

Synthesis of nickel nano-particles by EB irradiation

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ABSTRACT A new method, using electron beam, has been successfully developed to prepare nickel nano-particles at room temperature under ambient pressure, without any catalyst. The structure, morphology, size, size distribution, optical properties, magnetic properties and the melting point have been characterized by X-ray diffraction (XRD), laser scattering particle size distribution analysis (LSPSDA), transmission electron microscopy (TEM), ultraviolet-visible spectrophotometer (UV-vis), vibrating sample magnetometer (VSM) and differential scanning calorimeter (DSC), respectively. The LSPSDA and TEM results show that average size of the nickel nano-particles is about 39 nm, which is in agreement with the calculated value from XRD using Scherer formula.

KEYWORDS Nano-materials, Nickel nano-particle, Electron beam, Radiation, Electron accelerator

CLC O614.2, O572.2, O644.22, TF125.2⁺3, TH742, TB383

1 Introduction

Nano-particles of metals have been a subject of intense research due to their potential applications in catalytic properties, sensitive materials, electronics and magnetics etc^[1]. Transition metal nanoparticles, such as Fe, Co and Ni, have been given much attention due to their applications of magnetization, catalysis, electronic and conduction^[2]. Therefore, synthesis of the nanoparticles has become an active subject of studies. Many methods including hydrogen arc plasma^[3], borohydride reduction of metal salts^[4], extraction of transition metals from wood pulp fibers using supercritical carbon dioxide^[5], radiolytic system, sonochemical and thermal decomposition of organic metal complexes^[6,7], and electrode position on alumina template^[8] have been proved effective for the synthesis of these transition metals.

Among these preparation methods, radiolytic synthesis of nanocrystals from metal ions in solution can provide a wide variety of mono and multi-metallic systems with different structures^[9]. However, applications using high-energy electron beams as irradiation source to synthesize nano-particles in an aqueous solution are rarely reported in the literatures.

In this paper, we present a detailed study on synthesis, characterization of nano-particles with

nickel nano-particles for as an example.

2 Experimental procedure

All the chemicals used in this work are of analytical grade (A.R) without further purification, including NiSO₄·6H₂O, polyvinyl alcohol (PVA), isopropyl alcohol (IPA) and ammonia (NH₃·H₂O). Distilled water was used in the experiment as dissolvent. Solutions were prepared by dissolving certain amount of nickel sulphate in water. PVA was added to control the size of nano-particles and, moreover, to prevent aggregation of the nano-particles, IPA was added in appropriate proportions in the solution to act as scavenger of oxidative radicals (OH·). Ammonia was added in the solution to act as precipitator, and simultaneously, to control pH. Then nitrogen was added to the solution to scavenge dissolved oxygen. After the above procedures were finished, the solution was irradiated to different absorbed doses by 1.75MeV 1mA electron beam from an electron beam (EB) facility at Shanghai Applied Radiation institute, Shanghai University.

After irradiation, colour change of the solution could be observed, from aquamarine before the irradiation to black after the irradiation, as the radiation induced nickel nano-particles suspended in the solution. The suspended nickel nano-particles were

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treated by magnet, for nickel is a magnetic material. The residual PVA was removed by washing several times with distilled water and ethanol (99.7%, density 0.79g/mL) until no suspended materials could be found on the surface when the solution was poured off. After vacuum drying at room temperature for 12 hours, black nickel nano-particle powders were obtained.

X-ray diffraction ($\text{Cu } K\alpha \lambda = 0.15418\text{nm}$), was used to measure the particle structure. Morphology and particle size of the particles were determined by laser scattering particle size distribution analysis (Zeta Potential / Particle Sizer NICOMPTM 380ZLS) and a transmission electron microscopy (JEM-200CX), which was operated at 200 kV accelerating voltage. Visible absorption spectra of the nickel nano-particles were recorded by a UV-visible spectrophotometer (TU-1901). An NETZSCH STA 409 PG/PC differential scanning calorimeter was used to check the melting point and an EGG Princeton Applied Research Model 155 vibrating sample magnetometer was used to test the magnetic properties of the nickel nano-particles.

