissipate heat from the central components. Metallic materials are compelling in thermal conductivity application over decades. However, it is still a great challenge to synthetize metal nanomaterials which have specific structure. Here we report a one-step method to synthesis mono-dispersed nickel nanoparticles with durian structure in a large scale. These nickel nanoparticles can be prepared by mixing the nickel salts, reducing agents, coupling agents and nucleating agent in aqueous solution. The morphology of the nanoparticles can be well controlled by adjusting the reaction parameters. The average size of these nanoparticles is about 100 nm and extremely uniform. These nickel nanoparticles possess uniform cone-shape surface structure, which can provide excellent interconnection ability among themselves. Results show that, the thermal conductivity of the sample which nickel filler content of about 80 wt% embedded in a thermosetting-type insulating polymer resin reached 0.49 $W\cdot m^{-1}\cdot K^{-1}$. Due to the unique durian-like morphology, facile and efficiency synthetic method, and prominent thermal conductivity, the nickel nanoparticles can be widely used in some relatively low-end and large-scale applications of heat conductivity, such as high-power electrical heat sink, LED plastic shell, wireless signal base station.

Keywords—nickel nanoparticles; thermal conductivity; electronic; nanostructure

I. INTRODUCTION

Recently, there is an increasing demand for high power circuits with high performance and multi-function, smaller size, high efficiency and low cost, etc. [1] Accordingly, massive heat emerged from the central components, and thus thermal interface materials are needed to dissipate heat. Materials with a high thermal conductivity are becoming increasingly important with the need for more efficient heat removal from electronic devices such as LEDs[2], consumer electronics, automotive[3] and aerospace products[4, 5]. Hence, researches on those materials which can provide excellent heat dissipation ability have attracted extensive attention in recent years[6]. Traditionally, thermal problems of electronic devices can be solved in packages process by using high cost embedded heat sinks which exist thermal cracking risks and limits in thinner packages[7]. Polymers filled with thermal conductive fillers are considered as a feasible and cost effective candidate to address thermal management issues, in which the polymers provide mechanical properties while the fillers determine the thermal conductivity[8]. Hence, there were many researches on available conductive filler material, such as metal[9], carbon and ceramics, which provide thermally conductive channels. Accordingly, the morphology control of metal materials was considered as an effective method to improve the thermal conductive ability [7, 10-14]. As a base metal, nickel is easily obtained, low cost, chemically stable and exhibit good thermal conductivity (90.7 $W\cdot m^{-1}\cdot K^{-1}$ in bulk), the nickel nanomaterials have potential importance in the physics and chemistry as a transition metal[12, 15, 16]. To extend the application of base metal materials, it is of great significance to develop a facile and scalable method, which can fabricate special nanostructure with precisely controlled size and morphology[17-19].

Herein, we reported a one-step method to synthesis mono-dispersed nickel nanoparticles with durian structure in a large scale. The nickel nanoparticles can be prepared by mixing the nickel salts, reducing agents, complexing agents and nucleating agents in aqueous solution. The morphologies and nanostructures of the nanoparticle can be controlled by adjusting the reaction parameters. The average size of these nanoparticles is about 100 nm and extremely uniform. These nickel nanoparticles possess uniform cones structure on the surface, which provide excellent interconnect ability between each other. Results showed that, the thermal conductivity of the filling polymer with 80 wt% nickel filler and 20 wt% epoxy resin reached the level of 0.49 $W\cdot m^{-1}\cdot K^{-1}$, several times than the epoxy without filler. Due to unique durian structure, facile and efficiency synthetic method, prominent thermal conductivity, the nickel nanoparticles can be widely used in some relatively low-end and large-scale applications of heat conductivity, such as high-power electrical heat sink, LED plastic shell, wireless signal base station.

II. EXPERIMENTAL

A. Materials

Nickel (II) chloride hexahydrate ($NiCl_2\cdot 6H_2O$) powder, hydrazine hydrate ($N_2H_4\cdot H_2O$) solutions (85 wt% aq.), trisodium citrate dihydrate ($Na_3C_6H_5O_7\cdot 2H_2O$) and Hexadecyl trimethyl ammonium Chloride(CTAC) were purchased from Sinopharm Chemical Reagent Co.,Ltd., and the chloroplatinic acid hexahydrate was purchased from Aladdin. All the solutions in the experiments were prepared with analytical grade chemicals and deionized water.

The bisphenol A epoxy (Epon 828) and methyl tetrahydrophthalic anhydride(MTHPA) which serve as the binder were provided by Shell and Nanya, China, and hexamethylenetetramine (99%), which acts as the catalyst of the resin dispersant, was obtained from Guangzhou Chemical Reagent Factory, China.

