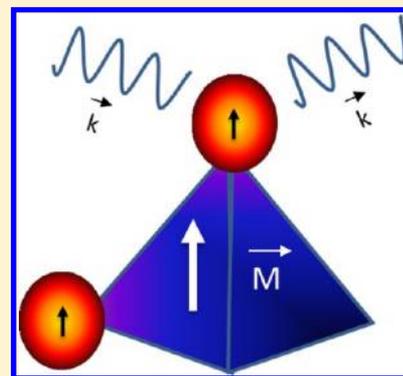


Tip Enhanced Silver Growth on Shaped Controlled Nickel Nanocrystals

Meital Shviro and David Zitoun*

Department of Chemistry, Bar Ilan Institute of Nanotechnology and Advanced Materials (BINA), Ramat Gan 52900, Israel

ABSTRACT: We report on the synthesis of Ni/Ag heterogeneous nanocrystals. Ag almost exclusively nucleates on the vertices of Ni nanopyramids and vertices and edges of Ni nanocubes. The synthesis is carried on using the decomposition of an organometallic Ni precursor to achieve a shape control (cubes and pyramids) followed by a nonaqueous galvanic replacement reaction of Ag(I). The colloids exhibit both plasmonic resonance and superparamagnetic behavior. Interestingly, the bimetallic nanocrystals display a magnetic moment higher than the pristine Ni nanocrystals, suggesting a specific magnetic polarization of the Ni/Ag interface or silver tips.



INTRODUCTION

The synthesis of bimetallic nanoparticles is generating large interest due to their unique chemical and physical properties.^{1,2} The properties of a monometallic structure can be modified by incorporating one more metallic component in the nanocrystal to form an alloy, a core/shell, or a Janus particle.³ The synergic and co-operative effects between the metallic components could lead to a more useful functionality and can ease the addressability of the particles with extensively studied surface state.⁴ An already classical case is the growth of Au tips on semiconductors or metals to specifically interface this tip with the microscale world, usually a microelectrode.⁵ Furthermore, plasmonic metals bring new optoelectronic properties that could be ideally combined with the magnetic or catalytic properties of transition metals like nickel.^{6–8}

There are several techniques to generate bimetallic nanostructures and galvanic replacement reaction (GRR) stands as a topotactic synthetic route when the redox potential allows for the spontaneous displacement of the metallic surface atoms by the more noble metal cation.^{9,10} GRR can convert monometallic nanostructures into complex multimetallic structures, using one or several steps to yield multimetallic colloids.¹¹ The growth of the second metal on the surface of the metal which act as a sacrificial anode depends on the similarity of both crystalline structures, the extent of lattice mismatch, the difference in metallic bonding strengths and the affinities with the ligands if present, which leads to a conformal or nonconformal growth.¹² This phenomenon is well established for noble metals in view of the stability of their metallic surfaces and has been studied in a few cases for more reactive 3d metals.^{13,14} The reactions can yield core/shell, hollow or Janus nanoparticles.³

The use of Ni as sacrificial anode has not been studied more extensively, since most of the synthetic pathways leads to a NiO shell¹⁵ or to strongly coordinated ligands (phosphines) which are

uneasy to displace.¹⁶ Interestingly, the GRR is not limited to metals and can be applied to transition metal oxides, like in the case of Ag on Fe/FeO_x core/shell,¹⁷ Rh on Fe/FeO_x core/shell,¹⁸ or in pure oxide systems (Fe(II) on Mn₃O₄).¹⁹ Organometallic synthesis stands as a unique route toward shape controlled particles without strongly coordinating ligands, since the synthesis occurs in mild conditions.²⁰ Organometallic precursor like Ni(cyclooctadiene)₂ (Ni(COD)₂ or Ni(η^4 -C₈H₁₂)₂) precursor shows a well-controlled decomposition process with amine ligands²¹ and microwave-assisted synthesis leads to cubic and pyramidal shapes.²² The ability to control the nanoparticles shape is an important step to monitor the growth anisotropy of the second metal during the GRR.²³ Indeed, the nanocrystal shape generally reveals the crystallographic planes of the lattice and the nucleation and growth of the second metal should be affected by the facet orientation.

In this work, we report on the synthesis of Ni/Ag heterogeneous nanocrystals by a two-step reaction. First, the Ni nanoparticles are produced by a decomposition reaction of the organometallic precursor in the presence of amine ligand to control the nanoparticle shapes. Then, galvanic displacement with silver leads to the growth of Ag nanocrystals on the edges and vertices of the pyramidal and cubic Ni nanocrystals. The Ni/Ag nanocrystals display outstanding magnetic properties.

