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# Polymer stabilized Ni–Ag and Ni–Fe alloy nanoclusters: Structural and magnetic properties

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### ARTICLE INFO

## ABSTRACT

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Keywords: Bimetallic alloy Nanocluster EPR Magnetic property We report here the structural and magnetic behaviors of nickel–silver (Ni–Ag) and nickel–iron (Ni–Fe) nanoclusters stabilized with polymer (polypyrrole). High resolution transmission electron microscopy (HRTEM) indicates Ni–Ag nanoclusters to stabilize in core-shell configuration while that of Ni–Fe nanoclusters in a mixed type of geometry. Structural characterizations by X-ray diffraction (XRD) reveal the possibility of alloying in such bimetallic nanoclusters to some extent even at temperatures much lower than that of bulk alloying. Electron paramagnetic resonance (EPR) spectra clearly reveal two different absorption behaviors: one is ascribed to non-isolated Ni<sup>2+</sup> clusters surrounded by either silver or iron giving rise to a broad signal, other (very narrow signal) being due to the isolated Ni–Fe nanoclusters have been further compared with the behavior exhibited by pure Ni nanoclusters in polypyrrole host. Temperature dependent studies (at 300 and 77 K) of EPR parameters, e.g. linewidth, g-value, line shape and signal intensity indicating the significant influence of surrounding paramagnetic silver or ferromagnetic iron within polymer host on the EPR spectra have been presented.

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## 1. Introduction

Magnetic nanostructures are found to have diverse applications today and have become the subject of key area of research in nanoscience and nanotechnology. The major potential area of applications not only includes magnetic recording media, sensors and importantly spintronic devices, but it also extends in the key area of biotechnological research, e.g. cell sorting, drug delivery, optical coding, ferrofluids, etc [1–8]. The tiny magnetic material objects can easily be manipulated by suitably changing their size, shape and composition giving rise to unique properties compared to bulk [9–11]. Besides, they can be addressable by externally applied magnetic field and thereby widen the scope of obtaining tunable magnetic nanodevices. The literature indicates a great deal of research carried out so far on various ferromagnetic materials like Fe, Co, Ni (d-block transition metals),  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> or γ-Fe<sub>2</sub>O<sub>3</sub>, etc. in their various nanostructures form, e.g. nanoparticles, nanorods and nanowires. In this context, of late bimetallic magnetic nanomaterials or nanoalloys have regained considerable research interests for their unique physical properties [12-15]. These bimetallic nanostructures are composed of either magnetic-nonmagnetic or magnetic-magnetic elements. Such bimetallic nanoalloys are found to exhibit several anomalies in terms of lattice constant, thermal expansion coefficient and average magnetic moments and chemical reactivity [16-19]. Recent experiments and molecular simulations indicate the significant decrease in melting temperature and latent heat in such nanoalloy systems compared to their bulk values [20–22]. Apart from few experimental and molecular simulations based work giving some generic features, various issues like atomic ordering, interdiffusion of atoms, structural stability and their effect on the physical properties in such nanoalloy systems needs to be explored.

In this paper we focus on such bimetallic systems consisting of Ni–Ag and Ni–Fe elements synthesized in the form of nanoclusters. Systems of Ni–Ag in nanoscale have scarcely been addressed because of immiscible nature of the bimetallic constituents [23]. These nanoclusters may find superiority in applications like high density magnetic recording media, sensors and spintronic devices. Such nanostructures also offer tremendous potentiality in carrying pharmaceutical particles and hence can be used in drug delivery applications. Here, we report on the chemical synthesis of such bimetallic Ni–Ag and Ni–Fe nanoclusters and obtain their structural and magnetic properties. We show how the temperature dependent magnetic relaxation behaviors change in such low-dimensional bimetallic systems investigated by electron paramagnetic resonance spectroscopy (EPR).