B. Preparation of the nickel nanoparticles with durian structure

The reaction condition can be adjusted to control the size and morphology of nickel nanoparticles precisely. Typically, 400 mL of deionized water containing 0.100M $NiCl_2$, 37.5mM $Na_3C_6H_5O_7$, 0.20mM H_2PtCl_6 was prepared (solution A). Then, the same amount of ion-exchanged water (400 mL) containing 8.5% (v/v, 1.4M) N_2H_4 and 4g Hexadecyl trimethyl ammonium Chloride (CTAC) was also prepared (solution B). The pH of the both solutions was adjusted to 12.5 using an aqueous KOH solution. The metallic salt solution and the N_2H_4 solution were mixed and maintained at 80^{o}C. In the same time, keep the reaction solution under the magnetic field intensity of 300Gs. Finally, The Ni nanoparticles was washed several times with deionized water and ethanol, and then dried in a vacuum desiccator at room temperature.

C. Characterization

The morphologies of the nickel nanoparticles were observed by the field emission scanning electron microscope (ZEISS SUPRA®55, Germany). The thermal diffusivity (D) was obtained through Netzsch Laser Flash Apparatus (LFA 447) measurement.

III. RESULTS AND DISCUSSIONS

A. Characterization of the nickel nanoparticles with durian structures

The morphology and crystalline structure of the nickel nanoparticles are shown in Fig. 1. As shown in Fig. 1(a)-(b), the nickel nanoparticles possess durian-like structure, and the particle size is about 150 nm. It is clearly observed in Fig. 1(a) that the nanoparticles contain the homogeneous spherical structure as a core and a large number of cones on the surface as exterior structures, and the particle size is uniform. As can be seen from Fig. 1(c), the particles showed narrow diameter distribution. By changing the chemical reaction parameter, such as the concentration of reducing agent, reaction time, the average size and morphology of nickel nanoparticles can be tailored precisely. It's notable that, the nanoparticles can be prepared in a very large scale, and showed good reproducibility, the dried nanoparticles powder which the mass is 15 g is shown in Fig. 2.

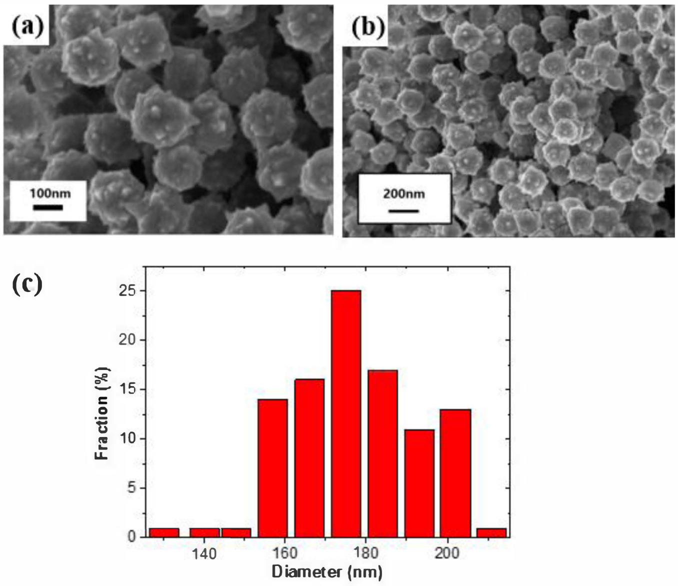

Fig. 1 (a) High magnification SEM image of the durian-like nickel nanoparticles. (b) Low magnification SEM image of the nanoparticles. (c) Diameter distribution of the nickel nanoparticles.

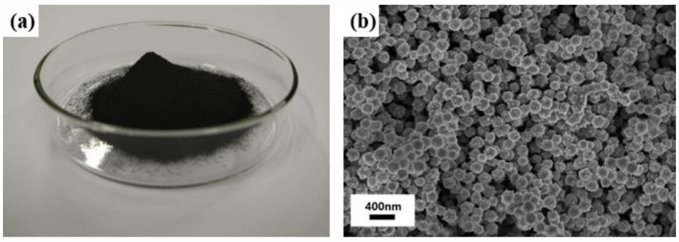

Fig. 2 The picture (a) and SEM image (b) of large-scale prepared durian-like nickel nanoparticles.

B. Effect of reaction parameters on nickel products

In order to control the size and morphology of the nickel product precisely, studying the function of reaction parameters is necessary. In this reaction system, the concentration of nickel chloride and hydrazine hydrate, reacting time, as the most vital reaction parameters, were investigated systematically.

