# 碳包覆纳米铁镍磁性颗粒的合成

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**摘要:** 通过在双温控的化学气相沉积炉中热解四吡啶并卟啉铁镍混合物, 合成了碳包覆铁镍纳米颗粒。原料中四吡啶并卟啉铁镍的质量比为 7:3; 扫描电镜和透射电镜的结果显示碳包覆铁镍纳米颗粒形貌均匀, 直径为 100~300 nm; 能谱结果显示碳包覆铁镍纳米颗粒是由铁、镍和碳组成; 拉曼光谱证明产物有大量的缺陷存在, 可能是由于球状结构上的碎片引起的; 此外, 磁性能测试表明室温下, 碳包覆铁镍纳米颗粒有很高的饱和磁化强度, 为 56.3 emu·g$^{-1}$; 而其产物的矫顽力趋近于零, 呈超顺磁性, 适合用于催化剂载体。

**关键词:** 碳包覆铁镍纳米颗粒; 化学气相沉积; 四吡啶并卟啉铁镍; 磁滞曲线
**中图分类号:** O614.81$^+$1; O614.81$^+$3　　**文献标识码:** A　　**文章编号:** 1001-4861(2011)07-1431-05

## Synthesis of Carbon Coated Nano Fe-Ni Magnetic Particles

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**Abstract:** Carbon coated nano Fe-Ni particles (C-FeNi-Ps) have been synthesized through pyrolysis of metal tetrapyrazinoporphyrazines (MPTpzs, M=Fe$^{2+}$, Ni$^{2+}$, $m_{FePTpzs}$:$m_{NiPTpzs}$=7:3) in a chemical vapor deposition furnace with two heating zones. The obtained C-FeNi-Ps show a uniform hair-bulb-like structure with diameter ranging from 100~300 nm; C-FeNi-Ps consist of C, Fe and Ni, and have lots of defects due to the edge planes on the ball structure, as supported by Raman spectrum. Besides, Hysteresis curve reveals that saturation magnetization (Ms) of C-FeNi-Ps is 56.3 emu·g$^{-1}$, and magnetic hysteresis tends to be 0, indicating superparamagnetic property, suitable for using as catalyst-support particles.

**Key words:** carbon coated nano Fe-Ni particles; chemical vapor deposition; hysteresis curve; metal tetrapyrazinoporphyrazines

## 0　Introduction

Nanostructured magnetic materials have caught great attention due to their much larger surface area compared to the corresponding bulk materials and magnetic properties[1-6]. Fe-Ni nano particles, as nanostructured magnetic materials, have special properties different from elemental iron and elemental nickel, and

special surface properties. Therefore, they have excellent potential applications in the fields of high-density magnetic recording materials, magnetofluid, electromagnetic shielding materials and highly efficient catalysts[7-13], and attracted more and more attention. Nowadays, there are mainly three methods to prepare Fe-Ni nano alloy, solid phase method[14-16], gas phase method[17-19] and liquid phase method[20-21]. However, most

of the methods mentioned above have some disadvantages, like high cost of equipments, poor product uniformity and morphology controlling, which limited their applications. Our method is different from traditional solid phase method. The process is quite simple and does not need large equipments, and can produce Fe-Ni nano particles with uniform structure.

Apart from the preparation methods, there is another problem with Fe-Ni nano particles. Because of the large surface area and metallicity of nanosized metal particles in the nanostructured magnetic materials, they are likely to react, to reunite or to be oxidized when they are used under high temperature or acidic, alkaline environments, which greatly limits their applications[22-23]. So, producing stable Fe-Ni nano particles has great practical and theoretical significance.

Carbon materials seem to be promising candidates to protect the Fe-Ni nano materials and maintain the catalytic properties attributed to their thermal and chemical stability. However, to date, few work on synthesis of carbon coated nano Fe-Ni particles (C-FeNi-Ps) has been reported.

