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Magnetic domain regime-controlled synthesis of nickel nano-particles by applying statistical experimental design in modified polyol process

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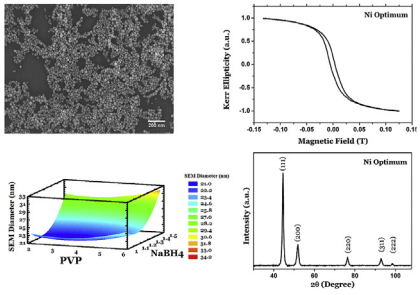
HIGHLIGHTS

- A central composite design (CCD) has been performed on the preparation of nickels NPs in the polyol process.
- Single domain or pseudo-single domain nickel nano-particles can be prepared based on Day's plot.
- Nickel NPs have been synthesized without agglomeration simply by controlling the injection rate of the reducing agent.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, central composite design (CCD) as a statistical experimental design method is performed to prepare nickel nano-particle of different magnetic domain regimes by the modified polyol process. It is shown that not only the concentration of the different chemicals but also the injection rate is determining for the morphology and magnetic properties. The average diameter of the synthesized nickel NPs is smaller than the critical single domain size and thus the single domain or pseudo-single domain nickel nano-particles can be prepared based on Day's plot.

1. Introduction

Nickel nano-particles (NP) have a wide range of application including catalysis [1], fuel cell electrodes [2], and magnetic storage media [3]. This is related to their specific properties at the nano-scale such as chemical activity, thermal resistance and magnetization. Nickel NPs can be synthesized by several methods such as ultrasound irradiation [4], evaporation [5,6], spray pyrolysis [7,8] or electrochemistry [9]. The polyol process with ethylene glycol (EG) is a method highly interesting for industry since it is energy-efficient and environmentally friendly, which can come in handy to scale up the production of nano-crystals with controlled particle size [10].

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Table 1
Central composite design and experimental results.

Run	PNi (Mol/Mol)	NNi (Mol/Mol)	SEM diameter (nm)	XRD diameter (nm)	M_r/M_s (a.u.)	H_C mT
1	2.0	1.5	43 ± 20	9	0.135 ± 0.005	2.384 ± 0.001
2	4.0	0.9	24 ± 8	6	0.198 ± 0.005	3.47 ± 0.001
3	4.0	1.25	18 ± 6	9	0.132 ± 0.005	1.530 ± 0.001
4	4.0	1.25	25 ± 11	10	0.154 ± 0.005	4.107 ± 0.001
5	6.8	1.25	23 ± 9	9	0.126 ± 0.005	1.651 ± 0.001
6	6.0	1.5	39 ± 20	9	0.149 ± 0.005	1.916 ± 0.001
7	4.0	1.6	22 ± 6	10	0.124 ± 0.005	2.048 ± 0.001
8	6.0	1.0	25 ± 8	10	0.205 ± 0.005	3.701 ± 0.001
9	2.0	1.0	29 ± 14	10	0.216 ± 0.005	4.597 ± 0.001
10	1.2	1.25	12 ± 4	10	0.147 ± 0.005	3.020 ± 0.001
11	4.0	1.25	22 ± 8	9	0.209 ± 0.005	2.941 ± 0.001

There are two different strategies, the conventional and the modified polyol process to synthesize nickel NP. In the conventional polyol (CP) process, the polyol such as EG serves as solvent as well as reducing and stabilizing agent. Agglomerated nickel NPs with a diameter larger than 100 nm can be synthesized with the CP method. If the CP process is combined with a microwave system or a reducing agent such as $NaBH_4$ or hydrazine, it is called modified polyol (MP) process. By this procedure, it is possible to decrease the particle size below 100 nm. As an example, Couto et al. [11] synthesized 4 nm nickel NPs by the MP process using $NaBH_4$ as reducing agent.