The effect of the concentration of nickel chloride on resulted nickel nanoparticles was studied, by fixing other parameters including the concentration of sodium citrate, CTAC and hydrazine hydrate, reaction temperature(80 ^{o}C), and reaction time (20 min)

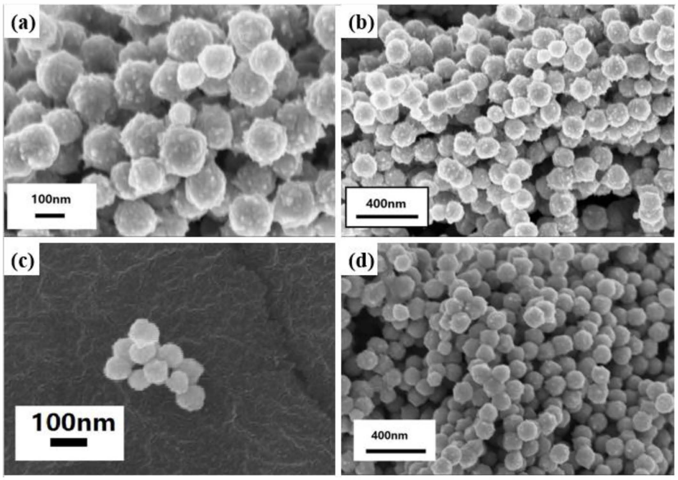

Fig. 3 SEM images of the nickel nanoparticles at the $NiCl_2$ concentration of 0.2 M (a, b) and 0.3 M (c, d).

As shown in Fig. 3(a)-(b), at the $NiCl_2$ concentration of 0.1M, the average diameter of Ni nanoparticles are 150 nm and possess typical durian-like structure. The length of these cones on the surface ranges from 10 nm to 20 nm. When the concentration of nickel chloride solution increased to 0.2M, the diameter of Ni nanoparticles decreased to about 120 nm, and the cones become extreme short and rare (the size of cone is only several nanometers). By further increasing the concentration of $NiCl_2$ to 0.3M, Ni nanoparticles exhibit a good spherical shape and smooth surface with decreased diameter at about 80 nm. This can be partly explained that, when at low Ni^{2+} concentration, Ni atoms tend to deposit on the active crystal faces which result in nanocones; while at high Ni^{2+} concentration, Ni atoms deposit uniformly on the surface of Ni particles and the cones on the surface are not apparent.

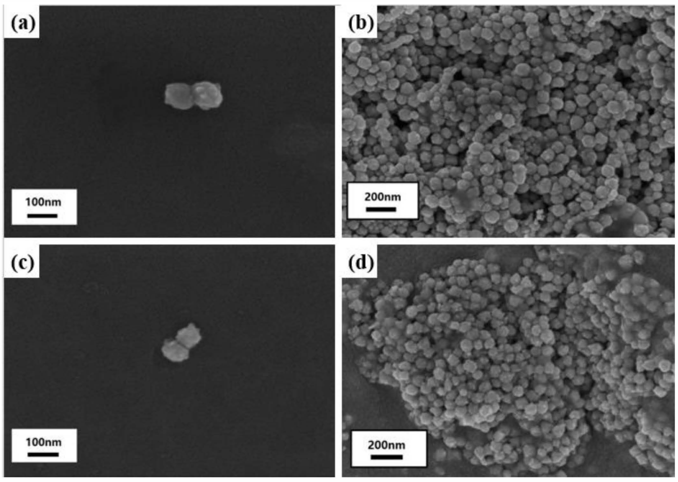

Fig. 4 SEM images of the nickel nanoparticles at the $N_2H_4 \cdot H_2O$ concentration of 0.75 M (a, b) and 0.35 M (c, d).

As to the reducing agent, the diameter of Ni particles decreased with the decrease of the concentration of $N_2H_4 \cdot H_2O$. As can be seen from Fig. 4(a)~(b), compared to the typical durian-like nickel nanoparticles synthesized at the hydrazine hydrate concentration of 1.4M (Fig. 1(a)~(b)), the cones on the surface of particles disappeared at a low concentration of hydrazine hydrate. Indeed, when the concentration of hydrazine hydrate solution decreased to 0.7M, the size of nickel nanoparticles is about 80~100 nm, smaller than the case of high concentration reducing agent. When the concentration of hydrazine hydrate solution decreased to 0.35M, the particles size is about 50~70 nm, it can be seen in Fig. 4(c)~(d). The nucleation and growing speed will be enhanced by increasing the concentration of reducing agent, thus the nanoparticles grown up to larger size. In addition, at the same reaction time, low hydrazine hydrate concentration provides very low reaction rate, resulting in that the cones have no enough time to grow. Hence, the smooth and uniform nanoparticles were obtained.

