Synthesis and characterization of Fe, Co, and Ni colloids in 2-mercaptoethanol

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Abstract
Metal colloids in 2-mercaptoethanol using nanoparticles (NPs) of iron (Fe), cobalt (Co), and nickel (Ni) were prepared by chemical liquid deposition method. Transmission electron microscopy, electron diffraction, UV-VIS spectroscopy, and scanning electron microscopy with electron dispersive X-ray spectroscopy characterized the resulting colloidal dispersions. The NPs exhibited sizes with ranges from 9.8 nm for Fe, 3.7 nm for Co, and 7.2 nm for Ni. The electron diffraction shows the presence of the metals in its elemental state Fe (0), Co (0), and Ni (0) and also some compounds FeO (OH), CoCo₂S₄, and NiNi₂S₄.

Keywords
Nanomaterials, 2-mercaptoethanol, colloidal dispersions, electron diffraction, X-ray analysis

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Introduction
Recently, research on mesoscopic to nanoscopic scale materials has gained great momentum. Advances in interdisciplinary fields between chemistry, physics, biology, and various engineering applications have provided such development. The application of construction techniques of materials atom by atom (molecule by molecule) allows the synthesis of materials of the order of nanometers called “nanomaterials.” This type of investigations has a strategic importance which it concerns to the development of new materials of great functionality and for the integration of inorganic, organic, and biological materials.

By being able to handle and control the shape and size of nanomaterials, it becomes possible to obtain desired characteristics for different applications. Within materials at this scale, there are all kinds of nanoparticles (NPs), some built from their bulk and others by molecule-to-molecule technique. One of the most important characteristics of NPs is their large surface area that gives them exclusive chemical properties. Specifically, metallic NPs can enhance the properties of the raw metal and/or acquire new characteristics, depending on the size, shape, and the media, among others. Heavy metals have unique properties of electricity and paramagnetism, and for this, they are used in electrochemical processes, synthesis, and catalysis. These properties give the metallic NPs (MNs) a great potential for application in areas such as linear optics, luminescence, electronics, optoelectronics, and catalysis.¹⁻⁴ One of the most common presentations

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of metallic NPs (MNps) is that of the colloidal system which has been taking more and more interest in materials science. These metal colloids have a wide variety of applications in many fields of science, paint and dye industries, medicine, photography, heterogeneous catalysis, and agricultural chemistry.

Recently, nanoscale zerovalent iron (nZVI) has gained much attention for its use in a wide range of water treatment applications due to its unique properties, including extremely high surface area to volume ratio and an ability to be injected into the subsurface as a colloidal suspension.\(^{5-18}\) The high efficacy of nZVI for the removal of Cu\(^{2+}\) has been reported in several empirical studies\(^{9,10}\); however, very little information exists on the physicochemical properties of the Cu NPs such as particles size, particle shape, or crystallinity when removed from solution by iron (Fe) zero NPs.

The cementation reaction between nZVI and aqueous Cu has been studied in a wide range of chemical conditions. More recently, some mechanistic studies were reported to understand the physicochemical composition of nanomaterial copper compounds.\(^{11}\)

On the other hand, although colloidal dispersions can be stable for long periods, sometimes years, they tend to settle slowly by the action of gravity, in prolonged rest. This occurs when suspended particles that are thermodynamically unstable form agglomerates of greater size and weight and finally flocculate.\(^{12}\) In this way, it is understood that the stabilization of the colloid dispersions can be controlled from its synthesis to obtain the desired characteristics and to manage to take advantage of them and to maintain them in the time. Solvated metal atoms are used as precursors of new organometallic compounds but also as precursors of catalysts dispersed catalysts called SMAD (“Solvated Dispersed Metal Atoms”). A characteristic of these new colloidal systems is their tendency to form films, when the solvent is evaporated.\(^{13}\)

In this work, to our knowledge is the first reports using 2-mercaptoethanol by chemical liquid deposition (CLD).\(^{14-16}\) These solutions were characterized by several techniques to describe composition, properties, and behavior in order to explain their stability based on the effects of the solution and the metal used.\(^{17}\)

**Experiment**

**Colloid synthesis**

The colloids of Fe, cobalt (Co), and nickel (Ni) in 2-mercaptoethanol synthesized by means of the method CLD. This method involves the co-deposition at 77 K (liquid nitrogen) of metallic vapors (Fe, Co, and Ni) with organic vapors of 2-mercaptoethanol in a metal atom reactor.