EXPERIMENTAL SECTION

Materials. Ni(COD)₂ (STREM, 98%) used as receive, AgNO₃ (99.9%, STREM Chemicals), 1-Hexadecylamine (HDA) (ACROS, 90%) is dried, degassed, and stored in the glovebox (N₂ filled, O₂ < 1 ppm, H₂O < 1 ppm). Mesitylene

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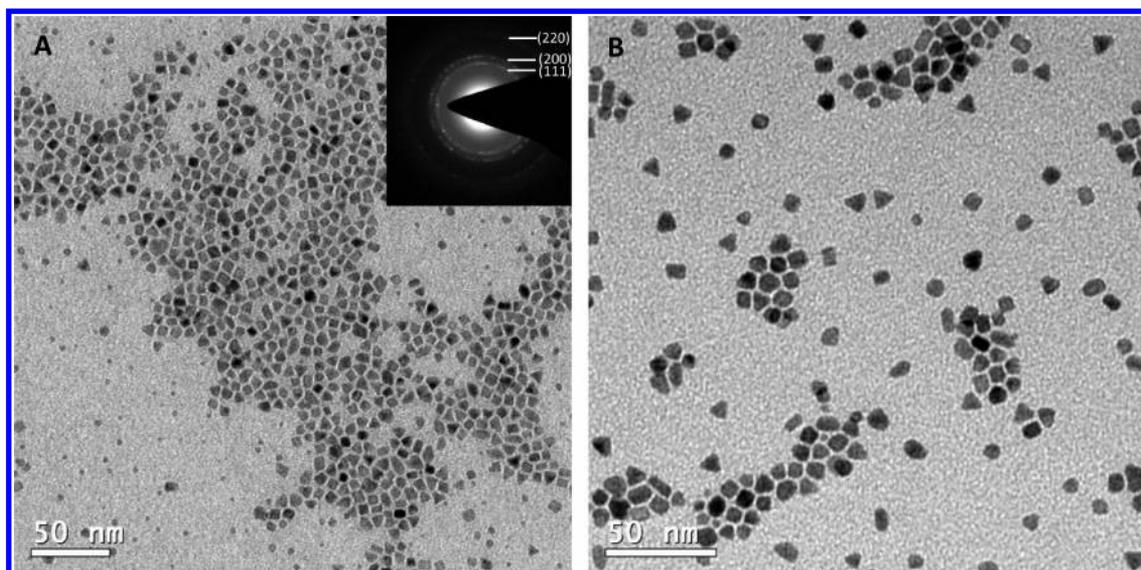


Figure 1. TEM images and electron diffraction of Ni nanoparticles: 80/20 cubes/pyramids (A) and 60/40 cubes/pyramids (B).