3 Results and discussion

Typical XRD result of the nickel nano- particles is given in Fig.1. The XRD peaks at $2\theta = 44.5$, 51.82 , 76.36 , 92.9 and 98.44 degrees were indexed as pure nickel atoms in ASTM powder diffraction card No. 04-0850. The obtained black powder was confirmed to be nickel atoms.

$$L = 0.9\gamma / B (\cos\theta) \quad (1)$$

Where θ is the diffraction angle, γ is wavelength of the X-ray, and B is correlated to the diffraction peak, $B = (\beta_{\text{sample}}^2 - \beta_{\text{reference}}^2)^{1/2}$, β is the full width at the half maximum (FWHM) of the peak.

For $2\theta = 44.5^\circ$ in Fig.1, $\beta_{\text{reference}}$ is 0.260 degrees and β_{sample} is 0.424 degrees, then average size of the nickel nano-particles is about 25.6nm. The largest average particle size ($2\theta = 92.9^\circ$) is about 34.5nm. The calculated particle size is in agreement with the results of LSPSDA analysis and TEM observation, which will be discussed later.

Typical TEM micrographs of the nickel particles are shown in Fig.2, 3 and 4. The nickel nano-particles

dispersed in different solvents exhibit various aggregated morphologies. Clearly, dispersibility of the nickel particles in ethanol was better than in carbon tetrachloride. The strong interactions between the nickel nano-particles and ethanol could make the nickel particles well dispersed in ethanol. As shown in

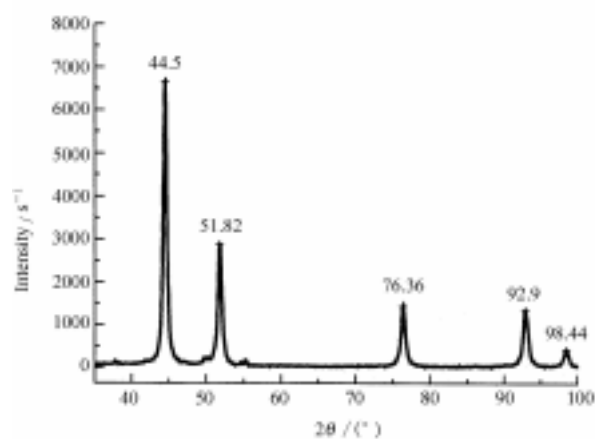


Fig.1 XRD pattern of nickel nano-particles by electron beam irradiation. Average size of the particles can be calculated by Scherer formula