**Solvent degasification.** Previously, 2-mercaptoethanol was degasified by means of the technique freeze-pump-thaw to evacuate the air. This operation is repeated three times or until no longer there is gas loosening. The operations of degasification to dryness avoid that during the co-deposition reaction the metallic atoms are oxidized by the humidity or present oxygen previously in the solvent.

**Co-deposition procedure.** A typical condensation was carried out using the equipment specially designed, previously reported\(^{18,19}\). An alumina tungsten crucible was charged with around 80 mg of Co metal lumps. Distilled and dried solvent (e.g. 100 mL) were placed in a ligand inlet tube and freeze-pump-thaw degassed for five cycles. The reactor was pumped to \(1 \times 10^{-4}\) torr, while the crucible was warmed to red heat. The temperature in the W-Al\(_2\)O\(_3\) crucible at red heat should be at the boiling point of Co. A liquid nitrogen (77 K) filled Dewar was placed around the vessel, and Co (1.35 \(\times\) \(10^{-2}\) moles) and 2-mercaptoethanol (60 mL) were co-deposited over 1 h period at rate of 0.65 mL min\(^{-1}\), approximately. The matrix was black at the end of a co-deposition. The matrix was allowed to warm slowly for 1 h to room temperature under vacuum by removal of the liquid nitrogen Dewar. Upon meltdown, a colorless dispersion was allowed to warm for another 30 min to room temperature. The sol was siphoned into a flask under nitrogen flow. Based on the amount of solvent consumed, the concentration of the colloid could be calculated.

**Colloid characterization**

**UV-VIS spectrophotometry.** For the studies of UV-VIS absorption, approximately 0.1 mL of colloidal dispersion was diluted in 3 mL of pure solvent avoiding the excessive agglomeration of colloidal particles and its high absorption. The diluted colloidal dispersions were poured in rectangular quartz cells of 1 cm of optical way and they analyzed in the rank 200–500 nm in spectrophotometer of double beam UV-2450 UV-Visible Shimadzu, Chemistry faculty of Universidad de Concepción. Pure solvent before each sample measured was used to reduce the noise signal.

**Transmission electron microscopy conventional, scanning electron microscopy, and electron diffraction.** For measurements of transmission electron microscopy (TEM), a drop of the colloidal dispersions just prepared was deposited on one copper grid of 150 mesh covered with coal (supplier Electron Microscopy Sciences, Universidad de Concepción) under a nitrogen atmosphere in a dry camera. The samples were analyzed in an EX-TEM JEOL-JEM 1200 II microscope (JEOL Technics Ltd, Tokyo, Japan) with a voltage of acceleration of 120 kV.

**Kinetic stability.** Stability for each of the colloidal dispersions studied through physical and chemical behavior of the same sample on time, at room temperature, and under inert atmosphere.
Electrophoresis. The electrophoresis measurements were performed in a Zeta Meter 3.0 Model and 0.1 mL of colloid in 2-mercaptoethanol is placed in a cell, which applies a potential difference and the rate of migration of the particles is measured.

Results and discussion

The colloids of Fe, Co, and Ni were obtained by simultaneous co-deposition of these metals with the solvent 2-mercaptoethanol as shown in Figure 1. The excess solvent was added in order to achieve stabilization of the agglomerates or clusters of metal solvated. With this technique were prepared monometallic colloids of Fe, Co, and Ni molar concentrations described in Table 1.

Stability

For colloidal dispersions, the kinetic stability was measured in terms of its power of flocculation at room temperature. The colloid stability measured when 50% of the particles remains in suspension, this is measured by UV-VIS absorptions of the colloidal suspensions. They have been studied the behavior of quantum dots of CdSe and relative colloidal stability in solution. They calculate the average NPs size theoretically, but in this system we obtained them by TEM.20 Table 1 summarizes the stabilities of metal ions in the solvent 2-mercaptoethanol to each of the different concentrations prepared.

From the results, we can observe that for colloidal dispersions obtained from Co and Ni are quite stable in 2-mercaptoethanol, indicating that there is a strong solvation. In contrast, Fe is stable but no to the same extent as other metals due to the higher oxidation potential of Fe over Co and Ni.19,21

The surface energy of a nano metal is different if their sizes are different.21,22 This is due to quantum size effect, which is relevant in the nanotechnology materials.23,24 The colloidal dispersions are systems that tend to produce clusters of low energy state. Henglein25,26 defined the concept of electronic instability to make clear the clustering and coalescence of small particles. But if the particles are quite stable, it should be certain electronic instability when the energy Fermi level is arranged different in the particles.

