Binary Roles of Schiff-bases as Capping Agent and Precursor for Synthesis of Metallic Nickel Ultrafine Nanoparticles

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This study focused on the synthesis and characterization of nickel nanoparticles by simple precipitation method. The various Schiff-bases such as: ethylenediamine (acacen), 1,3-propylenediamine (acacpn), and butane-1,4-diamine (acacbn) acetyl acetonate were prepared and were used for preparing of nickel-Schiff base complexes and then, these complexes as precursor were reduced in the presence of KBH₄, for the first time. In addition, the anti-aggregation effect of prepared Schiff bases was compared with common surfactants and results demonstrated that the huge ligands can be considered as novel surfactants. The obtained nickel nanoparticles were characterized by XRD, TEM, HRTEM, FT-IR, SEM and EDS.

Keywords Schiff-base, nickel, nanoparticles, precipitation method, anti-aggregation

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INTRODUCTION

In the past two decades metallic nanostructures have received more interest for possible applications in the field of catalysis, microelectronics, biology and material science ^[1-4]. Synthesis of some metals such as nickel, copper, and iron in the zero valence state are relatively difficult because they are easily oxidized. Among various routs developed for the production of metallic nanoparticles, chemical reduction is an economical technique because it is much faster, cleaner and it does not need special equipments. Various reducing agents such as hydrazine, alcohols, KBH₄ and many other reductants have been used to provide nanosized nickel particles ^[1-4].

Using of the novel compound can lead to nanomaterials with controlled size, shape and particle size distribution. Tetradentate Schiff base complexes of transition metal ions have attracted much attention in the field of coordination chemistry ^[5-9]. Schiff bases—the condensation proceeds of an amine and ketone or aldehyde with general formula of R₂C=NR are well-known organic repressors ^[10, 11]. The -N=CH-(imine) group is indicator of Schiff bases which is significant in explaning the mechanism of transamination and racemisation reactions in biological systems ^[12, 13].

There is a great interest in our group for novel precursors to control size and morphology of prepared nanoparticles $^{[14-21]}$. The Ni nanoparticles were synthesized with using of nickel-Schiff base complexes as new precursors in the presence of KBH₄, also synthesized Schiff bases were utilized as anti-aggregation, and this is the first report on the synthesis of metallic nickel nanoparticles by reducing of complexes [Ni(acacen)], acacen = bis(acetylacetonato)ethylenediimine; [Ni(acacpn)], acacpn = bis(acetylacetonato)propylene-1,3-diimine; [Ni(acacbn)], acacbn = bis(acetylacetonato)buthylene-1,4-diimine, in the presence of KBH₄. The operation of Schiff bases were compared with common surfactants

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and results demonstrated that the huge ligands can be considered as novel surfactant. The products were characterized by XRD, TEM, HRTEM, SEM, FT-IR spectroscopy and EDAX.

EXPERIMENTAL

Acetyl acetonate, (acac), butane-1, 4-diamine(bn), 1,3-propylenediamine(pn), ethylenediamine(en), toluene, hexane, different kinds of nickel salt (KBH₄), methanol and ethanol were purchased from Aldrich and used as received. Fourier transform infrared spectroscopy spectra were recorded on Magna-IR, spectrometer 550 Nicolet in KBr pellets in the range of 400–4000 cm⁻¹. Powder X-ray diffraction was carried out on a Philips diffractometer of X'pert company with mono chromatized Cu K α radiation (k = 1.5406 Å). Microscopic morphology of products was visualized by scaning electron (LEO 1455VP) and transmission electron microscope images were obtained on a JEM-2100 with an accelerating voltage of 60-200 kV in 50 V steps. Nuclear magnetic resonance spectrum of Schiff base precursors, were recorded by BRUKER (400 MHz) in acetone-d₆.

