

Preparation and Characterization of NiPd Nanoparticles

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ABSTRACT

Low Curie temperature NiPd seeds have been studied as potential materials for self-regulated hyperthermia. The invasive deposition of these seeds can be overcome by the use of NiPd nanoparticles with functionalized surfaces. The present work discusses two new methods of preparation of NiPd nanoparticles. The particles have been characterized by x-ray diffraction, energy dispersive spectrometry, transmission electron microscopy and alternating gradient magnetometry.

KEY WORDS

NiPd, nanoparticles, hyperthermia

INTRODUCTION

Hyperthermia has long been known as a potential therapeutic treatment for cancer. In hyperthermia the tumor tissue is heated to therapeutic temperature levels causing their necrosis without heating the healthy tissue¹. Such spatially constrained heating can be achieved magnetically. This involves localization of magnetic material in the tumor tissue followed by the application of an alternating magnetic field that causes hysteretic, eddy current or Néel relaxational losses in the magnetic material that is converted to heat.

Recently, it has been shown that using magnetic materials with a Curie temperature near the therapeutic temperature serves as a self regulating temperature control mechanism²⁻⁴. This avoids any damage caused due to overheating of the tissue. Nickel-Palladium (NiPd) alloy is one such material that has been studied for self-regulated hyperthermia⁵. These alloy seeds have to be introduced invasively into the tissue. It may be possible to overcome such invasive deposition by using nanoparticles of magnetic materials. Such treatment has been termed as Magnetic Fluid Hyperthermia (MFH). By using nanoparticles of low Curie temperature magnetic materials like NiPd alloy, the advantages of self-regulated heating and MFH can be coupled to achieve a practical therapy. The subject of this paper is to discuss and

compare the characteristics of NiPd nanoparticles synthesized by two different methods.

There have been several reports in the literature that describe the synthesis of NiPd alloy⁶⁻⁹ or Ni/Pd core/shell¹⁰⁻¹¹ nanoparticles. They focus on the catalytic activity and the magnetic properties of the nanoparticles. Our interest is to study the synthesis of NiPd alloy nanoparticles, since it is the bulk NiPd alloy whose Curie temperature is in the range of interest for self-regulated hyperthermia¹². Reports on synthesizing highly monodisperse nanoparticle alloys like FePt¹³⁻¹⁵ has motivated us to choose a wet chemical synthesis method. In the present work we describe two new methods to synthesize NiPd nanoparticles. We characterize these particles for their structure, size, composition and magnetic properties by X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Energy Dispersive Spectrometry (EDS) and Alternating Gradient Magnetometry (AGM) respectively.

EXPERIMENTAL SECTION

Materials

Nickel (II) acetylacetonate (95%) and palladium (II) acetylacetonate (99%), 1, 2-hexadecanediol, oleic acid (95%), and oleyl amine (70%) were purchased from Sigma Aldrich. Diphenyl ether (99%) and 1.0 M solution of lithium triethyl borohydride (LiEt₃BH) in THF were purchased from Acros. A three neck round bottom flask fitted with a reflux condenser on the middle neck, a thermometer on one of the side necks and an injection septum on the other side neck, was used for the synthesis. The ground joints were sealed using teflon sleeves. A 10 mm magnetic stirrer bar was used to mix the contents. The top of the condenser was fitted with a septum through which N₂ was supplied and withdrawn to provide an inert atmosphere during the synthesis. Heating was carried out using a resistive heating mantle, the rate of heating being controlled by a variac.

Preparation of NiPd nanoparticles

Method 1

A combined quantity of 1.0 mmole of nickel (II) acetylacetonate and palladium (II) acetylacetonate, 2.0 mmoles of 1, 2-hexadecanediol (0.517 g) and 20 ml of diphenyl ether were placed in a round bottom flask. The ratio between Ni (II) and Pd (II) precursors was varied depending upon the desired composition of the nanoparticles. Nitrogen gas was purged through the reaction flask. The contents were stirred and heated. The solution appears greenish yellow and later turns to a golden brown color at around 70°C. At 100°C, 0.5 mmole of oleic acid (0.16 ml) followed by 0.5 mmole of oleyl amine (0.17 ml) were injected through the side neck. Injection of oleyl amine changed the color of the solution back to greenish yellow. On continued heating, the solution color changed to black, indicating the formation of nanoparticles. The solution was then refluxed at ~260°C. After refluxing, heating was stopped and the solution was allowed to cool in air to 40°C before removing the contents. The contents were treated with ~80 ml of ethanol. Particles were collected by centrifuging and the supernatant was discarded. Particles were treated with ~5 ml of dispersing solution, that is, 1:1 mixture of hexane and octane containing 0.5% (vol %) of oleic acid and 0.5 % of oleyl amine. The solution is again treated with ethanol and particles collected by centrifuging. This process was repeated three times. Finally the particles were preserved in 5 ml of the dispersing solution that was used for further analysis.

