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PREPARATION AND CHARACTERIZATION OF Al-Ni COLLOIDAL BIMETALLIC NANOPARTICLES BY GAMMA- IRRADIATION METHOD

Alam Abedini*[,1], Farhad Larki[1], E. B. Saion[1], and M. Zobir Hussein[2]

[1] *Department of Physics, Faculty of science, University Putra Malaysia, 43400 Serdang, Selangor, Malaysia.*

[2] *Department of Chemistry, Faculty of science, University Putra Malaysia,43400 Serdang, Selangor, Malaysia.*

**Corresponding author: abedini_alam@yahoo.com*

ABSTRACT

Bimetallic Al-Ni nanoparticles are synthesized by gamma-ray irradiation from their corresponding metal salts in aqueous solution. The main objective is to find out the optimum parameters of the gamma reduction synthesized Al-Ni nanoparticles which include capping agent concentration and radiation dose. The products are characterized by UV–vis spectroscopy, transmission electron microscopy (TEM), and Energy-dispersive X-ray spectroscopy (EDX). UV–visible spectra and TEM images showed that as the radiation dose increases the particle size decreases and it may be explained due to the competition between nucleation and aggregation processes in the formation of metallic nanoparticles.

Keywords: Bimetallic nanoparticles; Gamma-ray; UV–vis spectroscopy; transmission electron microscopy (TEM);

INTRODUCTION

Alloy nanoparticles [1-5] of various compositions were studied because of their catalytic properties, optical and nonlinear optical properties. They have been prepared by both chemical and physical methods. Many researchers prepared the monometallic and bimetallic nanoparticles in an aqueous solution in the presence of a stabilizer using chemical reducing agents, because most of the monometallic and bimetallic precursors, which are called salts, have good - enough solubility in aqueous solution [6, 7]. A number of production techniques have been reported for preparation of metallic colloids using metal salts as starting materials, such as chemical, photochemical, electrochemical, Radiolytic [8-10], and sonochemical reduction [11]. Of these techniques, the radiation-induced synthesis is one of the most promising strategies because there are some important advantages to the use of the irradiation techniques, as compared to conventional chemical and photochemical methods[12]: (1) the process is simple and clean, (2) Reaction stops immediately when the radiation source ius removed, (3) controlled reduction of metal ions can be carried out without using excess reducing agent or producing undesired oxidation products of the reductant, (4) the

method provides metal nanoparticles in fully reduced, highly pure and highly stable state, (5) Radiation-induced reduction can be made at ambient temperature. Radiolytic reduction generally involves radiolysis of aqueous solutions that provides an efficient method to reduce metal ions. In the Radiolytic method, aqueous solutions are exposed to γ-rays creating solvated electrons, e_{aq}^-. These solvated electrons, in turn, reduce the metal ions and the metal atoms eventually coalesce to form aggregates. Even though several papers have been published about the irradiation-induced synthesis there has little been studied about the γ-irradiation-based reduction of bimetallic. The bimetallic nanoparticles in aqueous solution were difficult to prepare and analyze.

In this study Al-Ni colloidal bimetallic nanoparticles were synthesized by the gamma irradiation – induced technique and the characteristics of the synthesized nanocolloidals and the effect of gamma dose on the size of nanoparticles were examined.

EXPERIMENTAL DETAILS

Aluminium chloride and Nickel chloride were used as precursors. Polyvinyl alcohol (PVA) as a capping agent used to reduce the agglomeration and isopropanol as radical scavenger of hydroxyl radicals and distilled water as a solvent. $AlCl_3 \bullet 6H_2O$, $NiCl_2 \bullet 6H_2O$ and PVA (M.W=22000) were purchased from Systerm. The precursors, capping agent, and radical scavenger were used without further purification. Nitrogen gas used has a high purity of 99.5%.

$AlCl_3 \bullet 6H_2O$ and $NiCl_2 \bullet 6H_2O$ were mixed with various molar ratio to find the best one and dissolved into deionised water in the presence of polymer as colloidal stabilizer and isopropyl alcohol are able to scavenge $OH^\bullet$ and $H^\bullet$ under magnetic stirring to form clear liquid. After stiring for 1 h at 70◦C, ammonia was added to adjust the pH to 8 in which the colour of the solution was changed to light green. Nitrogen gas was bubbled through the solution (30 min) to remove oxygen and then was irradiated by gamma-ray (Co-60 source) under atmospheric pressure and ambient temperature.