Synthesis of Schiff base ethylenediamine ($H_2acacen$), 1, 3-propylenediamine ($H_2acacpn$), butane-1, 4diamine ($H_2acacbn$) acetyl acetonate

Various alkyl Schiff bases were synthesized by the condensation reaction of amines, namely: ethylene, propylene and buthelyne diamine. 5 ml of acetylacetonate dissolved in 20 ml methanol and was added to a stoichiometric amount of desired amine solution dissolved in 20 ml methanol. The reaction mixture was heated under reflux for 4 h. The brown precipitate was collected and then washed with ethanol and dried in vacuum oven in 50 °C. The chemical structures of the prepared Schiff bases were confirmed by using different analysis, (FT-IR and ¹H-NMR spectra). The prepared Schiff-bases NMR spectra (Fig. 1) have good agreement with the spectra which are consistent in references ^[22-24]. ¹H-NMR spectra of the produced ligands are presented in Fig 1, which conforms to the bonding structure of these compounds as

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follows: Fig. 1a-c are related to ethylenediamine, 1,3-propylenediamine, butane-1, 4-diamine acetyl acetonate, respectively. In this Figure (δ (ppm)): 10.9 (s, 2H, OH); 4.956 (s, 2H, -CH-); 3.496-3.510 (t, 4H, -CH₂-); 1.939 (s, 6H, -CH₃); 1.868 (s, 6H, -CH₃) is related to ethylenediamine acetyl acetonate and δ (ppm): 10.9 (s, 2H, OH); 4.963 (s, 2H, -CH-); 3.367-3.416 (m, 4H, -CH₂-), 2.055 (s, 6H, -CH₃); 1.951-1.969 (d, 6H, -CH₃); 1.837-1.887 (m, 2H, -CH₂-) and (δ (ppm)): 10.9 (s, 2H, OH); 4.956 (s, 2H, -CH-); 3.496-3.510 (t, 4H, -CH₂-); 1.939 (s, 6H, -CH₃); 1.868 (s, 6H, -CH₃) are related to acetyl acetonate 1, 3-propylenediamine and acetyl acetonate butane-1, 4-diamine, respectively. In Fig. 1b The FT-IR spectra of three Schiff-base acetyl acetonate butane-1, 4-diamine (H₂acacen), acetyl acetonate 1, 3-propylenediamine (H₂acacpn), and acetyl acetonate butane-1, 4-diamine (H₂acacbn) are shown in Fig. 2a, b and c, respectively. Their successful synthesis was confirmed by two index and important peaks at around 1610 cm⁻¹ and 1570 cm⁻¹ in every spectrum, which are related to stretching mode of C=O and C=N, respectively. These two peaks shifted due to intramolecular hydrogenic bonds. Although, the peaks at around 1510 cm⁻¹ and 3000 cm⁻¹ in each spectrum are indicating vibrations of C-N group in residual amine used for synthesis of Schiff-base.

Synthesis of Nickel-Schiff base complexes and Ni nanoparticles

For synthesis of nickel nanoparticles, 1 mmol of nickel salt was dissolved in 20 ml of distilled water and 50 ml solution of 0.02 M of synthesized Schiff-base (in methanol) was then added into the Ni solution under magnetic stirring at the room temperature for preparation of nickel-Schiff base complex. Then 90 ml of KBH₄ aqueous solution (0.2 M) was added drop-wise to the produced Ni-Schiff base complex solution. After a few minutes the color of solution changed slowly from emerald green to black. The black solution was centrifuged and then washed with distilled water and ethanol. These products could easily be dispersed in non-polar organic solvents, such as hexane or toluene.

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RESULTS

The effects of metal-to-ligand ratio, different metallic salts and Schiff-bases on the particle size and morphology of products were investigated. All of the preparation conditions were illustrated in Table1 with more details.

FT-IR spectroscopy

Infrared vibrational spectroscopy was used for confirming purity of the products. Fig. 2 shows the FT-IR spectra in the range 400–4000 cm⁻¹. Fig. 2d is related to the obtained Ni under explained condition for sample F. Presence of ligand group on the synthesized Ni nanoparticles is indicated by the peak of the C–N stretching at 1020 cm⁻¹ and a peak at 674.50 representing the CH₂ bending modes of the acetyl acetonate butane-1, 4-diamine (H₂acacbn) ligand capping the Ni nanoparticles. The peak at 1397.04 and 1587.62 cm⁻¹ are associated with the C–N bending mode and C=N group vibrations, respectively. The weak peak at 3435 cm⁻¹ can be assigned to the ethanol used in the separation step.