Method 2

It has been shown that when LiEt_3BH is used as the reducing agent for FePt synthesis¹⁴, the charged stoichiometry of metal precursors is maintained in the particles. This fact, in addition to our belief that a stronger reducing agent may change the size of the nanoparticles by effecting nucleation, has motivated us to use LiEt_3BH as the reducing agent for NiPd synthesis. The synthesis is the same as Method 1 up to the point where oleic acid and oleyl amine are injected. After the injection of surfactants, the solution was heated to 200°C at which point 2.5 ml of 1.0 M LiEt_3BH solution (2.5 mmoles) was injected. The injection was performed over a period of 5 minutes to avoid vigorous bubbling due to the escaping THF vapors. The solution was then refluxed at 260°C. The remainder of the synthesis is the exact same as Method 1.

Characterization of NiPd particles

The particle structure was determined by a Rigaku D/MAX-2BX Horizontal XRD Thin Film Diffractometer. XRD data was collected at a step size of either 0.02° or 0.05°. The size of the particles was determined from TEM micrographs acquired by a Hitachi 8000 - 200 kV Transmission Electron Microscope (TEM). A Phillips XL 30 Scanning Electron Microscope equipped with an energy dispersive spectrometer (EDS) was used to measure the composition. The magnetic hysteresis loop of particles was acquired using a Princeton Alternating Gradient Magnetometry (AGM).

RESULTS AND DISCUSSIONS

Typical therapeutic temperature for hyperthermia is 45°C. This temperature is the Curie temperature of bulk NiPd alloy of atomic composition $\text{Ni}_{30}\text{Pd}_{70}$ ¹². Therefore the nanoparticle synthesis was designed to achieve compositions around $\text{Ni}_{30}\text{Pd}_{70}$.

NiPd particles were prepared by method 1 with 0.5 mmole of each Ni (II) and Pd (II) precursor and refluxing for 30 minutes. The composition of these particles was measured to be $\text{Ni}_{40}\text{Pd}_{60}$. The TEM image and the XRD pattern for these particles are shown in figure 1(a) and figure 2(a), respectively. The TEM image shows a wide range of particle sizes, from 3 to 20 nm with irregular particle shape. The crystallite size calculated by Scherrer's equation from the full width half maximum of the (111) peak is 3.8 nm. This mismatch between TEM image size and crystallite size from XRD may probably be due to presence of multiple domains in the particles.

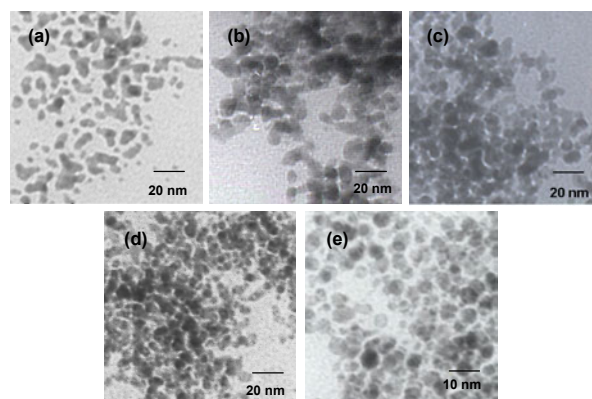


Figure 1. TEM images of (a) $\text{Ni}_{40}\text{Pd}_{60}$ prepared by method 1 and refluxed for 30 min (b) $\text{Ni}_{44}\text{Pd}_{56}$ prepared by method 1 (c) $\text{Ni}_{20}\text{Pd}_{80}$ prepared by method 1 (d) $\text{Ni}_{25}\text{Pd}_{75}$ prepared by method 2 and (e) $\text{Ni}_{20}\text{Pd}_{80}$ prepared by Toshima et al.⁸ procedure.

To study the effect of reflux time on particle shape and size, NiPd nanoparticles were synthesized by method 1 for a reflux time of 120 minutes. These particles had a composition of Ni₄₄Pd₅₆ as measured by SEM-EDS. The TEM image and the XRD pattern for these particles are shown in figure 1(b) and figure 2(b) respectively. The TEM image shows particles to be more uniform compared to figure 1(a). The particle size is in the range of 6-10 nm. Hence, increasing reflux time makes particle shape more regular and monodisperse. Scherrer analysis on the (111) peak in figure 2(b) indicates a crystallite size of 3.9 nm.

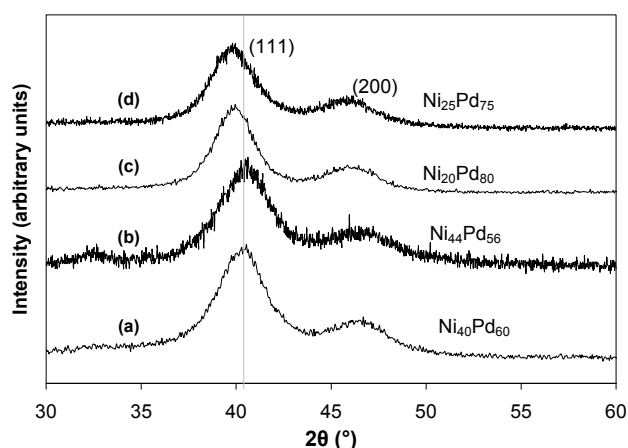


Figure 2. XRD patterns of (a) Ni₄₀Pd₆₀ prepared by method 1 (b) Ni₄₄Pd₅₆ prepared by method 1 (c) Ni₂₀Pd₈₀ prepared by method 1 (d) Ni₂₅Pd₇₅ prepared by method 2.