The colloids of Fe-2-mercaptoethanol are less stable than reported in previous works using other organic solvents such as ethanol, 2-propanol, and 2-methoxyethanol probably due to a size effect.27 Co colloids are considerably more stable at low concentrations (5.72 × 10⁻⁴ mol L⁻¹) than what is reported,24 which does not exceed 4 days, however here, are stable over 60 days. Much clearer is the case with Ni that compared to previous work21 is significantly higher than the period of stability, whereas solvents have similar characteristics and used the same method of production. This is due to the difference in redox potentials of these metals.

However, in the case of Fe and Co, the stability of colloidal dispersions is dependent on concentration, where lower concentrations for colloidal dispersions are more stable than for those with greater concentration. In fact, it is attributed to stabilize less concentrated colloidal dispersions with lower energy needed for particles to remain dispersed in the reaction and improved the solvation power of the NPs.

The Ni suspension exhibit another behavior, independent of the concentration of colloidal dispersions. Their stability over 60 days due to the strong interaction of the metal is observed with OH and SH bonds of the solvent.

Study of particle size

The particle sizes were determined by analysis of micrographs obtained in the transmission electron microscope JEOL JEM 1200 EXII with 4 Å resolution as shown in Figure 2, and these micrographs show the presence of agglomerated particles dispersed on a grid.

Fe particles have a considerably larger particle size than values reported in similar solvents, and Co particles have a size smaller than 4 nm that is lower than that reported by other systems before.28

Table 2 summarizes the particle size of the metallic colloids in the solvent.

These colloids show similar stability to Au-2-propanol being also spherical and negatively charged particles.29 The narrow particle size distribution becomes wider the time aging of the colloid. The values are summarized in Table 2. Also, Bi-2-propanol of Pd, Au, and Ag previously reported colloids just prepared exhibit a particle size of 5.1 nm very similar to (PdSn)-2-propanol. This is probably due to the similarities in the dielectric constant of the solvent.

Table 1. Stability of metal colloids in 2-mercaptoethanol.

| Metal | Concentration (mol L⁻¹) | Stability (days) | Color   |
|-------|------------------------|-----------------|---------|
| Fe    | 1.7 × 10⁻³             | 17              | Green   |
| Fe    | 2.2 × 10⁻²             | 10              | Green   |
| Co    | 1.2 × 10⁻³             | 1               | Red     |
| Co    | 5.7 × 10⁻⁴             | >60             | Red     |
| Ni    | 7.5 × 10⁻⁴             | >60             | Yellow  |
| Ni    | 2.2 × 10⁻²             | >60             | Brown   |

Fe: iron; Co: cobalt; Ni: nickel.
Accordin to TEM analysis, the clustering of particles is due to the association of several particles. Similar stability and behavior have been observed in other colloidal dispersions.31–35

**Electron diffraction**

This study was performed by electron diffraction (ED) for the systems Fe, Co, and Ni-2-mercaptoethanol in order to obtain diffraction patterns that have concentric rings or diffraction spots or in some cases both as shown in Figure 3. Table 3 presents a summary of the crystalline areas and their possible assignments of crystallographic planes for the most representative colloidal dispersions.

According to the results obtained from the diffraction measurements, the presence of metallic particles of each of the metals in its elemental state Fe (0), Co (0), and Ni (0) is observed. There is also the presence of Fe as FeO(OH), Co as CoCo₂S₄, and Ni as NiNi₂S₄. It is noteworthy that the particles thus formed are mainly amorphous in diffraction rings indicating that they have completely random oriented. Otherwise, it would be present as well-defined points.

One interesting point is the intensity of that form of the rings. If they are of very low intensity, it indicates that they are very small crystals that are in colloidal dispersions, which coincides with reports in the frequency histograms.

**Scanning electron microscopy and electron dispersive X-ray spectroscopy**

Scanning electron microscopy (SEM) revealed no differences in the morphology of the films obtained from the colloids synthesized Fe, Co, and Ni in 2-mercaptoethanol as shown in Figure 4.
Figure 3. Electron diffraction for (a) Fe-2-mercaptoethanol, (b) Co-2-mercaptoethanol, and (c) Ni-2-mercaptoethanol. Fe: iron; Co: cobalt; Ni: nickel.

