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PREPARATION AND CHARACTERIZATION OF NANOPOROUS NICKEL USING PS BEAD AS PHYSICAL TEMPLATE

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Abstract. Monodisperse PS beads were prepared by miroemulsion polymerization method. Styrene monomer (0.99%), potassium persulfate (0.44%), and sodium dodecyl sulfonate (0.27%) was used as precursor, initiator, and surface active agent, respectively, and then used a novel and simple electroless plating method coating nickel on PS beads substrate by pd-free activation process (nickel acetate 2.27%, sodium borohydrate 2.27%, and sodium hypophosphite 2.50%), lastly, the mixture samples were annealed at 500 °C for 5 h to obtain nanoporous nickel. SEM, EDS, XRD was used to characterize these samples. N_2 sorption was used to analyses of pore structure .The results indicate that pure PS beads show 120-150 nm of particle size, while the aperture of the nanoporous nickel is about 100-130 nm of particle size, the shell thickness is about 15-20 nm, and the specific surface areas is 161.69 m^2 g^{-1}.

1. INTRODUCTION

Micro- and nanoporous metals with high surface areas have attracted considerable interest in a wide range of industrial and environmental applications, including catalysis, sensors, actuators, fuel cells, and so forth [1,2]. Recently, nanoporous metals have been synthesized by different routes, including powder sinter, glancing angle deposition, colloidal crystal template and dealloying the less stable component in the alloys [3,4]. Among these routes to synthesize nanoporous metal, colloidal crystal template is a bottom-up candidate since this method can control the porosity (pore size, surface area, pore channel structure, and pore volume) of porous metals well and showed bigger relatively surface area [5-7].

It is known that, electroless plating has been used widely in many fields, generally, the deposition reaction of the electroless nickel occurs at the absorbed palladium catalytic active centers on the nonmetallic substrates [8-10]. However, this method involve numerous problems, such as the use of highly toxic Sn, the rare and cost metal of Pd and complex procedure involves pretreatment, activation and plating [11-13]. In this paper, we developed a novel and simple electroless plate method by pd-free activation process to plate nickel on polystyrene(PS) microspheres substrate ,and thus Ni nanoporous materials have been successfully prepared by annealing to remove polystyrene template.

2. EXPERIMENTAL

2.1. Synthesis of polystyrene microspheres

Nano-sized PS spheres were prepared by microemulsion polymerization method which

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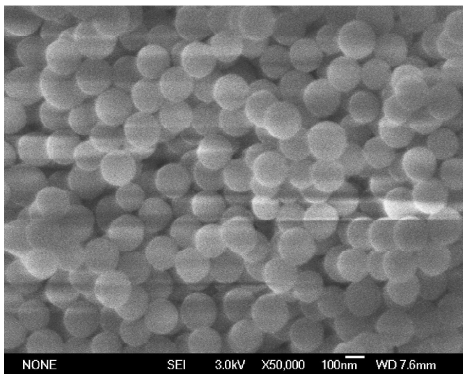

Fig. 1. SEM photograph of polystyrene microspheres.

comprises styrene monomer (St,), potassium initiator, and surfactant, respectively. In detail, 0.25 g SDS and 0.4 g $K_2S_2O_8$ were dissolved in 90 mL water solution, then add in 10 mL St, mixed by ultrasonic vibration. This solution was Shift into 250-mLfour-necked glass vessel equipped with a condenser, stirrer and thermometer. The vessel was immersed in a thermostated water bath. When the temperature rose to 70 °C, the reaction was carried out for 10 h under N_2 protection.

2.2. Synthesis of PS/Ni microspheres

1.5 g nickel acetate and 1.5 g sodium borohydride were dissolved in 30 mL and 20 mL methanol solution, respectively. Then add 1.0 g PS microspheres into nickel acetate alcohol. These two solutions were mixed under ultrasonic vibration for 30 min at 50 °C, at which point the activated PS microspheres were separated from the activating solution, rinsed with distilled water.

The activated PS microspheres were placed into 60 mL electroless plating bath which contained 1.5 g NaH_2PO_2, then the pH value was adjusted to 5.0 by H_3PO_2. The plating process was carried out for 6 h at 75 °C with stirrer treatment.