We have also synthesized Ni₂₀Pd₈₀ by method 1 with 0.25 mmole of Ni (II) and 0.75 mmole of Pd (II) precursor. The TEM image is shown in figure 1(c) and the XRD pattern in figure 2(c). The particle size by TEM is between 5-10 nm and that determined by Scherrer analysis on the (111) peak is 4.2 nm.

The XRD data in figure 2(a) shows the (111) peak at 40.5°. This corresponds to a lattice constant of 3.854 Å. But, the lattice constant for bulk Ni₄₀Pd₆₀ from literature is 3.766 Å¹⁶, displaying a positive deviation. The same is true for all other NiPd compositions that we have synthesized (figure 2). Toshima et al.⁸ have also observed such positive deviation for NiPd nanoparticles.

Method 2 was developed under the following two hypotheses: 1) The charged stoichiometry in the particles will be retained as LiEt₃BH is a strong reducing agent, as was observed with FePt synthesis¹⁴ and 2) Using a different reducing agent would effect nucleation and thus the size of the particles. We synthesized NiPd

nanoparticles by method 2 beginning with a charge of 0.3 mmole of Ni (II) and 0.7 mmole of Pd (II) precursor. The particle composition was found to be Ni₂₅Pd₇₅, which is less than the charged amount. This fails our first hypothesis. The TEM images and XRD pattern for these particles are shown in figure 1(d) and figure 2(d) respectively. TEM shows that the particle size range is between 3-10 nm. This indicates that LiEt₃BH has indeed affected the nucleation giving rise to smaller particles as compared to method 1. Scherrer analysis on the (111) peak in figure 2(d) also shows a low crystallite size of 3.6 nm.

Apart from the lattice parameters and the crystallite size, XRD patterns in figure 1 also prove that we have formed alloyed NiPd particles and not core/shell particles. This is confirmed by observing the shift in the (111) peak position corresponding to the composition of the particles. For instance, (111) peak position for Ni₂₅Pd₇₅ and Ni₄₀Pd₆₀ is 39.96° and 40.55°. Since Ni₄₀Pd₆₀ has more nickel we would expect the lattice parameter to decrease and thus increase the 2θ value. Core/shell particles would not show such a shift.

The magnetic hysteresis loops of NiPd nanoparticles prepared by method 1 were acquired at room temperature and are shown in figure 3. Ni₄₄Pd₅₆ shows a coercivity of 280 Oe and Ni₂₀Pd₈₀ shows a coercivity of 130 Oe, displaying their ferromagnetic behavior at room temperature.

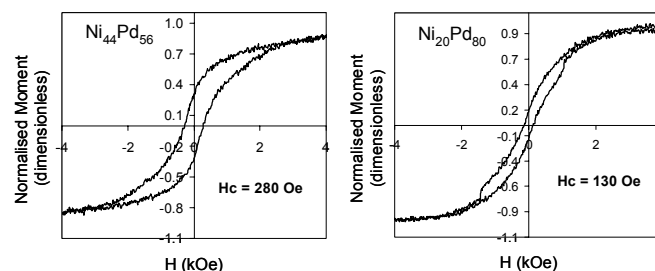


Figure 3. Hysteresis loops of NiPd at room temperature prepared by method 1.

Both methods 1 and 2 do not provide NiPd nanoparticles that form stable dispersions. One possible explanation could be that oleic acid and oleyl amine do not bind strongly enough to keep the nanoparticles apart. Ideally we would like to make stable dispersions of these particles. We have synthesized NiPd nanoparticles by the procedure developed by Toshima et al.⁸ that uses PVP as the surfactant. This procedure produces a stable dispersion of NiPd nanoparticles, most likely due to the long polymer chain sticking to the particles. These particles are about ~3 nm (figure 1(e)) and reasonably

monodisperse. The major issue with these particles for our application is in removing the polymer.

CONCLUSIONS

Two methods of synthesizing NiPd nanoparticles, inspired by the synthesis of FePt, were developed. With increased refluxing time, shape of the particles becomes more regular and tends towards becoming spherical. In both the methods, the precursor stoichiometry did not match the particle composition as nickel could not be reduced completely. The shift in the x-ray diffraction peaks confirms that a NiPd-alloy was formed. The method that uses LiEt_3BH as the reducing agent produced smaller NiPd particles. Magnetometry with AGM revealed that NiPd nanoparticles have coercivity of the order of 100 Oe at room temperature. The particles did not form a stable dispersion. New surfactant systems need to be explored to form stable dispersions of NiPd nanoparticles.

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