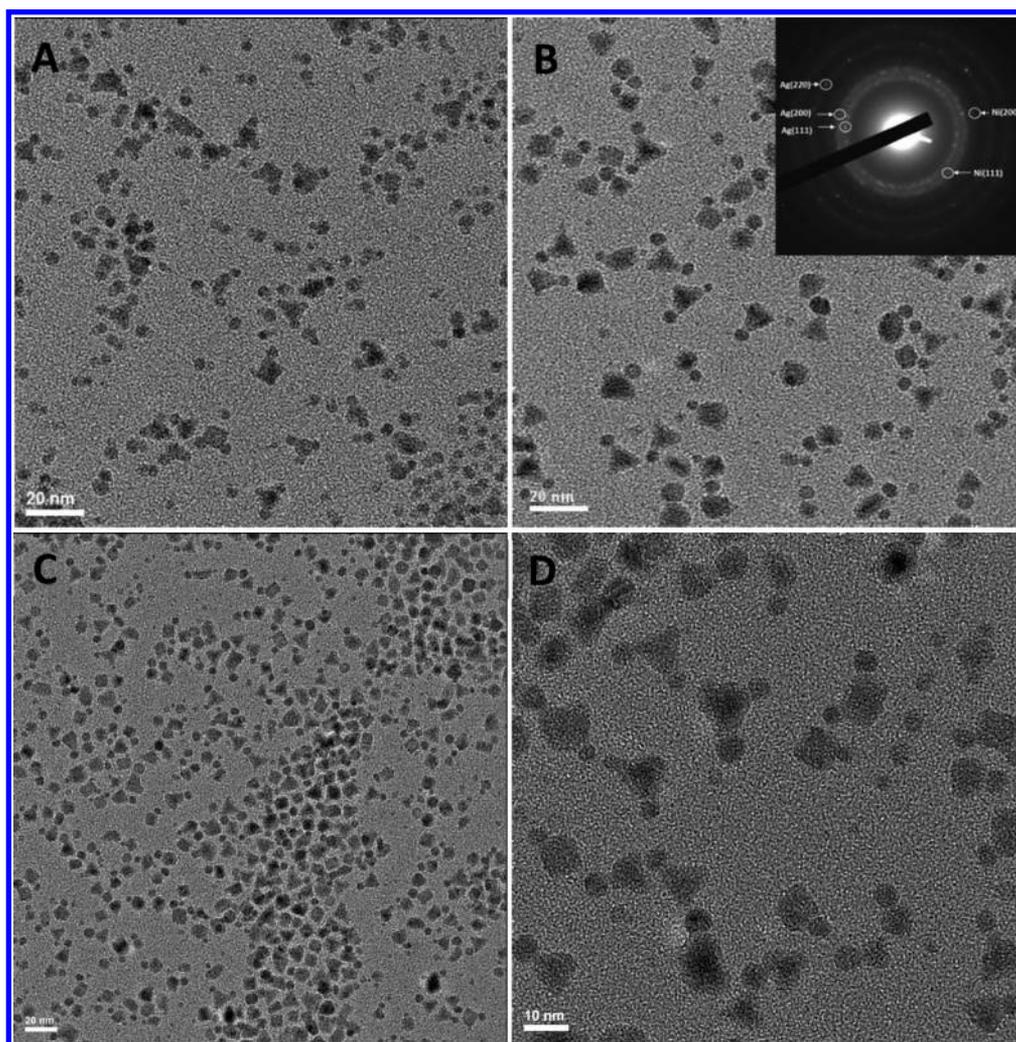


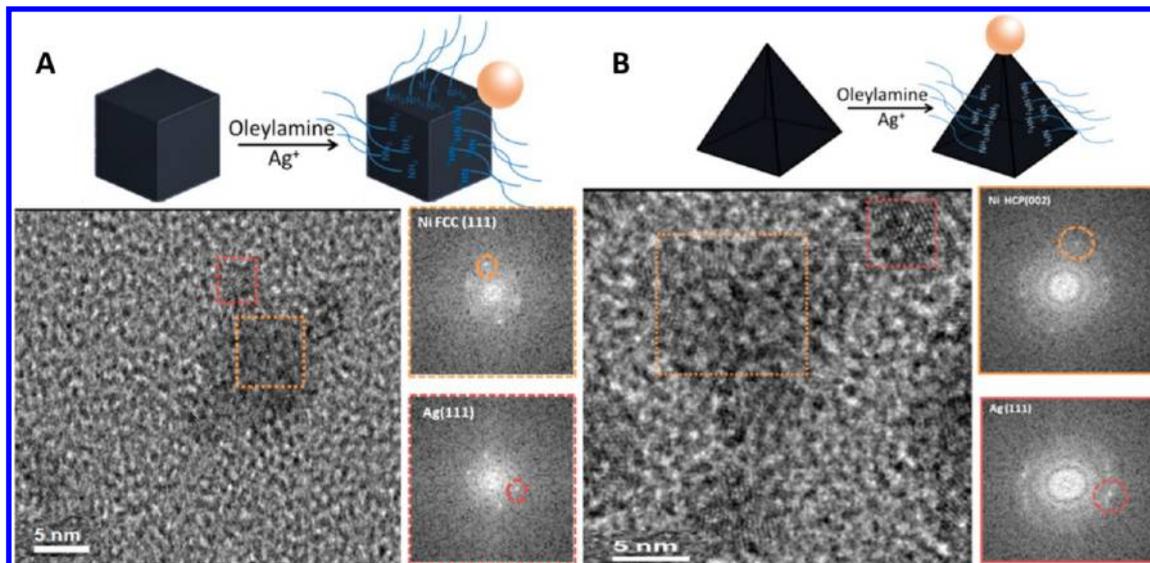
Figure 2. TEM images of Ni/Ag nanocrystals 2:1 without heating (A); 2:1 ratio after heating (B); 8:1 ratio large scale (C); and 8:1 ratio higher magnification (D).

(ACROS, 97%) and Oleylamine (ACROS, 80–90%) are dried, degassed, and stored on molecular sieves in the glovebox.

Synthesis of Ni Nanocrystals. Ni(COD)₂ (9.0×10^{-5} mol, 25 mg), 10 equiv of HDA, and 3 mL of mesitylene are added to a

Table 1. Nanoparticle Size and Frequency of Nucleation on the Vertices and Edges of the Nanocrystals

sample	Ni size (nm)	Ag size (nm)	tip growth (Ag on vertices) %	Ag growth on edges %	Ag tips/Ni particle
Ni pyramids/Ag (2:1)	7 ± 1	3.5 ± 1	95	5	2.2
Ni pyramids/Ag (8:1)	7 ± 1	3.5 ± 1	95	5	1.2
Ni cubes/Ag (2:1)	7 ± 1	3.5 ± 1	60	40	2
Ni cubes/Ag (8:1)	7 ± 1	3.5 ± 1	46	54	1.13

**Figure 3.** Schema of nucleation site, HRTEM image, and FFT of the selected area of Ni nanocube with Ag dots (A) and Ni nanopyramid with Ag dots (B).

special sealed vial for microwave reaction (CEM Discover) and heated at 170 °C (run time 20 min, hold time 2 or 30 min). The dispersion is centrifuged three times at 4000 rpm for 10 min to separate the solid product. The black solid is redispersed in toluene.