## 2. Experimental

Synthesis of Ni, Ni–Ag and Ni–Fe nanoclsuters is accomplished by simple wet chemical technique. All the regents used here are

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analytically pure and no further purifications are done. For the synthesis of Ni nanoclusters, the procedure takes place first by exchanging Ni<sup>2+</sup> ions into the pyrrole and then the nickel ions are reduced to nickel metal by sodium borohydride (NaBH<sub>4</sub>). Two separate solutions of Ni(NO<sub>3</sub>)<sub>2</sub> (Purified Merck Limited, India) and sodium borohydride (Spectrochem, India) are prepared in a solvent of ethanol (GR, Jiangsu Huaxi, China) and distilled water. The volume ratio of ethanol and water is maintained 2:3 throughout to prepare the solution. Both the solutions are continuously stirred for two hours keeping the bath temperature  $\sim$ 60 °C. Finally, the sodium borohydride solution is slowly added to the nickel  $(Ni^{2+})$  solution keeping the bath temperature same and stirred for one hour. This instantly results in the formation of Ni within polypyrrole (PPY) matrix. The precipitate is washed in distilled water for three times, filtered and dried at room temperature in vacuum. The redox type of reaction mechanism for the formation of Ni in polypyrrole matrix can be proposed in the following way:

$$Ni^{2+} + (PPY)_{complex} \rightarrow Ni^{2+} (PPY)_{complex}$$

# $Ni^{2+}(PPY)_{complex} + NO_3^- + 2NaBH_4 + 6H_2O \rightarrow Ni(PPY)_{complex}$ + 2B(OH)<sub>3</sub> + 2NaNO<sub>3</sub> + 4H<sub>2</sub>

The same procedure is adopted while preparing Ni–Ag and Ni–Fe nanoclusters in polypyyrole matrix. In the latter cases, initially separate solutions of AgNO<sub>3</sub> (Purified Merck Limited, India) and Fe(NO<sub>3</sub>)<sub>2</sub> (Purified Merck Limited, India) are prepared. These solutions are then separately added to the stock solution of Ni(NO<sub>3</sub>)<sub>2</sub> to obtain mixed precursor solution of Ni–Ag and Ni–Fe, respectively. These solutions are then reacted with sodium borohydride under rapid stirring and are continuously stirred for two hours keeping the bath temperature ~60 °C. The precipitates of Ni–Ag and Ni–Fe in polypyyrole obtained in this way are finally washed in distilled water for three times, filtered and dried at room temperature in vacuum.

#### 3. Results and discussion

It is found that bimetallic nanoclusters can form alloy or segregate with each other in core-shell structures [19]. In case of Ni-Ag system, Ni and Ag are immiscible in their bulk form in any proportion as indicated by their phase diagram. Various efforts have been made to synthesize Ni-Ag alloys, but giving no signature of the formation of alloy, only in some cases giving rise to the segregation of Ni atoms onto the core and with Ag atoms preferentially at the surface forming core-shell clusters [22]. The structural characterization done by transmission electron microscope (TEM) clearly indicates the possible formation of nanoalloy clusters for Ni, Ni-Ag and Ni-Fe and is given in Fig. 1. Fig. 1 shows the typical TEM and that of HRTEM for Ni (a, d), Ni-Ag (b, e) and Ni–Fe (c, f), respectively. The TEM images indicate that although there is a distribution of nanoclusters size, the average crystallite size didn't change appreciably for all the three samples. The average nanoclusters size is found to be D (=2R, R being the radius)  $\sim 20 \pm 2$  nm and plausibly caused by the similar experimental conditions while synthesizing such nanoclusters. We also present the HRTEM images of individual alloy nanoclusters in Fig. 2. The image given in Fig. 2(a) shows the nanocluster of Ni-Ag and clearly the formation of core-shell structures, while that of a (inter-) mixed type of cluster for Ni-Fe as indicated by Fig. 2(b). Both these structures are possible patterns of formation of alloy nanoclusters as indicated by theoretical calculations [19]. The core-shell configuration of Ni (core)-Ag (shell) as observed earlier is possibly caused by the lower surface energy of Ag and large lattice mismatch between the constituents leading to a loosely bonded silver shell covering the nickel core [24]. On the other hand, intermixed type of nanocluster is common to many bimetallic systems like Ni-Fe [25,26]. Of course, the process of coordination of atoms segregating each other to form core-shell, mixed or any other configurations is complex and the surface kinetics is largely influenced by the chemical nature of individual



Fig. 1. Typical TEM (a-c) and HRTEM (e-f) images obtained for Ni, Ni-Ag and Ni-Fe samples, respectively.