The particle size and particle distribution were determined from the transmission electron microscopy (TEM) micrographs (HITACHI H-7100 TEM). The TEM characterization was carried out at 100 keV. The optical properties of nanoparticles were characterized using UV–vis absorption spectroscopy (UV-1650PC SHIMADZU). Energy dispersive X-ray analysis (EDX-LEO 1455) was used to determine the composition of the bimetallic nanoparticles and their weight percentage of the samples.

RESULT AND DISCUSSION

We prepared Al-Ni bimetallic nanoparticles from their respective salt solutions by using ɣ-irradiation reduction at various irradiation doses. Isopropanol and PVA were used as a radical scavenger and colloidal stabilizer respectively. The radiation crosslinking of PVA molecules is known to be induced mainly by OH radicals in aqueous medium [13].

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$$PVA\ (H) + {}^{\bullet}OH \rightarrow \quad PVA^{\bullet} + H_2O \qquad (1)$$

$$2PVA^{\bullet} \rightarrow PVA - PVA\ (\text{Crosslinked polymer}) \qquad (2)$$

Whereas, the hydroxyl radicals almost exclusively react with PVA and the reduction of metal ions takes place both by strongly reducing hydrated electrons and the polymeric radicals $PVA^{\bullet}$ (having similar structure to alcohol radicals) formed by H atom abstraction reaction from PVA chains by hydroxyl radicals.

The dose of gamma radiation has a great effect on the size of the resulting nanoparticles. Since nanometer-sized metal clusters usually exhibit unique optical properties with their specific absorption and scattering, the resulted bimetallic colloids were characterized with UV-visible spectrometer.

Figure 1 shows typical SPR absorption spectra of Al-Ni bimetallic nanoparticles at different radiation doses. As the dose increase, the colour of the nanocolloidal solution changes from light green to brownish green. This shows that the absorbance increases with the increase of the radiation dose.

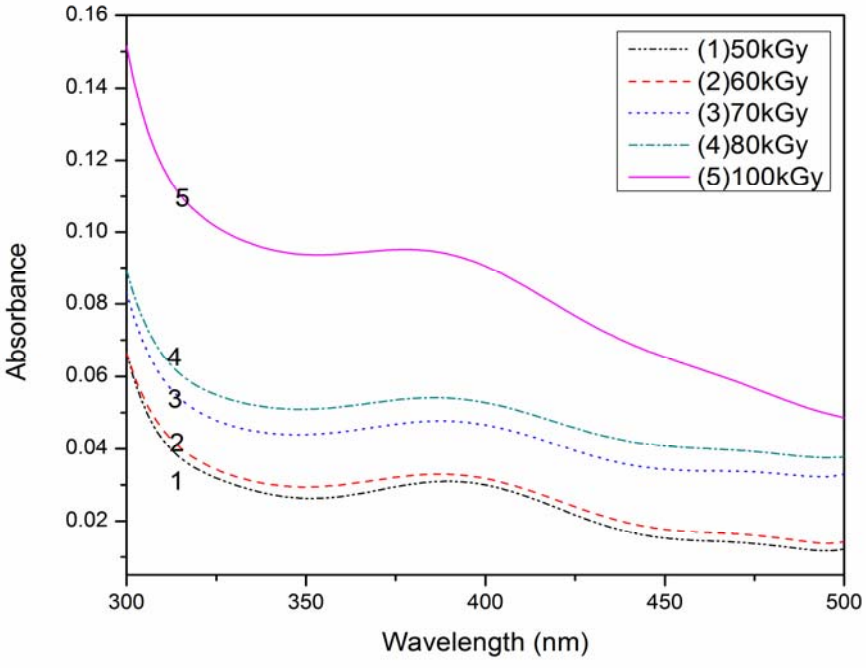

Figure 1: The UV–vis absorption spectra of Al-Ni colloidal nanoparticles for several dose of irradiation

The absorption peaks λmax of colloidal nano particles gives SPR bands in the ultraviolet region. As the dose increased from 50 to 100 kGy, The SPR maximum absorption peak λmax increased and blue shifted from 391 to 377 nm. It is as a result of increasing concentration of reduced particles and decreasing diameter of the bimetallic nanoparticles with increasing dose.