Synthesis of Ni/Ag Nanocrystals. A solution of Ag-oleylamine complex is prepared by dissolving AgNO_3 (4.5×10^{-5} mol) in an excess of oleylamine (2 mL). The solution is added to the Ni nanoparticles dispersion dropwise under giving a stoichiometry of 2:1 between Ni and Ag. The colloidal dispersion is stirred overnight at room temperature and turns dark yellowish. Afterward, the solution is heated at 80 °C for 2 h. A small volume (~ 1 mL) of methanol and toluene is added to the dark yellow dispersion to help precipitation; the dispersion is then centrifuged at 4000 rpm for 10 min and redispersed in toluene/methanol 3/1. This process is repeated three times to separate a dark brown solid product. Finally, the dark yellow dispersion is obtained by dispersing the solid in 2 mL toluene. The same procedure yields 8/1 Ni/Ag nanocrystals by simply adjusting the stoichiometry of AgNO_3 (1.1×10^{-5} mol).

Characterization. The structure of the NPs is investigated by transmission electron microscopes (TEM): FEI Tecnai-12 at 120 kV and JEOL JEM-2100 (LaB6) at 200 kV for high resolution imaging (HRTEM). Fourier transform analysis (FFT) of high-resolution images technique was used for structural analysis. High Resolution Transmission Electron Microscopy (HRTEM) images together with energy dispersive X-ray spectroscopy (EDS) were obtained by a JEOL JEM-2100F Field Emission Electron Microscope operated at 200 kV.

X-ray Diffractograms are collected on a Rigaku Smartlab X-ray Diffractometer. Ni/Ag nanocrystals are drop-cast on a glass slide. Magnetic properties are measured using a Superconducting Quantum Interference Design (SQUID) magnetometer MPMS

XL7, in the range of temperature 2–300 K and of field 0–5 T. The temperature-dependent susceptibility was measured using Direct Current (DC) mode. The samples are cooled to 2K under zero magnetic field, low magnetic field (5.0 mT) was applied and data collected from 2 to 300 K (zero-field cooled, ZFC). Field Cooled (FC) measurements were performed from 2 to 300 K with an applied field during the cooling. Hysteresis loop was measured at 2 K. optical properties are measured using Cary 100, Digital UV–visible absorption spectrometer, in the range 190–900 nm.

RESULTS

After purification by repeated centrifugations and dispersion in toluene, the thermal decomposition of $\text{Ni}(\text{COD})_2$ in hexadecylamine under microwave irradiation yields Ni NPs with polyhedral shapes. Cubes and pyramids are the most frequent shapes, as previously reported.²² The highest ratio between cubes and pyramids is obtained after only 2 min of irradiation with 4/1 ratio between cubes and pyramids (Figure 1A). While reaction time is increased from 2 to 30 min, the amount of the pyramidal particles increases with a ratio of 3/2 (cubes/pyramids) (Figure 1B). The nanocrystals display a face-centered cubic (FCC) phase with lattice parameters corresponding to bulk Ni ($Fm\bar{3}m$, $a = 3.52$ Å, JCPDS-04-0850) as shown from electron diffraction (inset Figure 1A). Nevertheless, an HRTEM study shows that the pyramidal nanoparticles crystallize in the HCP phase.²²

The Ag seeds nucleate on Ni through a nonaqueous galvanic displacement of Ni by Ag(I) at room temperature, followed by the overgrowth of Ag at 80 °C. The silver source forms a complex with oleylamine by in situ mixing of oleylamine with AgNO_3 in a 1/1 ratio. The Ag(I)oleylamine complex is soluble in toluene and stable for days, no Ag nucleation could be observed optically or