X-ray diffraction (XRD) patterns

XRD analysis was employed to investigate the prepared sample. Fig. 3a shows XRD pattern of the obtained Ni nanoparticles without calcination. A solid with fractional crystallization was formed as illustrated by the low intensity of diffraction peaks in the pattern. Fig. 3b depicted pattern of the obtained nickel nanoparticles that calcinated in 800 O C for 30 min under N₂ atmosphere. Increasing temperature from 25 to 800 O C led to arising of the crystalline phase. All diffraction peaks can be indexed to cubic Ni. Three characteristic peaks at 44.3, 52.1, 76.6 for cubic nickel (JCPDS, no. 87-0712) were observed. Some other minor peaks exist that may be obtained from oxidation of Ni nanoparticles. The average crystallite diameter of the as-synthesized nickel, Dc, was calculated from the major diffraction peaks using the Scherer equation: Dc = Kλ/βcosθ; where K is a constant (ca. 0.9) ^[25], λ is the X-ray wavelength used in

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XRD (1.5418 Å), θ is the Bragg angle and β is the pure diffraction broadening of a peak at half-height which is enlargement due to the crystallite dimensions. The average crystallite diameter calculated by the Scherer equation is 8 nm.

SEM and TEM

The surface morphological study of the nickel nanoparticles was carried out by using scanning electron microscope. Since presence of surfactant is an important parameter on the shape and particle size of the products, therefore much attention has been paid to the study of such supramolecular structures. Surfactants played an important role as both template and micro-reactor for producing nanomaterials ^[26-28]. Schiff bases of acetyl acetonate ethylene diamine (acacen), acetyl acetonate 1, 3-propylenediamine (acacpn) and acetyl acetonate butane-1,4-diamine (acacbn) as ligand and stabilizing agent have been used to make the stable nanoparticles and to prevent their agglomeration. Schiff-bases provided great steric hindrance thus this agent can decrease ripening process and create smaller particles. Scheme 1 steric hindrance effect of ligand investigated. Comparison to different surfactant sodium dodecyl sulfate(SDS), sodium dodecyl benzene sulfonate (SDBS) and cetyl trimethyl ammonium bromide(CTAB) are illustrated in Fig. 4a-c, respectively. Fig. 4a shows that the produced nanoparticles have average diameter of 70 nm, while by using SDBS the products with larger diameter were achieved (Fig. 4b). In the presence of CTAB the smallest nanoparticles have been synthesized while it seems nickel nanoparticles are agglomerated (Fig. 4c).

The effects of various ligands acetyl acetonate ethylenediamine (H_2 acacen), acetyl acetonate 1, 3propylenediamine (H_2 acacpn) and acetyl acetonate butane-1,4-diamine (H_2 acacbn) are shown in Fig. 4d-f, respectively. The results proved using ligands with higher steric hindrance led to particles with lower size. So nanoparticles that have been synthesized by using acetyl acetonate butane-1,4-diamine (H_2 acacbn)

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(Fig. 4f) are the smallest ones, and the produced particles with acetyl acetonate 1, 3-propylenediamine
(H₂acacpn) (Fig. 4e) are smaller than those prepared by acetyl acetonate ethylenediamine (H₂acacen) (Fig. 4d) complexes. Ultimately, the huge ligands can operate instead of common stabilizers.

The influence of utilized salt to prepare precursor on size of obtained Ni nanoparticles was investigated and outcome SEM images are depicted in Fig. 5. When Ni(NO₃)₂.6H₂O was used, nanoparticles of Ni with particle size of about 15 nm were attained (Fig. 5a). Fig. 5b, c are related to NiCl₂.6H₂O and Ni(ClO)₄.6H₂O, respectively, which led to nanoparticles of Ni with diameter of about 20 nm. Also, the type of salt played an important role in produced particle size. Nickel Chloride and nickel per chlorate led to larger particles while synthesized Ni nanoparticles by using nitrate salt were smaller. As shown in Fig. 6, structures of Ni with nanometer dimensions were investigated by different molar ratios of ligand to nitrate salt. According to SEM images when the molar ratio is 1:2, the average size of produced particles is 180 nm (Fig. 6a) and with increasing of the ratio to 1:1 (Fig. 6b), the size of nanoparticles reaching 15 nm while increasing of the ratio to 2:1 (Fig. 6c) larger particles are produced that their size is about 30-40 nm.