2.3. Synthesis of hollow nickel microspheres

After the electroless plating reaction, the complexed microspheres were filtered and rinsed with distilled water, then dried at 50 °C. The hollow nickel microspheres were obtained by heating the PS/Ni microspheres at 500 °C for 5 h in an oven with nitrogen flow.

2.4. Characterization

The surface morphologies of the PS, PS/Ni, and hollow Ni microspheres were investigated by scanning electron microscopy (SEM, LEO 1530VP). Element analysis was carried out on an energy dispersive X-ray analytical system (EDX, INCA 3294). The structural state of the products was identified by the measurement of X-ray diffraction (XRD, Bruker D8 ADVANCE) using Cu K_α radiation. Nitrogen adsorption and desorption isotherms at 77.35K were measured by a NOVA2000e system.

3. RESULTS AND DISCUSSIONS

3.1. Preparation of the PS microspheres

The PS microspheres with diameter of 120-150 nm were obtained by microemulsion polymerization method. SEM photograph of the polystyrene microspheres is shown in Fig. 1, which indicates that the PS microspheres are monodisperse with uniform size distribution, spherical in shape and smooth on the surface.

3.2. Preparation of the PS/Ni microspheres

When coating Ni on PS microspheres, methanol solution, as activating solvent, was used due to that the solution from this solvent showed favorable spreadability on the surface of PS microspheres which is in favor of gaining even activating microspheres and nicer coat. Fig. 2 shows the SEM images of as-synthesized Ni/PS microspheres. It could be seen from the Fig. 2 that microspheres with compact and continuous nickel coatings were obtained, which is attributed to the following reasons. First, The first ions of nickel reduced by $NaBH_4$ aggregate on the PS surface to form the nuclei as catalytic centers, because nickel is also a catalyst for the reaction, as a result, nickel deposition

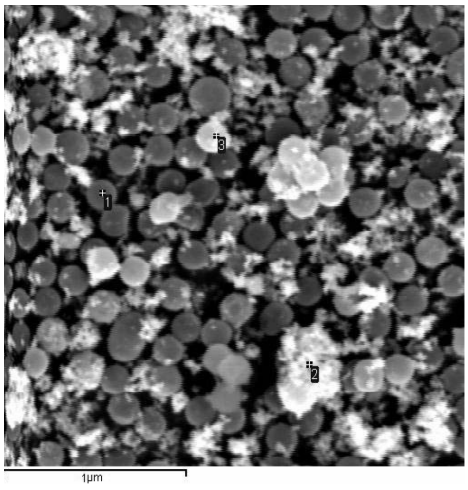

Fig. 2. SEM photograph of PS/Ni microspheres.

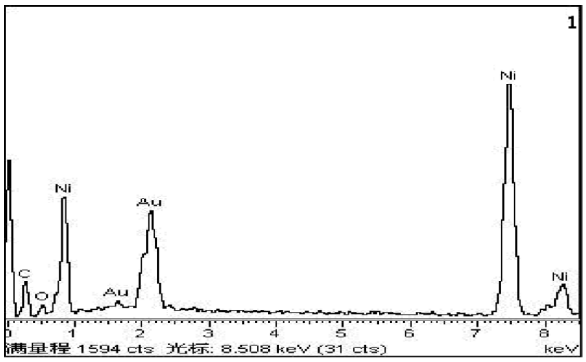

Fig. 3. EDS spectrum of the PS/Ni microspheres hollow.

continues automatically. Second, ultrasonic wave is used to assist the electroless plating, because the cavitation of ultrasound wave can release hydrogen bubbles instantly and accelerate the reactants transportation in the elctroless plating solution [14].

The chemical composition of PS/Ni microspheres is shown in Fig. 3. It indicates that the coating deposited on the PS microspheres is nickel as the major element. The small peak of carbon and oxygen is attributed to PS substrate, for the depth of the electron beam rip into the coating. Similarly, the peak of Au is attributed to the deposition on the samples when they were measured for increasing the conductivity.