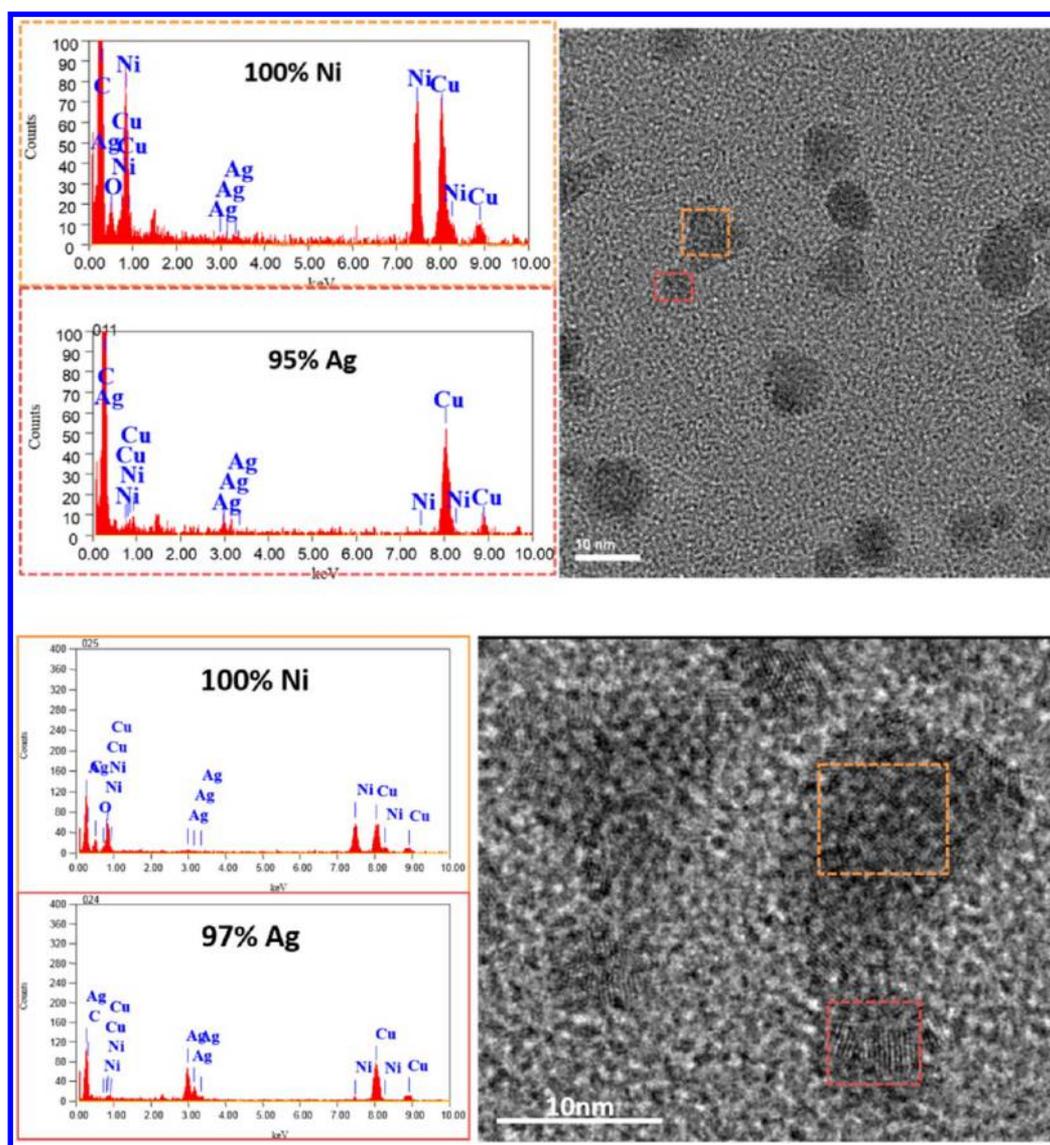


Figure 4. HRTEM images and corresponding EDS spectra recorded from the Ni nanoparticles (orange square) and on the silver tip (red square) on the vertex on two different areas.

by observation in TEM (not shown). The Ag(I)oleylamine is added dropwise to the Ni colloidal dispersion and stirred overnight at room temperature in inert atmosphere. The dispersion results in the nucleation of Ag(0) on the Ni NCs (Figure 2A), as noticed from the dark yellowish color of the dispersion. In a final step, the dispersion is heated at 80 °C for 2 h to complete the overgrowth reaction (Figure 2B). Figure 2 shows TEM images of Ni/Ag nanoparticles obtained for different atomic ratio between Ni and Ag(I) complex, namely 2/1 (Figure 2A,B) and 8/1 (Figure 2C,D). The atomic ratio between the two metals has been quantified by ICP-AES and EDX measurements, the atomic ratio is fully consistent with the initial stoichiometry of the reagents (Ni/Ag = 2/1 or 8/1). The reaction does not modify the overall shape of the nanocrystals, cubes or triangles. The TEM reveals the formation of hemispherical particles on the vertices and the edges of the pristine particles, together with the occurrence of individual spherical nanoparticles with a diameter below 3 nm. The electron diffraction (Figure 2B inset) shows the formation of a face-centered cubic (FCC) Ag ($Fm\bar{3}m$, $a = 4.090$ Å, JCPDS 04-0783) together with face-centered cubic (FCC) Ni ($Fm\bar{3}m$, $a = 3.52$ Å).