Fig. 2. HRTEM images obtained for an isolated (a) Ni-Ag and (b) Ni-Fe nanocluster.

constituents, composition, growth process, thermodynamical parameters, etc.

The XRD pattern of synthesized Ni, Ni–Ag and Ni–Fe nanorods is given in Fig. 3(a-c). For the sake of clarity, bulk XRD data of Ni is also included in Fig. 3(d). The XRD of synthesized Ni nanoclusters shows mainly two distinct peaks at  $2\theta$  ~39.7° and 71°, respectively. The peak centered at  $2\theta \sim 39.7^{\circ}$  is broad, making it difficult to index the characteristic peak within the limit of resolution. However, in comparison with the bulk Ni data, the peak in the range  $2\theta$ =37–42° can be identified as the characteristic Ni peaks (110) and (006) superposed with each other. The other peak at  $2\theta \sim 71^\circ$  is well resolved and also broad, can be indexed to Ni (300). The broad nature of the peaks is indicative of the nanocrystalline nature of the sample and also to some extent due to the inherent strain present in such synthesized nanoclusters. The addition of silver into nickel results in significant changes in the XRD pattern as obtained for synthesized Ni-Ag nanoclusters, in terms of position of the peaks, relative orientations and intensities. The intense peaks Ni (1 1 0) and Ni (300) observed for Ni nanoclusters are drastically broadened and almost subdued for Ni-Ag nanoclusters. On the other hand, new peaks at  $2\theta \sim 44.5^{\circ}$  and  $76.5^{\circ}$  appears which can be indexed to (1 1 1) and (2 2 0) reflections of cubic silver present in a mixed state with nickel. The only peak at  $2\theta \sim 51.7^{\circ}$  can be assigned to (111) reflections of Ni-Ag nanoalloy phase. Such a formation of Ni-Ag alloy phase has been recently reported for laser ablated and solution grown films [27,28]. In case of Ni-Fe, in addition to the (110) and (300) reflections of Ni, some new Bragg reflections appear at  $2\theta \sim 24.9^\circ$ ,  $45^\circ$  and  $85.5^\circ$ , which can be indexed to alloy phase of Ni-Fe. These peaks are broad and not well resolved compared to Ni peaks. The nickel peaks observed in both Ni-Ag and Ni-Fe is quite similar to that of Ni nanoclusters apart from a slight shift in peak positions. Clearly, both the Ni-Ag and Ni-Fe samples indicate a coexistence of isolated Ni as well as nanoalloy phase due to interfacial mixing and segregation of the bimetallic constituents. The composition analysis of the alloy clusters are performed by energy dispersive X-ray analysis (EDAX) and indicate the following composition of the elements: Ni-Ag: Ni-7.2% and Ag-92.8%, Ni-Fe: Ni-45% and Fe-55%.

Figs. 4 and 5 present the first derivative of EPR signals [(dP/dH) vs H] for Ni, Ni–Ag and Ni–Fe nanoclusters recorded at room temperature (300 K) and liquid nitrogen temperature (77 K), respectively. EPR measurements are carried out at 9.833 GHz using a Bruker BioSpin GmbH spectrometer with a judicious choice of modulation frequency (50–100 kHz) and modulation amplitude (10–15 G), and without any appreciable spurious signals. The EPR parameters calculated are given in Table 1. The



**Fig. 3.** X-ray diffraction (XRD) spectra obtained for Ni, Ni–Ag and Ni–Fe samples. The data has been compared with bulk obtained from JCPDS file. The asterisk (\*) indicates the corresponding alloy phase of bimetallic nanoclusters.

room temperature spectrum for Ni nanoclusters consists of two lines: a weaker sharp line not properly resolved (indicated by the arrow mark) superposed on a broader resonance line. We call the broad signal at the lower resonance field as I-type and that of the sharper one as II-type. The broad I-type signal of Ni nanoclusters becomes narrower with reduction in temperature to 77 K and shows a single, nearly symmetric line. The II-type line gets vanished with lowering in temperature to 77 K. The g-value obtained for I-type line is found to significantly increase from 1.9679 to 2.2449 as the temperature changes from 300 to 77 K. In contrast to pure Ni nanoclusters, both the spectra for Ni-Ag and Ni-Fe nanoclusters at 300 K consist of two distinct lines: a very sharp line superimposed on a broader line with a significant difference in their resonance field. For Ni-Ag nanoclusters, the integral EPR intensity at 300 K of II-type line (g=1.9690) is very low compared to that of I-type line (g=2.1902). With lowering in



Fig. 4. Room temperature (300 K) EPR spectra obtained for Ni, Ni-Ag and Ni-Fe samples.