In this paper, we report for the synthesis of C-FeNi-Ps with many edge planes by chemical vapor deposition (CVD) using metal tetrapyrazinoporphyrazines (MPTpzs, M =Fe$^{2+}$, Ni$^{2+}$ chemical structure is shown in Fig.1) as precursors. Due to the carbon coating, the C-FeNi-Ps have good stability. The planes on the edges of C-FeNi-Ps which greatly increase their surface area, combined with the transition metal particles, C-FeNi-Ps have promising applications in electrochemical field. The high saturation magnetization (Ms), combined with its negligible magnetic hysteresis make it a good candidate as catalyst supports[24].
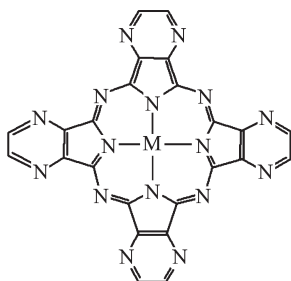


Fig.1　Structure of MPTpz

# 1　Experimental

## 1.1　Synthesis of MPTpz

MPTpz (M=Fe$^{2+}$, Ni$^{2+}$) was prepared by microwave reaction[25]. The route to synthesize FePTpz is as follows. A mixture of 1.37 g 2,3-Pyrazinedicarboxylic acid, 1.96 g urea, 1.56 g NH$_4$Cl, 1.65 g (NH$_4$)$_2$Fe(SO$_4$)$_2$·6H$_2$O and 0.17 g (NH$_4$)$_2$Mo$_2$O$_7$ in a 100 mL crucible was irradiated in a microwave oven (Galanz G80F20CN2L-B8(S0)) at 600 W for 8 min, and then at 800 W for 8 min. After cooling to room temperature, the as-product was washed with water, ethanol, and acetone several times in a centrifugal filter.

To prepare NiPTpz, a mixture of 1.37 g 2,3-Pyrazinedicarboxylic acid, 1.96 g urea, 1.56 g NH$_4$Cl, 1.10 g NiCl$_2$·6H$_2$O and 0.17 g (NH$_4$)$_2$Mo$_2$O$_7$ in a 100 mL crucible was irradiated in a microwave oven at 600 W for 8 min, and then at 1 000 W for 10 min. After cooling to room temperature, the as-product was washed with water, ethanol, and acetone several times in a centrifugal filter.

The results of elemental analyses and IR spectra of the obtained products are as follows.

FePTpz: 59% yield; m.p. >300 ℃; IR (KBr pellet, cm$^{-1}$): 1 628 (s), 1 527 (m), 1 111 (s), 935 (m), 755 (s); Anal. cald. for C$_{24}$H$_8$N$_{16}$Fe: C, 50.02; H, 1.40; N, 38.89; Found: C, 49.73; H, 1.58; N, 39.12.

NiPTpz: 57% yield; m.p. >300 ℃; IR (KBr pellet, cm$^{-1}$): 1 639 (s), 1 531 (m), 1 121 (s), 933 (m), 754 (s); Anal. cald. for C$_{24}$H$_8$N$_{16}$Ni: C, 49.77; H, 1.39; N, 38.70; Found: C, 49.55; H, 1.45; N, 39.03.

## 1.2　Synthesis of C-FeNi-Ps

The synthesis procedure of C-FeNi-Ps was carried out in a CVD furnace with two heating zones. The reaction chamber was a quartz tube with 30 mm in diameter and 1 700 mm in length. First, 0.14 g FePTpz, 0.06 g NiPTpz and 0.2 g sulfur were mixed together, ground for ~5 min and equally distributed in three quartz boats. Then three boats were put into the CVD furnace. One was in the low temperature zone, while the other two in the high temperature zone. The CVD growth was carried out under a nitrogen atmosphere with flow rate remaining at 200 sccm during the whole

synthesis procedure. The heating procedure is as follows: first, the two zones were heated to 550 ℃ in 1.5 hours and held for 20 min. Next, the high temperature zone was heated to 900 ℃ in 40 min and held for 1 hour. While the low temperature zone was heated to 800 ℃ in 20 min and remained at this temperature for 80 min. Finally, the furnace was cooled to 380 ℃ within 2 h, and then to room temperature. The product was washed by water, ethanol and acetone for several times, and vacuum dried for 12 h.

The morphology of the products was observed using scanning electron microscopy (SEM, ZEISS-SUPRA55). The detailed microstructures of the samples were analyzed by a transmission electron microscopy (TEM, JEOL, JEM-3010, 300kV) with an energy dispersive spectroscopy (EDS). The hysteresis curve of the C-FeNi-Ps was obtained by using a vibrating sample magnetometer with an applied field of −11 000~11 000 Oe at room temperature.