The nucleation of Ag occurs during the room temperature GRR step before the heating step (Figure 2A). During this reaction, Ag nucleates on the vertices and the edges of Ni nanocrystals to form 2.5 ± 1 nm Ag dots (Ni/Ag ratio 2/1). Ag grows during the heating step at 80 °C up to 3.5 ± 1.5 nm. After decreasing the Ag(I) concentration (Ni/Ag: 8/1), Ag presents the same particle size but fewer Ag dots per Ni particles are formed. An average of one Ag dot/Ni particle has been counted from the TEM images (2 dots for Ni/Ag: 2/1 ratio). The Ag(I) concentration increases the number of nucleation sites without influencing the dots size.

Ag nucleates preferentially on vertices of pyramidal Ni (95%, see Table 1) for both Ag concentrations, while cubic particles lead to two nucleation sites with equal probability of nucleation on the vertices and on the edges. The statistical analysis of TEM images is summarized in Table 1.

The bimetallic nanocrystals are characterized by high-resolution transmission electron microscopy (HRTEM) (Figures 3 and 4). For both shapes, the particles present the same average number of Ag dots per Ni particle for each Ni/Ag ratio (Table 1). The cubic shape NCs display {111} planes of FCC Ni

crystal lattice and {111} planes of a face-centered cubic (FCC) Ag ($Fm\bar{3}m$, $a = 4.090 \text{ \AA}$) (Figure 3A). The same results are obtained for the two atomic ratios.

The pyramidal shape nanocrystal consists of hexagonal closed packed (hcp) Ni (Figure 3B). The fast Fourier transform (FFT) of the image shows the occurrence of {002} lattice planes corresponding to hcp Ni ($P63/mmc$, $a = 2.622 \text{ \AA}$, $c = 4.321 \text{ \AA}$). The hemispherical tip formed on the vertex of the pyramid is a single-crystal of FCC silver as observed from the FFT corresponding to {111} lattice plane of a FCC Ag crystal lattice. No oxide phase has been noticed.

EDAX analyses are performed on single particle using the nanobeam mode to monitor the metallic interdiffusion (Figure 4). The spectra recorded on the cubic or pyramidal shapes (orange square) show exclusively the K line of Ni at 7.47 keV (apart from the Cu and C lines from the TEM grid), whereas the spectra recorded on the tips on the vertices or edges show almost exclusively the L line of Ag at 2.98 keV with weak Ni K lines (red square on Figure 4). The presence of weak Ni signal is due to small drift of the sample resulting in the exposure of the electron beam to the Ni shape. The EDAX spectrum also shows the presence of oxygen only on the Ni particle and not on the Ag tip. The presence of an oxide is expected from the GRR mechanism but has not been revealed by diffraction techniques.

Nanobeam has been used on several nanocrystals, and all the results are consistent with the formation of pure Ag nanocrystal without any noticeable interdiffusion process within the accuracy of EDAX measurement. Those microscopic analytical results give convincing proof for the growth of pure Ag tips on Ni nanocrystals.

The XRD pattern of the Ni/Ag nanocrystals has been collected for two different stoichiometric ratios (Figure 5). The XRD

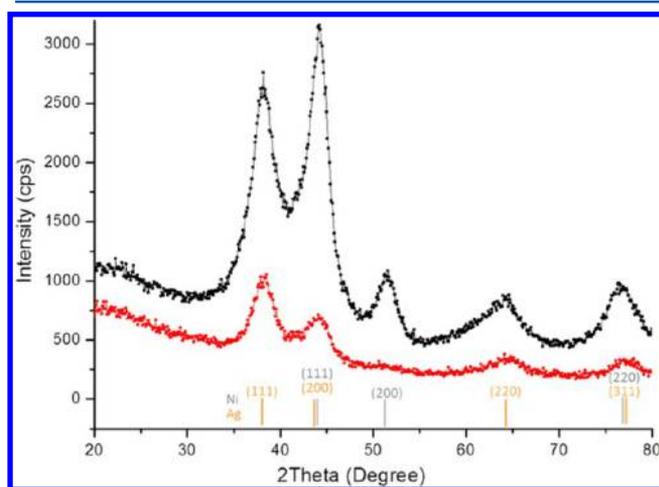


Figure 5. XRD pattern for Ni/Ag nanocrystals with two atomic ratios: 8/1 (Black curve) and 2/1 (red curve).

pattern of the Ni/Ag nanocrystals is typical of two different phases corresponding to FCC Ni and Ag. All peaks are widely broadened by the disorder of such small nanocrystals, and the overall width of the peak is fully consistent with sub-10 nm nanocrystals. While the XRD pattern clearly reveals two phases for the 8:1 ratio between Ni and Ag. The XRD of 2:1 ratio corresponds almost exclusively to FCC Ag with very broad Ni peaks. No oxide phase can be noticed on the patterns while EDAX reveals its presence, leading us to conclude on the amorphous character of the oxide.