The TEM images of sample F are presented in Fig. 7a. It was observed that the particles were spherical shape with average size of 5 nm and the ligand covered nickel nanosphere. Fig. 7b showed high-resolution TEM (HRTEM) image of the nanoparticles, the crystalline nature of the nanoparticles is obvious. The lattice fringes clearly observed and the spacing of the two neighboring plane is about 0.1 nm.

Energy dispersive X-ray spectroscopy (EDAX)

To further confirmation the chemical composition of the as-prepared Ni, EDAX spectrum was recorded for sample F. In the EDAX spectrum of related sample (Fig. 8), Ni and O elements are detected. Synthesis

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of nickel in the zero valence states not easy because they are easily oxidized, thus the sampling oxidized and the oxygen are recognizable.

CONCLUSION

Nickel nanoparticles have been prepared via a simple and facile precipitation method at the room temperature in water. Nanoparticles were prepared by using nickel–Schiff base complexes [Ni(acacen)], acacen = bis(acetylacetonato)ethylenediimine; [Ni(acacpn)], acacpn = bis(acetylacetonato)propylene-1,3-diimine; [Ni(acacbn)], acacbn = bis(acetylacetonato)buthylene-1,4-diimine, as new precursors. The effects of metal-to-ligand ratio, different salts and Schiff-bases on the particle size and morphology of products were investigated. In addition, the anti-aggregation effect of Schiff bases was compared with common surfactants and results demonstrated that the huge ligands can be considered as novel surfactants. FT-IR, EDAX, XRD, SEM and TEM analyses confirmed the successful synthesis of Ni nanostructures by this method.

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REFRENCES

- 1. G. Schmid and L. F. Chi, Advanced Materials, 1998, 10, 515-526.
- J. H. Fendler Nanoparticles and Nanostructured Films: Current Accomplishments and Future Prospects. Weinheim: Wiley–VCH; 1998.
- 3. J. D. Aiken and R.G. Finke, Journal of molecular catalysis A: chemical, 1999, 145, 1-44.
- 4. B. L. Cushing, V. L.Kolenichenko and C. J. O'Connor, Chemical Review, 2004, 104, 3893-3946.
- 5. A. Berkessel, M. Frauenkon, T. Schwenkreis and J. Steinmetz, Journal of molecular catalysis A: chemical, **1997**, 117, 339-346.
- 6. L. A. Kovbasyuk, I. O. Fritzy, V. N. Kokozay and T. S. Iskendevov, Tetrahedron, 1997, 16, 1723.
- 7. A. Nishinaga, T. Tsutsui and H. Moriyama, Journal of molecular catalysis, 1993, 83, 117-123.
- M. Amirnasr, R. Vafazadeh, A. H. Mahmoudkhani, Canadian Journal Chemistry, 2002, 80, 1196-1203.
- A. Bottcher, T. Takeuchi, K. I. Hardcastle, T. J. Meade, H. B. Gray, D. Cwikel and M. Kapon, Inorganic Chemistry, 1997, 36, 2498-2504.
- M. Hosseini, S. F. L. Mertens, M. Ghorbani and M. R. Arshadi, Journal of Applied Electrochemical, 2003, 38, 1629–1636.
- 11. Y.A. Balaban, S. Kandemir, G. Bereket and Y. Erk, materials chemistry and physics, 2004, 85, 420–429.
- 12. K. Y. Lau, A. Mayr and K. K. Cheung, Inorganic Chemical Acta, 1999, 285, 223–229.
- A. S. Shawali, N. M. S. Harb and K. O. Badahdah, Journal of Heterocyclic Chemistry, 1985, 22, 1397–1403.
- 14. M. Salavati-Niasari, F. Davar, M. Mazaheri, Materials Letters, 2008, 62, 1890–1892.