### 1.3　Preparation of the absorbing sample

The obtained products and sodium dodecyl sulfate (SDS) were mixed at the mass ratio of 1:4, which was dissolved in acetone completely. Then the mixture was followed by a ultrasonic treatment for 30 min, and dried in air. After this, the mixture was mixed with paraffin used as binder at the mass ratio of 1:1, which then was made as a coaxial sample with the inside diameter of 3 mm, outside diameter of 7 mm, and thickness of 10 mm.

The wave absorbing test was carried out in an electromagnetic vector network analyzer (Agilent 8722s).

## 2　Results and discussion

From the SEM image of the products (Fig.2a), we can see that the C-FeNi-Ps shows a uniform structure with many planes on the edge, and the diameter ranges from 100~300 nm, which is well consistent with the TEM image in Fig.2b. And the EDS result (Fig.2e) shows the presence of C, Fe, Ni and Cu, among which, the Cu atoms come from the copper grid used in the experiment. So the C-FeNi-Ps is mainly composed of Fe, Ni and C.
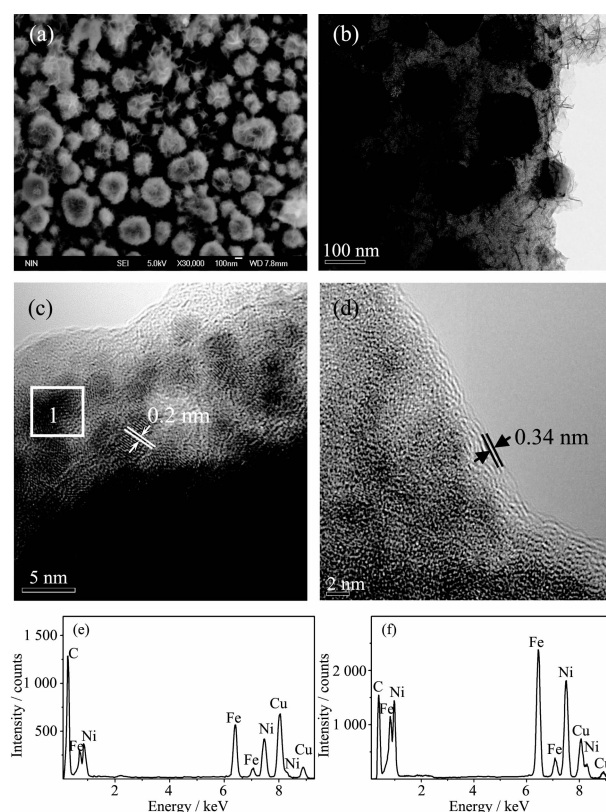


Fig.2　(a) SEM image of C-FeNi-Ps, (b) TEM image of C-FeNi-Ps, (c), (d) HRTEM images of C-FeNi-Ps and the nano-film, (e) EDS spectrum of C-FeNi-Ps, (f) EDS spectrum of selected area 1 in Fig.2(c)

The high resolution TEM (HRTEM) image of C-FeNi-Ps shows that the edge planes are very thin, nearly transparent, which largely increase the specific surface area. And each plane of the products consists of many metal particles coated by nano-film (Fig.2c). The metal particles are 2~4 nm in diameter. The nano-film consists of several sheets with a lattice fringe spacing of 0.34 nm (Fig.2d), related to that of the graphite (002) plane[26]. The spacing of the metal particles has a lattice fringe spacing of 0.20 nm (Fig.2c), which is very close to the (111) plane of the γ-Fe and (111) plane of Ni crystal[27]. These are well consistent with the EDS results of selected area 1 in Fig.2c, in which it shows the metal particles mainly consist of Fe, Ni and C surrounding the particles. The small amount Cu is from the copper grid used in the experiment (Fig.2f).

The Raman spectrum (Fig.3a) reveals that there are two main bands, D band and G band. The ratio of D and G band is a value to show the defective structure.

And the ratio is calculated to be 1.35, which indicates the existence of great amount of defects. These defects may contain many active sites and benefits the improvement of electrochemical properties[28].