Magnetic properties of Ni/Ag nanocrystals are measured for the two ratios (Figure 6 and Table 2). We have measured both the temperature and magnetic field dependence of the two Ni/Ag atomic ratios in a SQUID magnetometer. For the Zero Field Cooled (ZFC) measurement, the sample is cooled down to 2 K without external magnetic field and for the field cooled (FC) measurement the sample is cooled to 2 K in a constant external magnetic field of 5.0 mT, then the magnetization is measured at 5.0 mT while increasing the temperature (Figure 6A). The ZFC/FC curves display a very rare characteristic with two maxima found on the ZFC. The absolute maximum corresponds to a blocking temperature (T_B) of 32 K and 37 K, respectively, for Ni/Ag 2:1 and 8:1 ratio. Since the blocking temperature depends mainly on the magnetic volume of the NC and its magnetic anisotropy, the low blocking temperature observed for 2:1 ratio reveals a smaller magnetic size and/or a lower anisotropy. As already observed from XRD, crystalline Ni reacts with Ag in the GRR step leading to a disordered phase with a nickel oxide shell. Such a reaction should decrease both magnetic size and magnetocrystalline anisotropy. The second maximum is observed at the same temperature of 10 K for the two samples and origins from the reaction with silver. Nevertheless, the exact nature of the second maximum is still a matter of investigation as it could be attributed to Ni/Ag interface, NiO/Ag interface or Ag tips.

Figure 6B shows the hysteresis loops measured at 4 K. In both cases, the nanocrystals exhibit a ferromagnetic behavior with a symmetric coercive field of 180 mT for the 2:1 ratio and an asymmetric loop with an average coercive field of 70 mT for the 8:1 ratio. Pristine Ni nanocubes display a ferromagnetic behavior at low temperature with a coercive field of 152 mT, nearly 10 times higher than the bulk value of 17 mT and nearly 4 times higher than the spherical NPs of equivalent size.²² The saturation magnetization for the 8:1 ratio of Ni/Ag nanocrystals is $86 \text{ Am}^2\text{kg}_{\text{Ni}}^{-1}$ and for the 2:1 ratio is $55 \text{ Am}^2\text{kg}_{\text{Ni}}^{-1}$. Bimetallic nanocrystals display higher magnetic moment than the corresponding pristine Ni nanocrystals $44 \text{ Am}^2\text{kg}_{\text{Ni}}^{-1}$, while the bulk value is $58 \text{ Am}^2\text{kg}^{-1}$.

The UV-vis absorption spectrum of Ni/Ag nanocrystals is given in Figure 7. Spherical particles of colloidal silver coated by oleylamine and dispersed in toluene display a plasmon resonance at $\lambda_{\text{max}} = 410 \text{ nm}$.²⁴ The same volume fraction of particles in toluene is used for all the optical measurements. Ni/Ag (8/1 ratio) displays an absorption at $\lambda_{\text{max}} = 433 \text{ nm}$. When a higher amount of Ag (2:1 ratio) is reacted on Ni nanoparticles, the band is sharper and blue-shifted to $\lambda_{\text{max}} = 423 \text{ nm}$. The dispersion is dark yellowish, and the yellow color is more intense for the higher content of Ag. The larger intensity of plasmon resonance probably results from the increase in Ag particles frequency (Table 1).

DISCUSSION

Nickel and silver do not form any alloy according to the bulk phase diagram, and their crystallographic bulk lattice parameter mismatch is as large as 14% (FCC structure for Ni), while Ni can also crystallize in HCP polymorph in pyramidal, elongated or multipods particles.²⁵ In the literature, a single example of epitaxial growth has been demonstrated for Au@Ni with similar lattice mismatch,²⁶ while growth of CdSe on Ni nanocubes with a smaller lattice mismatch (3.9%) is governed by the formation of a strong Ni–Se bond.²⁷ XRD and EDAX measurements on the nanocrystals show the occurrence of two monometallic phases without interdiffusion. This result is also evidenced by the