Table 3. Crystal space and possible assignments for colloidal dispersions of Fe, Co, and Ni in 2-mercaptoethanol.

| Colloidal dispersion        | $d$ (nm$^{-1}$) | $d$ (hkl) theoretic | $d$ (hkl) experimental | Compound and crystallographic |
|----------------------------|-----------------|---------------------|------------------------|-----------------------------|
| Fe-2-mercaptoethanol       | 9.86            | 2.027               | 2.028                  | Fe$^0$ (-1,0,1)             |
|                            | 6.24            | 3.291               | 3.205                  | FeO(OH) (0.2, -1)           |
| Co-2-mercaptoethanol       | 10.5            | 1.916               | 1.905                  | Co$^0$ (-1,1,1)             |
|                            | 5.99            | 3.317               | 3.333                  | CoCo$_2$S$_4$ (-1,1,3)      |
| Ni-2-mercaptoethanol       | 9.931           | 2.035               | 2.013                  | Ni$^0$ (1,1, -1)            |
|                            | 5.9             | 3.317               | 3.338                  | NiNi$_2$S$_4$ (-1,1,3)      |

Fe: iron; Co: cobalt; Ni: nickel.
SEM micrographs obtained for Ni show a scattered surface irregularity. In addition, electron dispersive X-ray spectroscopy (EDS) confirmed the presence of the metal surface with a rate of 65% in the films, as shown in Figure 5. This high value of metal embedded in the colloid can be explained by the higher affinity to form bonds through metal solvent –OH group of solvent molecules.

In the case of Fe a rough surface atoms was observed, that follow a certain order, these groups could correspond to growth of the agglomerates of colloidal particles. From EDS, it was confirmed the presence of metal with a low percentage (22.6%). Unlike the case of Co, the micrograph shows a uniform surface roughness, and the EDS analysis gave a rate of 47% metal surface.

**Zeta potential**

Electrophoretic measurements were carried out for the concentration of colloidal dispersion using a computer more...
stable Zeta Meter 3.0. Table 4 provides a summary of the values obtained experimentally from electrophoretic mobility, charge, and the estimated value of Zeta potential for more stable concentration of colloidal dispersions.

The colloidal systems of Fe and Co particles in 2-mercaptoethanol have a positive nature, which is consistent with previous studies. The difference is that the particles in 2-mercaptoethanol have the potential for a significantly lower charge than the one previously reported, and this could be due to the dielectric constant of the solvent which is less than other reported cases.

Table 4. Electrophoretic mobility and zeta potential of colloidal dispersions.

| Metal | Concentration (M) | μₑ | ζ (mV) | Charge | T (°C) | Standard deviation (σ) |
|-------|-------------------|----|--------|--------|--------|------------------------|
| Fe    | 1.7 × 10⁻³        | 76.890 | 14.027 | +      | 20     | 3.945                  |
| Co    | 5.7 × 10⁻⁴        | 51.726 | 9.436  | +      | 20     | 3.571                  |
| Ni    | *                 | *     | *      | *      | *      | *                      |

Fe: iron; Co: cobalt; Ni: nickel.

*It was not possible to determine the zeta potential of suspensions of nickel as they present an anomalous behavior, independent of the concentration of the suspension.

Figure 6. UV-VIS spectrum for colloids (a) Fe-2-mercaptoethanol 1.7 × 10⁻³ M, (b) Co-2-mercaptoethanol, and (c) Ni-2-mercaptothanol. Fe: iron; Co: cobalt; Ni: nickel.
The TEM micrographs and frequency histograms reveal a particle size distribution for each metal, Co = 3 nm, Ni = 7 nm and Fe = 10 nm.

In EDs, the presence of the metal in the elementary state is confirmed for each of them Fe$^0$ (−1,0,1), Co$^0$ (−1,1,1), and Ni (1,1,−1), in addition to other species present FeO(OH) (0,2,−1), CoCo$_2$S$_4$ (−1,1,3), and NiNi$_2$S$_4$ (−1,1,3).

According to the SEM analysis, surfaces for irregular and dispersed Fe and Ni are shown, and for Co, a uniform distribution is observed. EDS identified metals on each of the surfaces analyzed, with a percentage of 22.59%, 47.0%, and 65.0% for Fe, Co, and Ni, respectively.