From Fig.3b, we can see that when the magnetic field strength is less than 10 kOe, the magnetization intensity of the C-FeNi-Ps rises sharply with the increase of C-FeNi-Ps. When the magnetic field strength is larger than 10 kOe, the magnetization intensity grows slowly, and then becomes saturated, with saturation magnetization ($M_s$) of 56.3 emu·g$^{-1}$, indicating strong magnetic signal. In addition, the magnetic hysteresis of the obtained C-FeNi-Ps is

nearly 0, suggesting almost no magnetic aggregation under an changing magnetic field [24]. The C-FeNi-Ps show super-paramagnetic property, which can be explained by Herzer′s anisotropic model[29]. Due to the extremely small size of C-FeNi-Ps, the magnetic anisotropy energy can be as small as the thermal motion energy. In addition, the exchange interaction of neighboring grains and the electrostatic coupling effect, make the effective magnetic anisotropy energy approximately zero. Therefore, the easily magnetized direction will change irregularly, resulting in superparamagnetism of C-FeNi-Ps[30].
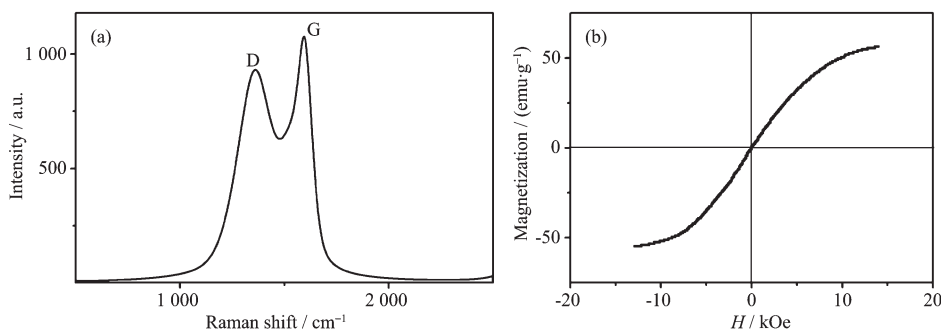


Fig.3　(a) Raman shift of the obtained C-FeNi-Ps, (b) Hysteresis curve of the C-FeNi-Ps at room temperature

The reflective loss curve of the sample (Fig.4) shows that when the frequency ranges from 4.5 ~9.1 GHz, the reflective loss is less to −10 dB. And the reflective loss reaches its maximum value (27.1 dB) at the frequency of 7.4 GHz. All of this suggest that the sample has excellent absorbing properties at low frequency, which has a close relationship with the ferromagnetic Fe and Ni[31]. Because the magnetic loss of Fe and Ni is very strong, magnetic nano Fe and Ni
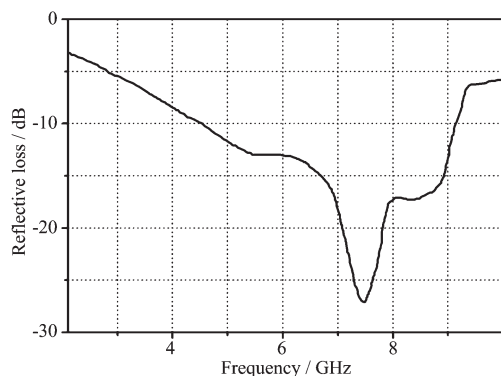
particles have high permeability and low conductivity, resulting in great eddy current loss. In addition, the size of the nano particles are much smaller than the wavelength of electromagnetic waves. Therefore the reflectivity of electromagnetic waves decrease largely. So the C-FeNi-Ps have potential applications as electromagnetic shielding materials. And its strong absorbing properties at low frequency has great significance for preparation of broadband absorbing composite materials.

In summary, C-FeNi-Ps have been synthesized by pyrolysis of MPTpzs in a CVD furnace. The abtained C-FeNi-Ps show uniform hair bulb-like structure. The C-FeNi-Ps have stable thermal and chemical stability, and superparamagnetic property, which enable it to have large potential applications in the fields of high-density magnetic recording materials, magnetofluid, electroma-gnetic shielding materials and highly efficient catalysts.



Fig.4　Reflective loss curve of the absorbing sample containing C-FeNi-Ps

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