⁹ ACCEPTED MANUSCRIPT

- 15. M. Salavati-Niasari and F. Davar, Materials Letters, 2009, 63, 441-443.
- 16. M. Salavati-Niasari, F. Davar and M. Mazaheri, Materials Research Bulletin, 2009, 44, 2246–2251.
- 17. M. Salavati-Niasari, N. Mir and F. Davar, Journal of Alloys and Compounds, 2009, 476, 908–912.
- 18. M. Salavati-Niasari, Z. Fereshteh and F. Davar, Chemical Engineering Journal, 2009, 146, 498–502.
- 19. N. Bouropoulos, G. C. Psarras and N. Moustakas, Physical Status Solid A, 2008, 205, 2033–2037.
- 20. S. Baskoutas, P. Giabouranis, S. N. Yannopoulos, V. Dracopoulos, L. Toth, A. Chris-santhopoulos and N. Bouropoulos, Thin Solid Films, 2007, 515, 8461–8464.
- 21. M. Salavati-Niasari, J. Javidi and F. Davar, Ultrasonics Sonochemistry, 2010, 17, 870–877.
- 22. R. Vafazadeh and M. Kashfi, Bulletin Korean Chemical Society, 2007, 28, 1227-1230.
- 23. M. Salehi, M. Amirnasr and K. Mereiter, Transition Metal Chemistry, 2009, 34, 373–381.
- 24. E. Larsen and K. Schaumburg, Acta Chemica Scandinavica, 1971, 25, 962-968.
- 25. R. Jenkins and R. L. Snyder, Chemical Analysis: Introduction to X-ray Powder Diffractometry. New York: John Wiley and Sons Inc.; 1996.
- F. Mohandes, F. Davar and M. Salavati-Niasari, Journal of magnetism and magnetic materials, 2010, 322, 872-877.
- F. Mohandes, F. Davar, M. Salavati-Niasari and K. Saberyan, Current Nanoscience, 2011, 7, 260-266.
- E. Esmaeili, M. Salavati-Niasari, F. Mohandes, F. Davar and H. Seyghalkar, Chemical Engineering Journal, 2011, 170, 278-285.

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Figure captions:

- **Fig. 1** ¹H-NMR of Schiff-base; (a): H₂acacen (b): H₂acacpn (c): H₂acacbn
- Fig. 2 FT-IR spectra of Schiff-base; (a) H₂acacen, (b) H₂acacpn, (c) H₂acacbn, and (d) sample F.
- **Fig. 3** XRD pattern of sample F; (a) without calcination, and (b) calcination in 800 ^OC for 30 min

Fig. 4 SEM images of Ni nanoparticles obtained from samples: (a) A, (b) B, (c) C, (d) D, (e) E, and (f) F.

Fig. 5 SEM images of Ni nanoparticles obtained from samples: (a) F, (b) G, and (c) H.

Fig. 6 SEM images of Ni nanoparticles obtained from samples: (a) I, (b) F, and (c) J.

Fig. 7 Images of Ni obtained from sample F; (a) TEM, (b) HRTEM.

Fig. 8 EDAX spectrum, Ni nanoparticles obtained from sample F.

Scheme.1 Pattern illustration of the Schiff-base effect on the morphology of Ni nanoparticles.

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Sample	Surfactant type	Precursor type	Molar ratio of surfactant to precursor
A	SDS	Ni(NO ₃) ₂ .6H ₂ O	1:1
В	SDBS	Ni(NO ₃) ₂ .6H ₂ O	1:1
С	СТАВ	Ni(NO ₃) ₂ .6H ₂ O	1:1
D	H ₂ acacen	Ni(NO ₃) ₂ .6H ₂ O	1:1
Е	H ₂ acacpn	Ni(NO ₃) ₂ .6H ₂ O	1:1
F	H ₂ acacbn	Ni(NO ₃) ₂ .6H ₂ O	1:1
G	H ₂ acacbn	NiCl ₂ .6H ₂ O	1:1
Н	H ₂ acacbn	Ni(ClO ₄) ₂ .6H ₂ O	1:1
Ι	H ₂ acacbn	Ni(NO ₃) ₂ .6H ₂ O	1:2
J	H ₂ acacbn	Ni(NO ₃) ₂ .6H ₂ O	2:1

Table 1. Preparation conditions of samples A to J.

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Fig. 1

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Fig. 2

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Fig. 3

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Fig. 4

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Fig. 5

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Fig. 6

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Fig. 7

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Fig. 8

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Scheme 1.

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