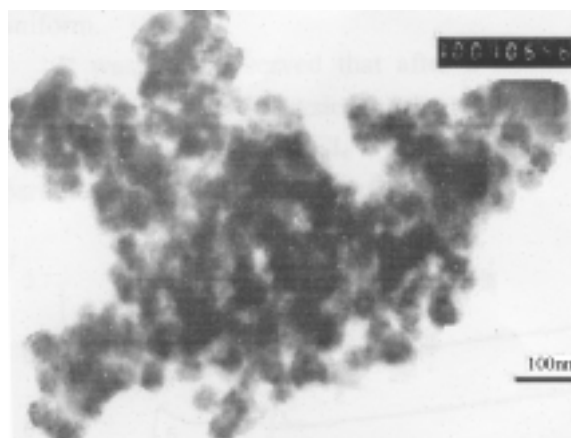


Fig.2 TEM micrographs of nickel nano-particles dispersed in ethanol

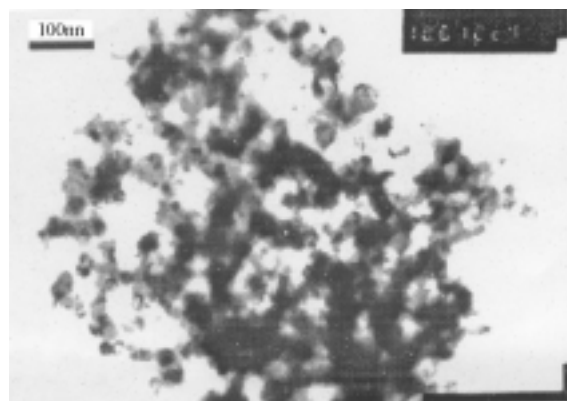


Fig.3 TEM micrographs of nickel nano-particles dispersed in carbon tetrachloride

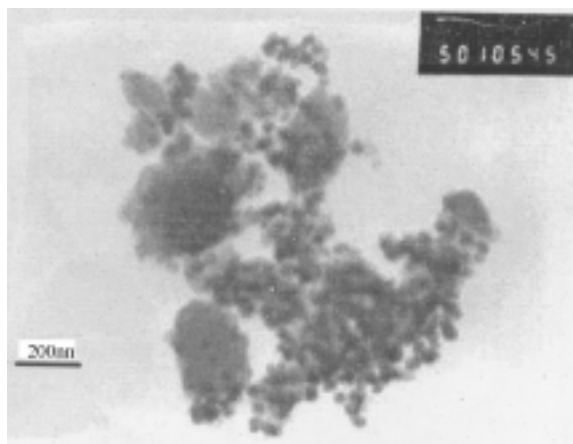


Fig.4 TEM image of nickel nano-particles in ethanol. The particles had been used to do the XRD

Fig.4, size of the nickel nano-particles is 26nm with the smallest, and average size of the particles is about 37nm.

The nickel nano-particle sample used for TEM observation had been used for the XRD measurement. Laser scattering particle size distribution analysis was used to study distribution of nickel nano-particles in solvent. The nickel nano-particles dispersed in chloroform was shown in Fig.5.

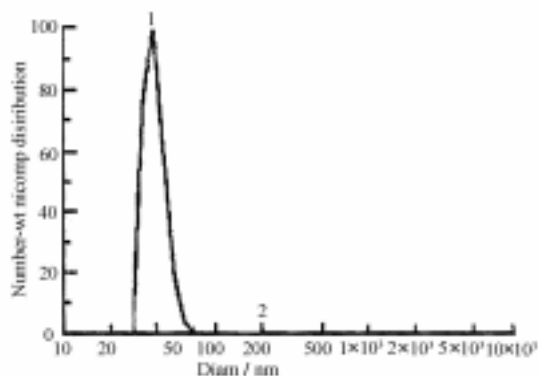


Fig.5 LSPDA pattern of nickel nano-particles dispersed in chloroform

NICOMP SUMMARY:

Peak #1: Mean Diam. = 39.4 nm, S.Dev. = 8.0 nm (20.3%) Num = 100.0%

Peak #2: Mean Diam. = 214.9 nm, S.Dev. = 24.3 nm (11.3%) Num = 0.0%

Mean Diameter = 39.9nm, Fit Error = 9.934, Residual = 38.178

Fig.5 shows the distribution of the nickel nano-particles by LSPDA. From the analysis of the

main peak, it can be seen that the mean diameter of the nickel nano-particles is 39.4nm, which is in agreement with the TEM results.

UV-visible spectrophotometer was used to study dispersibility of the nickel nano-particles in different solvents. An ultrasonic device vibrated the nickel nano-particles to help dissolution in different solvents. UV-vis absorption spectra of the nickel nano-particles dispersed in different solvents are shown in Fig.6. The absorption peaks of the nickel nano-particles are different in different solvents. In each case, the absorption by the nickel nano-particles was done relative to a blank containing the same solvent, in this way, only the absorption spectra of the nanoparticles are visible. Also, it can be seen from Fig.6 that there was no absorption by nickel nano-particles in both water and ethanol, and the absorption in acetone seems to be the most complicated. This is because that acetone has a low polarity and the size distribution of the nickel nano-particles in acetone is not very uniform.

It was also observed that after a month of storage at 4°C, the dispersion of the nanoparticles in both chloroform and CCl₄ was still good, and the particles remained in suspension.

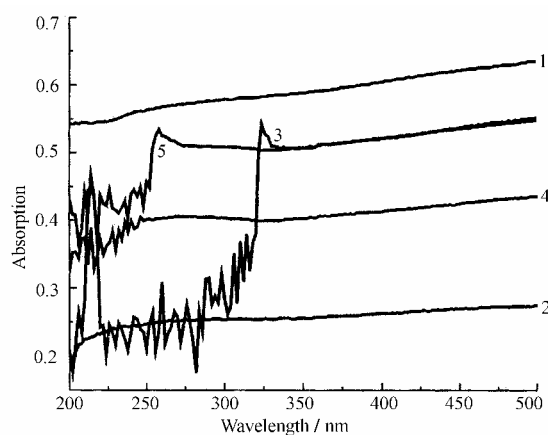


Fig.6 UV-VIS absorption of 200mg/L nickel nano-particles dispersed in different solvents

1, distilled water; 2, Ethanol; 3, acetone; 4, chloroform; 5, caborn tetrachloride

Being a magnetic material, the σ -H hysteresis loop of the prepared nickel nano-particles was measured at room temperature. A typical pattern is shown in Fig.7. Its coercivity (3541.2A/m) was inferior to that of the bulk nickel (7957.8A/m)^[10].