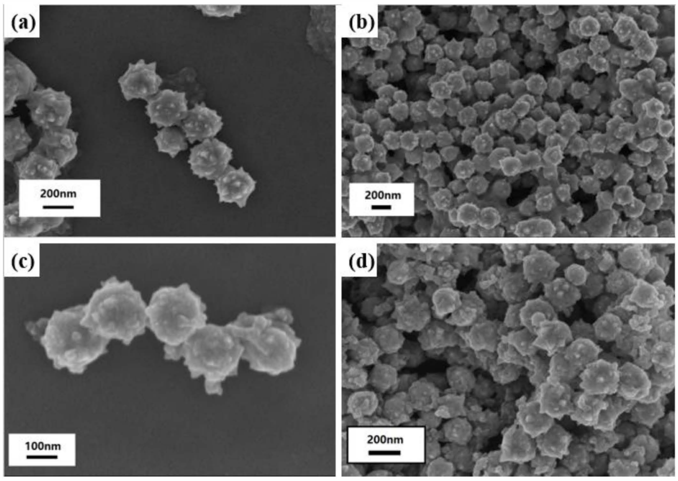

Fig. 5 SEM images of the nickel nanoparticles at the reaction time of 40 min (a, b), 60 min (c, d).

It is well known that the products are bound to be larger at longer reaction time. As we can see from the Fig. 6(a)~(f), when the reaction time prolonged, the nickel particles size gradually become larger. When the reaction time is 40 min, the particles diameter ranges from 170 to 200 nm. When the reaction time prolong to 60 min, the diameter ranges from 250 to 310 nm. In addition, the size of cones on the surface also increased with the reaction time.

C. Application in thermal conductive fillers

Due to the unique structure of the durian-like nickel nanoparticles, we developed their applications as thermal conductive filler in heat radiation. Typically, we select the reaction parameter that the nickel dichloride solution concentration is 0.1M, the hydrazine hydrate solution is 1.4M, and the overall reaction time is 30 min. Then, the nickel products were dried in a vacuum desiccator at room temperature.

The epoxy binder was consist of the bisphenol A epoxy and methyl tetrahydrophthalic anhydride (MTHPA) at the mass ratio of 1:0.85. A small amount of catalyst was added to the resin dispersant to accelerate crosslinking. After that, the dried Ni products were dispersed in the binder and mixed thoroughly by a planetary rotary mixer (Hasai. Co., Shenzhen) at 1500rpm for 5 min. Typically, the content of nickel particles in the filling polymer was 80 wt%. After that, all the samples were cured at 190 ^{o}C for 30 min.

Thermal conductivity of the cured sample in a through-plane mode was evaluated using a Netzsch Laser Flash Apparatus (LFA 447). The thermal diffusivity (D) obtained was used to calculate the thermal conductivity (λ) by:

$$\lambda = D \times \rho \times C_p$$

Where ρ and C_p is the density and thermal capacitance of the adhesive respectively.

The value of C_p was evaluated as:

$$C_p = a \times C_{Nickel} + (1 - a) \times C_{epoxy}$$

Where a is the ratio of nickel by weight. C_{Nickel} and C_{epoxy} are the specific heat capacity of nickel($0.45 \mathrm{J \cdot g^{-1} \cdot K^{-1}}$) and epoxy($1.2\ \mathrm{J \cdot g^{-1} \cdot K^{-1}}$) respectively. The average λ for each square sample was thus obtained[6].

Finally, the thermal conductivity of the primary sample was measured as 0.49 $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ at 80 wt% of nickel loading.

As can be seen from the nickel thermal conductivity sample, there are some pore in the bulk of sample. Due to the existence of these pores and the very poor thermal conductivity of air, so the thermal conductivity of these samples is able to suffer extremely harmful effect. In other words, the thermal conductive performance of nickel nanoparticles has a tremendous potential to improve. For instance, the method that get rid of bubble in slurry system or use the anneal process to modify the nickel particles, maybe improve the thermal conductivity to a great extent.

IV. CONCLUSIONS

In summary, we demonstrate a facile and one-step method to fabricate mono-dispersed nickel nanoparticles with durian structure in a large scale. The nickel nanoparticles can be prepared simply by mixing the nickel salts, reducing agents, complexing agents and nucleating agent in aqueous solution and reacting at a relative low temperature. The morphologies and nanostructures of the nanoparticles can be controlled by adjusting the reaction parameters. The average diameter of these nickel nanoparticles can be controlled range from 50 nm to 300 nm and kept the size extremely uniform. These nickel nanoparticles possess unique cones structure on the sphere surface, which can provide excellent interconnect ability between each other. Results show that, The thermal conductivity of the sample which nickel filler content is about 80wt% embedded in a thermosetting-type insulating polymer matrix for mechanical reached the level of 0.49 $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$, several times than the epoxy without filler, and it is sure that the performance have a great potential to improve. Due to unique durian-like structure, facile and efficiency synthetic method, prominent thermal conductivity, the nickel nanoparticles can be widely used in some relatively low-end and large-scale applications of heat conductivity, such as high-power electrical heat sink, LED plastic shell, wireless signal base station.

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