3.3. Preparation of hollow nickel microspheres

Fig. 4 shows particle morphology of the Ni hollow microspheres annealed at 500 °C for 5 h in nitrogen separately, it can be seen that the hollow

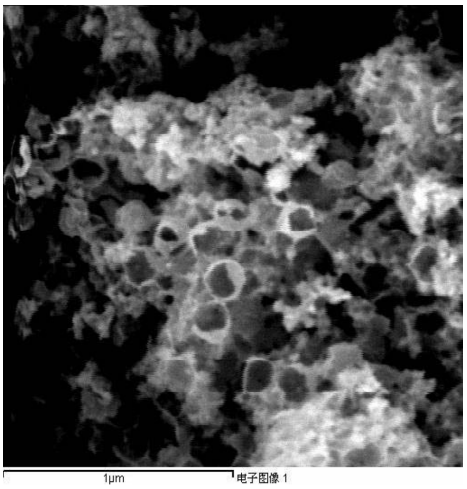

Fig. 4. SEM photograph of nickel microspheres annealed at 500 °C.

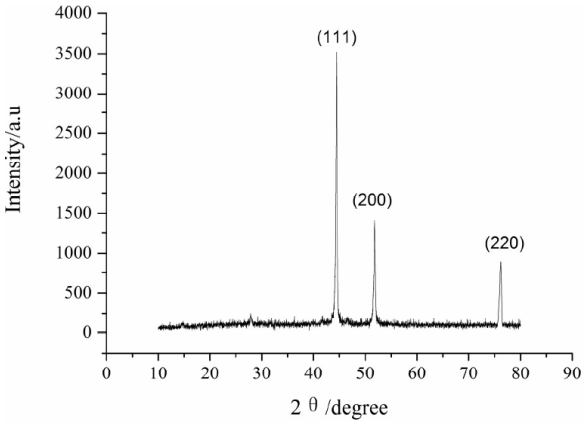

Fig. 5. XRD pattern of hollow nickel microspheres adsorption–desorption.

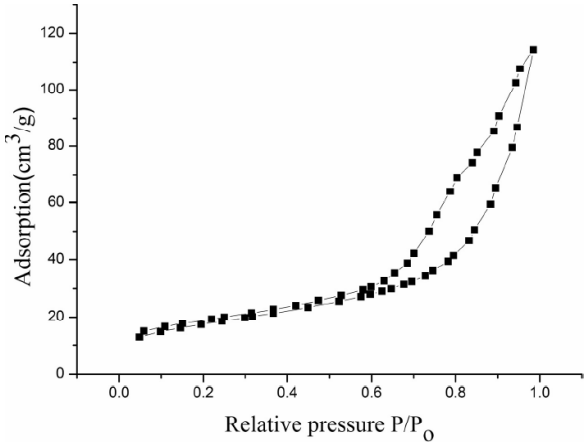

Fig. 6. Nitrogen isotherm curve of hollow nickel microspheres.

microspheres have been abtained successfully. The aperture of the samples is about 100-130 nm, which is less than PS microspheres, and the shell thickness of hollow nickel microspheres is about 15-20 nm. Some of these microspheres adhered to each other, it may be that some Ni Ions were deposited instead of coated on PS surface in the process of electroless plating reaction. The XRD pattern of the hollow nickel microspheres is shown in Fig. 5, the diffraction peaks of the microspheres can be indexed to the standard pattern (JCPDS No. 87-712), indicating the sample is pure Ni. Three peaks located at 44.40°, 51.72°, and 76.18° are respectively assigned to Ni (1 1 1), Ni (2 0 0) and Ni (2 2 0) planes, which demonstrates that nickel is coated on the surface of PS microspheres by electroless plating method used pd-free activation process in this work.

3.4. N_2 sorption analyses of hollow nickel microspheres

In order to determine the porous structure of nickel microspheres, nitrogen adsorption and desorption

isotherm at 77.35K was measured and the result is shown in Fig. 6. The nitrogen adsorption–desorption isotherm of nickel microspheres shows a typical IUPAC type IV pattern with an H3 type hysteresis loop[15], indicating the existence of mesopores. It is believed that this type of loop, exhibiting no limiting adsorption at high P/P_0, results from the assembly of loosely coherent particles. The Brunauer Emmett Teller (BET) specific surface areas of Ni is 161.69 $m^2 g^{-1}$.

4. CONCLUSIONS

The PS microspheres with diameter of 120-150 nm were obtained by microemulsion polymerization method. Then a novel, simple, and environment-friendly electroless plating method by pd-free activation process was used to obtain monodisperse microspheres with compact and continuous nickel coatings. Finally, we have successfully abtained hollow nickel microspheres with aperture of 100-130 nm, the shell thickness is about 15-20 nm, the specific surface areas of hollow Ni is 161.69 $m^2 g^{-1}$.

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