**Fig. 5.** EPR spectra obtained for Ni, Ni–Ag and Ni–Fe samples at liquid nitrogen temperature (77 K).

temperature to 77 K, the II-type line for Ni-Ag is completely smeared out and the spectrum shows only a single Lorentzian inhomogeneously broadened and suffered a significant change (increase) in the resonance field compared to room temperature. The g-value is appreciably reduced to 1.8956 and the integral intensity becomes higher as the temperature reduces to 77 K. The spectrum for Ni-Fe at 300 K evolves quite similar to Ni-Ag, but there is a significant change in g-values and EPR intensities for both the lines. In this case, the II-type line is guite sharp and intense than what observed for Ni and Ni-Ag nanoclusters. The gvalue is observed to be  $\sim$  1.9673 for the broad I-type line and that of  $\sim$ 1.9431 for II-type line, respectively. Interestingly, as the temperature decreased to 77 K. EPR spectrum retains both the lines with marked changes in intensity, g-values and linewidth. The integral intensity of I-type line is found to increase than the corresponding room temperature EPR signal. Also, the I-type line is largely broadened with significant decrease in resonance field and increase in g-value at 77 K. The g-value is calculated to be  $\sim$ 2.0372 for I-type line and  $\sim$ 1.9557 for II-type line, respectively.

The origin of II-type line (Lorentzian in shape) can be ascribed to isolated Ni<sup>2+</sup> ion clusters or nanoalloy clusters dispersed in polymer [29]. Such isolated region of Ni<sup>2+</sup> ions in the polymer may also be found in our samples. In true sense to say, those isolated ions are surrounded by largely diluted paramagnetic silver or iron ions, presence of which making no significant interactions with Ni<sup>2+</sup> ions to influence the EPR signals. Note that at room temperature the intensity for the II-type line is very low for pure Ni nanoclusters sample and subsequently increases with the modified interface Ni/Ag and Ni/Fe. The sharp narrow II-type resonance line occurs due to the superparamagnetic Ni clusters for pure Ni sample or nanoallov clusters in case of Ni-Ag and Ni-Fe samples. The observed weak intensity of II-type line for pure Ni sample indicates a very dilute concentration of isolated Ni ion clusters. On the other hand, for Ni-Ag and Ni-Fe samples the intensity of II-type line plausibly enhanced because of the presence of superparamagnetic nanoalloy clusters. Superparamagnetic relaxation is further confirmed by the broadening of linewidth with reduction in temperature [30]. Now the possibility of Ni-Fe alloy formation is higher (miscible in bulk) than that of Ni-Ag and quite reasonably making a significant difference in their respective II-type line intensity. At room temperature, faster spin relaxation of magnetization directions of superparamagnetic clusters results in the narrow resonance line [11]. As the temperature decreases, linewidth increases (without any appreciable change in the resonance field and g-value) due to the reduction of thermal fluctuation rate of the magnetization directions of the superparamagnetic clusters, usually called the blocking effect. Such thermally blocked state results in complete smearing out or weaker resonance line when cooled to lower temperature as observed in our case. The blocking temperature of course depends on the size or size distribution of the nanoclusters and their interface. In our case, complete blocking of the superparamagnetic state occurs for Ni and Ni-Ag nanoclusters at 77 K and results in smearing out of the II-type line or too weak to be observed, while for Ni-Fe nanoclusters, there are some fraction of small Ni clusters still undergoing superparamagnetic oscillations giving rise to weaker resonance line at 77 K.

The broad I-type line observed for all the samples is not superparamagnetic in origin. The origin of this line can be attributed due to the interaction of Ni nanoclusters with the surroundings [31]. For pure Ni sample, the interaction is between magnetically non-isolated Ni clusters within polymer matrix. The linewidth of I-type spectrum can arise out of the dipole–dipole and exchange interaction between the interacting spins. The dipole–dipole interactions superimposed on the Zeeman's interactions can give rise to the broadening of the EPR spectrum [32].