The colloids of Fe and Co have electric charge of character (+) with a ζ of 14.027 mV and 9.436 mV for Fe and Co, respectively; in Ni’s case, it was not possible to measure the zeta potential (ζ).

Colloids have continuous absorption into the visible spectrum and are increased in the ultraviolet with values for Ni, Co, and Fe of 216.20 nm, 219.20 nm, and 329.40 nm, respectively, which is coincident with the theoretical values except for Fe with a larger wavelength due to its larger particle size.

The active solids are thermally stable and have a decomposition at 100°C that could correspond to the presence of moisture in the samples. The solids in question have decomposition temperatures higher than 200°C, specifically Fe 222.45°C, Co 244.91°C, and Ni 288.29°C, respectively.

The results obtained by atomic absorption were different from one metal to another, Fe 22.7% Co 39.3%, and Ni 58.2%, but always similar content in each preparation.

Fourier transform infrared spectrograms reveal the interaction of metals with the solvent under study, and this is mainly carried out through the displacement to a longer wavelength of the link –OH, in addition to being of relevance is the disappearance of the link –SH which indicates that the interaction would be carried out in this place forming the link –S Metal.

Interaction with organic solvent are also observed in the results obtained from atomic absorption, where the results of the metals percentage are higher for Ni (64%) the Co (58%) and finally Fe with the lowest percentage (22%). Another indication is the particle size because being bound of the solvent the particles avoid agglomeration by repulsion of load between them so they do not agglomerate, obtaining particle sizes much smaller for Ni and Co than for Fe. Besides, the interaction with the solvent is fundamental corresponds to the stability of colloidal suspensions when the particles are more agglomerated. The colloidal suspension is less stable over time causing it to float, in this way the Ni suspensions (<60 days) being the least stable Fe suspension (10-17 days).