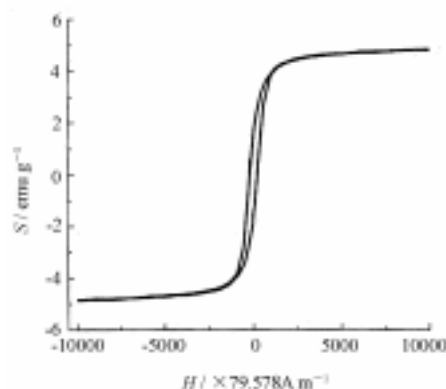


Fig.7 σ -H hysteresis loop of nickel nano-particle

DSC measurement was performed to check the melting point of the nickel nano-particles. As shown in Fig.8, melting point of the nickel nano-particles is about 524.3°C, far less than 1455°C^[11], the normal melting point of nickel. When particle sizes are in nanometer scale, their physical properties can differ greatly from the bulk materials. Decreased melting points can be observed with other nano-particle materials^[12].

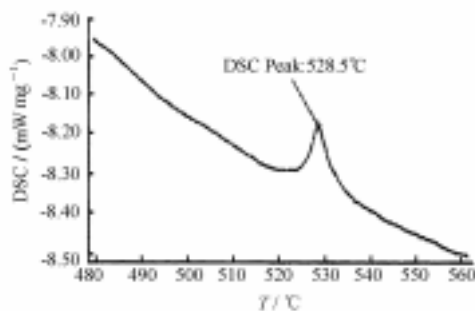
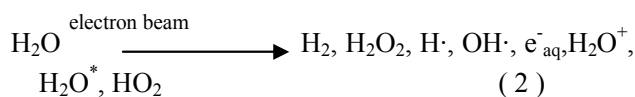
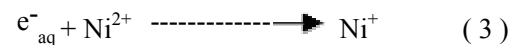


Fig.8 DSC spectra of the nickel nano-particles (heating rate 20°C / min)

Irradiation of water produces the hydrated electrons in addition to other radicals and species as given in Eq.(2)^[13]



Electron beams produce nickel nano-particle as a result of nickel ion reduction by hydrated electron formed in solutions under electron beam irradiation. As a hydrated electron has a standard electrochemical potential of -2.77V and the standard potential (E° of Ni^{2+}/Ni) is -0.25V, the reduction of nickel ions can occur according to the following reactions:



4 Conclusion

The following conclusions can be drawn from the experimental study.

(1) Nickel nano-particles were prepared, without any kind of catalysts, at room temperature and ambient pressure, by electron beam irradiation of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ solutions with isopropyl alcohol as scavengers of oxidative radicals.

(2) Melting point of the nickel nano-particles is much lower than bulk nickel.

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电子束辐照制备纳米镍

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摘要 在水溶液中, 常温常压下不加入任何催化剂, 用电子束加速器辐照作为一种新的方法可成功制备纳米镍。利用 X 射线衍射 (XRD)、透射电子显微镜 (TEM)、激光衍射粒度分布仪 (LSPSDA)、紫外可见光分光光度计 (UV)、样品振荡磁力计 (VSM) 和差热分析仪 (DSC) 来分别表征材料的结构、形貌、大小、粒径分布、光学特征、磁学性能以及材料的熔点。TEM 图像和 LSPSDA 分布图证明颗粒大小为 39nm, 这与 XRD 实验通过 Scherer 理论公式计算的结果相一致。

关键词 纳米材料, 纳米镍, 电子束, 辐照, 电子加速器

中图分类号 O614.2, O572.2, O644.22, TF125.2⁺3, TH742, TB383