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EPR parameters obtained for Ni, Ni-Ag and Ni-Fe samples at 300 and 77 K, respectively.

Sample	Temperature (K)	Resonance field (mT)		Linewidth $\Delta H$ (mT)		g-value		A/B
		I-type line	II-type line	I-type line	II-type line	I-type line	II-type line	I-type line
Ni	300	337.8	338	$\sim 300$	2.5	1.9679	1.9667	1.05
	77	296.1	-	131	-	2.2449	-	1.07
Ni–Ag	300	303.5	337.6	77	1.5	2.1902	1.9690	1.3
	77	350.5	-	342	-	1.8965	-	1.63
Ni–Fe	300	337.9	342.1	119	1.4	1.9673	1.9431	1.06
	77	326.3	339.9	301	5.4	2.0372	1.9557	1.09

The magnitude of broadening of course depends on the concentration of spins and the distance between them. On the other hand, exchange type of interactions lead to the narrowing of linewidth. The competing effect of the above two effectively determines the linewidth. Due to large magnetocrystalline anisotropy coupled with strong spin-spin interaction, the linewidth of the EPR spectra (I-type) significantly increases in case of Ni-Ag and Ni-Fe with reduction in temperature. For pure Ni sample, the exchange takes place between identical Ni spins giving rise to the narrowing of the resonance signal when cooled to lower temperature. As observed for pure Ni and Ni-Fe samples, the effective g-value increases with decrease in temperature indicating gradual strengthening of magnetic ordering. While for Ni–Ag, g-value is found to decrease with lowering in temperature to 77 K, clearly indicating a different resonance behavior. We also comment on the effect of surroundings on the line shape of the EPR spectra. This can be viewed by calculating the asymmetry parameter A/B, where A and B are the low field and high field amplitudes of the EPR signal, respectively (Table 1) [11]. In case of Ni and Ni–Fe samples, A/B is found to be  $\approx 1$  within the error limit and nearly temperature independent. To be noted that slight error may always be encountered in the calculation of A/B due to difficulties in obtaining the correct baseline of the broad EPR signal due to the mismatch in low field and high field baselines. However, Ni-Ag sample exhibits a characteristic Dysonian line shape i.e. A/B > 1 at room temperature and becomes more asymmetric with the decrease in temperature. This symmetric Dysonian line shape results from the mixture of absorptive and dispersive components of susceptibility and hence results in a non-uniform distribution of the microwave fields for nanoclusters of size larger than the skin depth [33,34]. Clearly, the presence of paramagnetic silver in the surroundings of nickel than polymer (for pure Ni) and ferromagnetic iron seems to introduce more asymmetry in the line shape of the EPR spectra. This is also reflected in the temperature dependent linewidth behaviors of Ni-Ag and Ni-Fe. At low temperature, the large linewidth for Ni-Ag appears due to the microwave absorption in a randomly oriented Ni-Ag sample and an anisotropic orientation of the magnetic moments. Increase in temperature results into magnetic moments more isotropic causing the linewidth to decrease, as observed at 300 K. This effect is less pronounced in Ni-Fe ferromagnets than Ni-Ag.

## 4. Conclusions

In conclusion, we described electron spin resonance behaviors of Ni-Ag (Ni-7.2% and Ag-92.8%) and Ni-Fe (Ni-45% and Fe-55%) nanoclusters in polypyrrole host matrix. Structural characterizations reveal the coexistence of nanoalloy phase and mixed phase of such bimetallic clusters. The nanoalloy cluster stabilizes either core-shell (Ni-Ag) or mixed pattern (Ni-Fe) in conformity with theoretical calculations. Existence of such nanoalloy phase is further confirmed by the EPR spectra. Influence of paramagnetic silver or ferromagnetic iron on the spin resonance behavior of Ni<sup>2+</sup> is further analyzed with the temperature dependent variation of EPR parameters. Indeed, as our discussion is restricted to the data available for temperatures 300 and 77 K only, a detailed analysis of the EPR parameters recorded in a wide range of temperature may provide more insight into the resonance behaviors of such important magnetic nanoclusters and their interfacial alloying behavior.

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