The application of nickel NPs in different fields requires the synthesis of large amounts with accurate control of morphology and magnetization. For example, Everson et al. [12] demonstrated that the methanation reaction is magnetic-structure sensitive and multidomain nickel particles show lower catalytic activity in comparison to single domain structures. However, nickel NPs with controlled morphology were obtained with limited success by the polyol processes since the influence of the different factors affecting the particle morphology were not well enough known. Moreover, most studies were limited to particle sizes above 100 nm or below 10 nm [11,13–16]. Consequently, a systematic study of the influence of the different factors on the polyol process is missing.

In this article a central composite design (CCD) is performed to investigate the effect of surfactant (PVP), reducing agent ($NaBH_4$) and its injection rate on the preparation of nickel NP. Central composite designs is a standard two-level factorial design, plus additional runs, called star points, located at a small distance below the low and high level. These star points are used to model the curvature of the response with respect to each parameter.

2. Experimental

2.1. Synthesis

The experiments were carried out using Nickel (II) acetate tetrahydrate ($Ni(Ac)_2.4H_2O$) and PVP40 (average molecular weight 40,000) both purchased from Sigma–Aldrich as metal precursor and surfactant, respectively. Specified amounts of the metal precursor (0.1 mmol, 0.0249 gr) and the surfactant were dissolved in 20 ml of ethylene glycol until a clear green solution was formed. Then, the solution was transferred to a flask with reflux attachment and placed in an oil-bath held at a preselected temperature under gentle mechanical stirring. At the desired temperature the specified volume of sodium borohydride ($NaBH_4$) solution (0.15 M) purchased from Sigma–Aldrich was added with different injection rates. The green solution turned black indicating the formation of NPs.

2.2. Experimental design

Central composite design (CCD) is used to extract the particle size as a function of selected variables. PVP/Ni ion mole ratios (PNi) of 2–6 (0.0222–0.0666 gr of PVP) and $NaBH_4$/Ni ion mole ratios (NNi) of 1–1.5 (0.0038–0.0057 gr of $NaBH_4$) are investigated. The CCD with these two variables is carried out in a single block and 11 combinations are generated (Table 1).

Response surfaces are represented by a second-order polynomial containing terms representing the main effects as well as second-order interactions and quadratic effects, Eq. (1) is used to generate the contour plots:

$$D = \beta_0 + \beta_1\xi_1 + \beta_2\xi_2 + \beta_{12}\xi_1\xi_2 + \beta_{11}\xi_1^2 + \beta_{22}\xi_2^2 + \varepsilon \quad (1)$$

D denotes the nickel particle size, ξ_1 and ξ_2 represents independent variables, PNi and NNi. In addition, β and ε are coefficients and the experimental uncertainty, respectively.

2.3. Characterization

The structure of the particles is analyzed using X-ray powder diffraction (Brucker D8 Discover XRD) with a copper target ($\lambda_{Cu\text{-}k\alpha} = 0.154$ nm). The average crystallite size (L) is calculated using the Scherrer's formula $L = 0.9\lambda/\beta\cos(\theta)$ at the (111) Bragg reflection, where λ is the wavelength of the X-ray radiation, θ and β are the Bragg angle and the full width at half maximum (FWHM) of the corresponding peak, respectively. Complementary, the morphology of the particles is determined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Model: EM10C-100 KV) on a Zeiss instrument. The magnetic hysteresis curves of the nickel NPs is measured via the magneto-optical Kerr

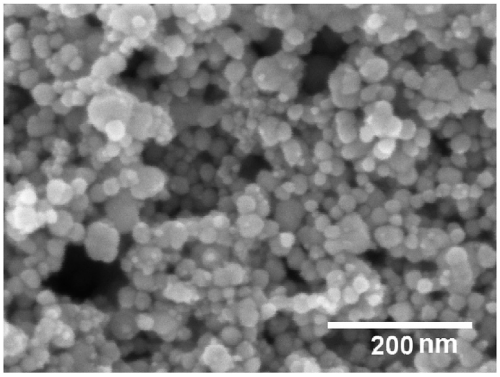

Fig. 1. The SEM image of nickel nanoparticles with drop-wise injection of $NaBH_4$ according to Ni_{11} experiment.