Figure 2 shows the TEM images of Al-Ni nanocolloids prepared by irradiation with a histogram of particle size distribution. Only the TEM images obtained from two doses of irradiation 60 and 100 kGy are showed here.

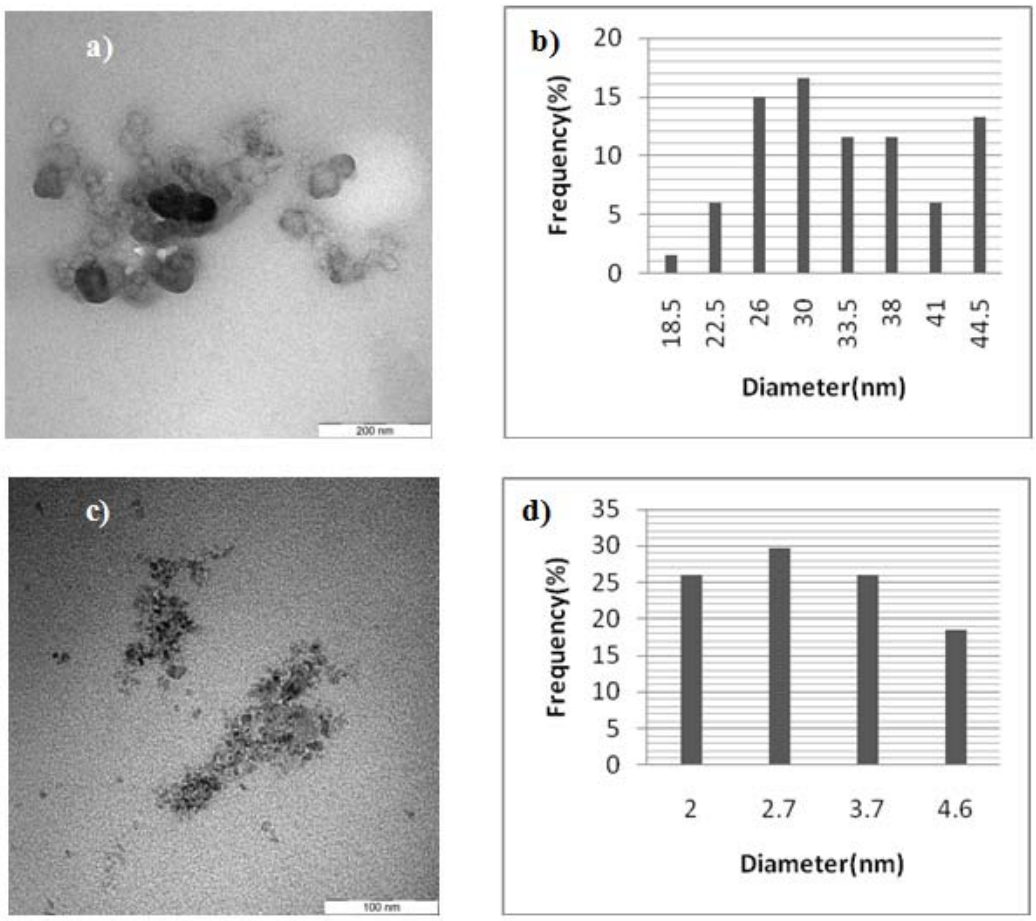

Figure 2: TEM images of colloidal Al-Ni nanoparticles sizes and their distribution of 60 kGy (a and b) compared with TEM images of Al-Ni nanoparticle sizes and their distributions of 100 kGy (c and d)

The size of Al-Ni nanocolloids decreases from 30 nm at 60 kGy to 3 nm at 100 kGy dose of irradiation. Our results show by increasing the radiation dose, the diameter of nanoparticles decrease. Because the reducing agents, which are generated by the radiation penetrating deeply in the sample, are randomly distributed as the metal ions in

the solution, the atoms are formed with a homogeneous distribution throughout the solution. The binding energy between two metal atoms is stronger than the atom-solvent or atom-ligand bond energy [14]. Therefore the growth of clusters are generated.