**Declaration of conflicting interests**

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References
1. Henglein A. Small-particle research: physicochemical properties of extremely small colloidal metal and semiconductor particles. Chem Rev 1989; 89: 1861–1873.
2. Steigerwald ML and Brus LE. Semiconductor crystallites: a class of large molecules. Acc Chem Res 1990; 23: 183–188.
3. Schmid G. Large clusters and colloids. Metals in the embryonic state. Chem Rev 1992; 92(8): 1709–1729.
4. Fendler JH and Meldrum FC. The colloidal chemical approach to nanostructured materials. Adv Mater 1995; 7: 607–632.
5. Crane RA and Scott TB. Nanoscale zero-valent iron: future prospects for an emerging water treatment technology. J Hazard Mater 2012; 211: 112–125.
6. Crane RA, Dickinson M, Popescu IC, et al. Magnetite and zero-valent iron nanoparticles for the remediation of uranium contaminated environmental water. Water Res 2011; 45: 2931–2942.
7. Popescu IC, Filip P, Humelnicu D, et al. Removal of uranium (VI) from aqueous systems by nanoscale zero-valent iron particles suspended in carboxy-methyl cellulose. J Nucl Mater 2013; 443: 250–255.
8. Crane RA, Pullin H, Macfarlane J, et al. Field application of iron and nickel–nickel nanoparticles for the ex situ remediation of a uranium-bearing mine water effluent. J Environ Eng 2015; 141(8): 04015011.
9. Scott TB, Popescu IC, Crane RA, et al. Nano-scale metallic iron for the treatment of solutions containing multiple inorganic contaminants. J Hazard Mater 2011; 186: 280–287.
10. Karabelli D, Uzum C, Shahwan T, et al. Batch removal of aqueous Cu2+ ions using nanoparticles of zero-valent iron: a study of the capacity and mechanism of uptake. Ind Eng Chem Res 2008; 47: 4758–4764.
11. Crane RA and Sapsford D. Tunable formation of copper metal oxide, chloride and hydroxyl chloride nanoparticles from aqueous copper solutions using nanoscale zerovalent iron particles. Nanomater Nanotechnol 2019; 9: 1–16.
12. Cárdenas G, Sáez C, and Cruzat C. Preparation of gold nanoparticles using 2-ethoxyethanol, 2-methoxyethanol and 1,3-butyleneglycol supported in chitosan. J Clust Sci 2016; 28: 1127–1144.
13. Klabunde KJ, Li YX, and Tan BJ. Solvated metal atom dispersed catalysts. Chem Mater 1991; 3: 30–39.
14. Cárdenas-Trivino G, Klabunde KJ, and Dale EB. Living colloidal palladium in nonaqueous solvents—formation, stability and film-forming properties. Clustering of metal atoms on organic media-14. Langmuir 1987; 3(6): 986–992.
15. Cárdenas G, Leon Y, Moreno Y, et al. Synthesis and properties of NiSn colloids using different metal ratios by CLD. Colloid Polym Sci 2006; 284: 644–653.
16. Cárdenas G, González G, Salgado M, et al. Au–Cu bimetallic colloids prepared by cocondensation with nonaqueous solvents. Mat Res Bull 1999; 34: 1911–1919.
17. Cárdenas G. Chemical reactions at nanomaterial particles. J Chil Chem Soc 2005; 50(3): 603–612.
18. Cárdenas G. and Oliva R.Colloids and films of Cu, Ag and Au from nonaqueous solvents. Bol Soc Chil Quim 1993; 38: 301–308.
19. Cárdenas G. and Delgado V. Iron colloids prepared by chemical liquid deposition. J Chil Chem Soc 2010; 55: 301–303.
20. Mansur HS and Mansur AAP. CdSe quantum dots stabilized by carboxylic-functionalized PVA: synthesis and UV-VIS spectroscopy characterization. Mater Chem Phys 2011; 125: 709–717. DOI:10.1016/j.matchemphys.2010.09.068.
21. Cárdenas G. and Acuña J.Nickel nanoparticles and solids using organic solvents. Colloid Polym Sci 2001; 279: 442–448.
22. Creighton J, Blatchford C, and Albrretch M. Plasma resonance enhancement of Raman scattering by pyridine adsorbed on silver or gold sol particles of size comparable to the excitation wavelength. J Chem Soc Farady Trans 1979; 75: 790–798.
23. De Caro D and Bradley JS. Investigation of the surface structure of colloidal platinum by infrared spectroscopy of adsorbed CO. New J Chem 1998; 22: 1267–1273.
24. Cárdenas-Triviño G and Lillo V. Synthesis and characterization of Co-Ni colloids prepared in nonaqueous solvents. J Chil Chem Soc 2007; 52(2): 1182–1185.
25. Henglein A. Mechanism of reactions on colloidal micrometer- and size quantization effects. Top Curr Chem 1999; 143: 113–180.
26. Henglein A. Physicochemical properties of small metal particles in solution: “microwave” reactions, chemisorption, composite metal particles, and the atom-to-metal transition. J Phys Chem 1993; 97: 5457–5471.
27. Díaz-Visurraga J, Cárdenas G, Melendrez M, et al. Colloidal Cu nanoparticles/chitosan composite film obtained by microwave heating for food package applications. Polym Bull 2009; 62: 511–524.
28. Cárdenas G, Muñoz C, and Vera V. Au and Pd nanoparticles prepared from non-aqueous solvents. Bol Soc Chil Quim 1996; 41: 235–241.
29. Cárdenas G, Vera V, González V, et al. Particle-size of Bi-2-propanol and Au-2-propanol colloids. Mat Res Bull 1997; 32: 97–106.
30. Puech K, Blau W, Grund A, et al. Picosecond generate four-wave mixing in colloidal solutions of gold nanoparticles at high repetition rates. Optic Lett 1995; 20: 1613–1615.
31. Cárdenas G, Vera V, and Muñoz C. Silver colloids from nonaqueous solvents. Mat Res Bull 1998; 33: 645–653.
32. Creighton JA and Eadon DG. Ultraviolet-visible absorption spectra of the colloidal metallic elements. *J Chem Soc Faraday Trans* 1991; 87(24): 3881–3891.

33. Bezryadin A, Dekker C, and Schmid G. Electrostatic trapping of single conducting nanoparticles between nanoelectrodes. *Appl Phys Lett* 1997; 71: 1273–1275.

34. Kotkov A, Chen R, and Likharev K. Possible performance of capacitively coupled single-electron transistors in digital circuits. *J Appl Phys* 1995; 78: 2520–2530.

35. Cárdenas G and Oliva R. Ni–Cu bimetallic colloids prepared in nonaqueous solvents. *Colloid Polym Sci* 2003; 281: 497–504.