$$M^0 + M^0 \longrightarrow M_2 \quad (3)$$

$$M_m + M^0 \longrightarrow M_{m+1} \quad (4)$$

The bonding between atoms or clusters with unreduced ions is also strong and these association processes are fast, which gradually guides to the formation of nanoparticles:

$$M^0 + M^+ \longrightarrow M_2^+ \quad (5)$$

$$M_m + M^+ \longrightarrow M_{m+1}^+ \quad (6)$$

$$M_{m+1}^+ + e^-_{aq} \longrightarrow M_{m+1} \quad (7)$$

The fast reactions (6) and (7) of ion association with atoms or clusters play an important role in the cluster growth mechanism. The competition between the reduction of free metal ions and absorbed ones is controlled by the rate of reducing radical formation, therefore the cluster formation by direct reduction followed by coalescence is dominant at high dose and the final cluster size is smaller (Figure 2(c)- (d)) [15].

In fact, in lower dose, the amount of solvated electrons is not enough to reduce metal ions to atoms. Thus they are essentially reduced by are adsorption on the nuclei generated by radiolysis at the start of irradiation, which results in larger size particles or clusters (Figure 2(a)-(b)).

Actually, when a mixed solution of two ionic precursors M^+ and M'^+ is irradiated, both situations of alloyed or, more often, bilayered cluster formation were encountered without clear prediction [16].

Energy dispersive X-ray spectroscopy (EDX) analysis (Figure 3) of the sample indicates that the atomic percentage of Al was 28.12% and for Ni was 71.88% while molar ratio of Al/Ni sample before irradiation was 70/30.

Since EDX is a somewhat surface-sensitive tool [17], we suggest that Ni might exist mostly inside the composite nanoparticles formed as a core with Al-Ni nanoparticles shell outside.

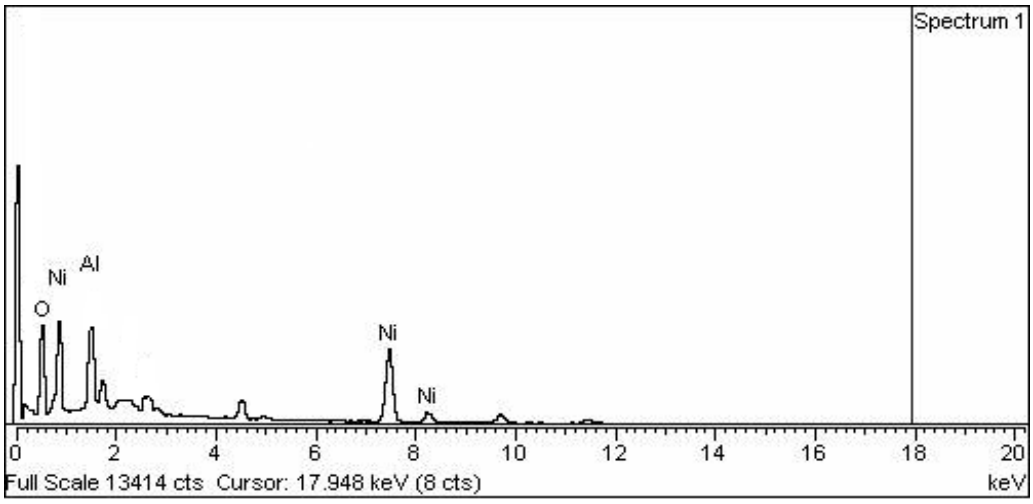

Figure 3: Energy dispersive X-ray spectroscopy (EDX) analysis of the colloidal Al-Ni nanoparticles

CONCLUSION

Al-Ni colloidal bimetallic nanoparticles are synthesized from $AlCl_3$ and $NiCl_2$ solution stabilized in PVA by gamma irradiation– induced thechnique. The UV-vis spectra of bimetallic colloids shows when dose increases, absorption peak shifted to lower wavelengths and shows higher absorption, indicating that with increasing irradiation dose the particle size decreases and the density of reduced ions to atoms increase. Particle size and distribution are determined by transmission electron microscopy. The results clearly indicate that when the dose increases, the size of nanoparticles decreases.

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