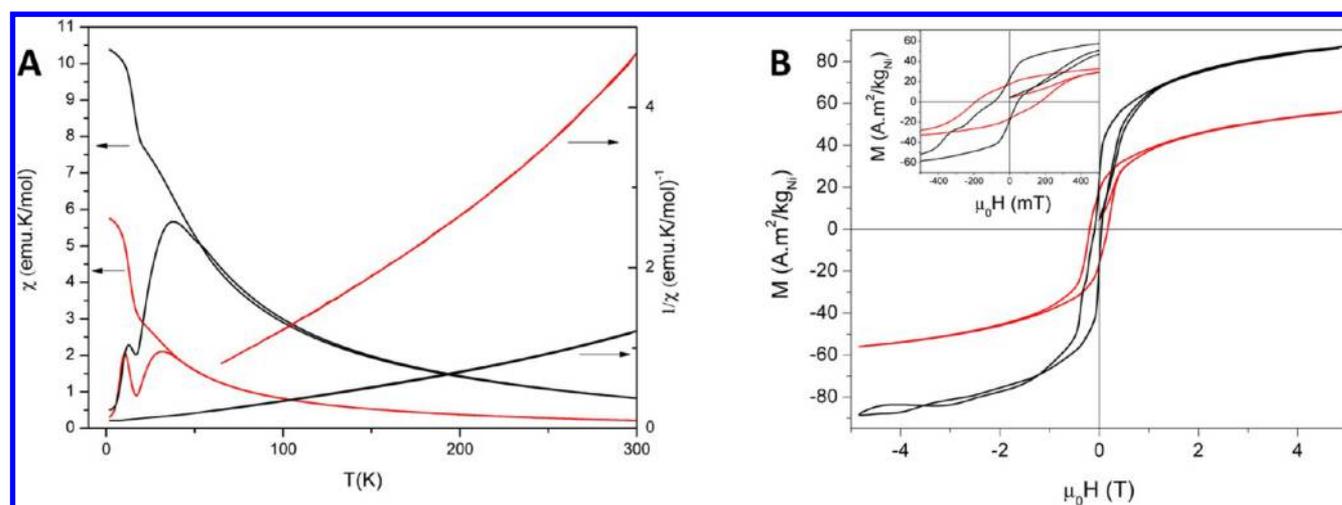


Figure 6. Magnetic measurements of Ni/Ag nanocrystals with 8:1 ratio (black curve) and 2:1 ratio (red curve): magnetic susceptibility during Zero Field Cooled/Field Cooled (ZFC/FC) with an applied field of 5.0 mT (A); Hysteresis curves measured at 4 K and inset of the low field feature (B).

Table 2. Optical and Magnetic Data of the Samples

sample	λ_{\max} (nm)	magnetic moment ($\text{A}\cdot\text{m}^2/\text{kg}_{\text{Ni}}$)	coercive field (H_C)	T_{Blocking} (K)
bulk Ni		58	17	
Ni/Ag (8:1)	433	86	70	10; 37
Ni/Ag (2:1)	423	55	180	10; 32

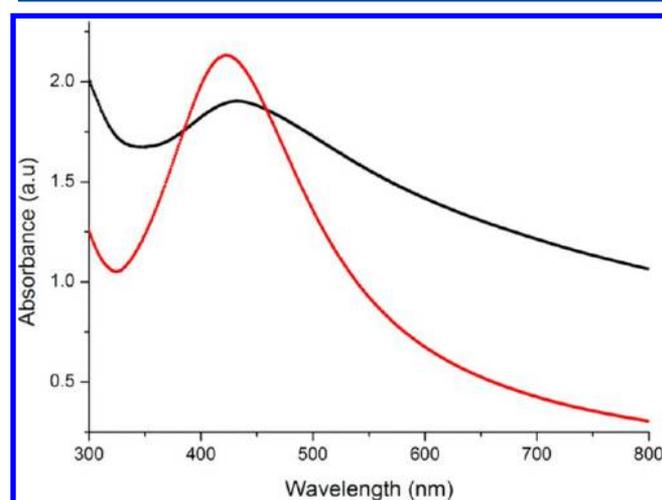


Figure 7. UV-vis absorption spectra of Ni/Ag nanocrystals with a stoichiometry of 8/1 (black curve) and 2/1 (red curve).

electronic properties typical of Ag plasmon resonance and the high magnetic moment which will be discussed below.

Before further discussion, we shall briefly expose a reasonable reaction mechanism for the reaction. As shown from the conservation of the atomic ratio, the reduction of Ag does not lead to substantial Ni leaching out of the particle. The conservation of Ni is also demonstrated by the invariance of the mean size of Ni NCs. However, XRD clearly reveals the vanishing of Ni FCC phase upon reaction with Ag (2:1 ratio). Since a GRR reaction should yield Ni(II) species, NiO seems to be the most relevant product to consider. The presence of Bronsted base in the medium (alkylamine) is also in favor of NiO formation. The GRR reaction is the dominant reaction at room temperature during the first step of the reaction, resulting in 2.5 nm Ag tips selectively on Ni. The second step at 80 °C is an

overgrowth on the Ag tips which display a size increase to 3.5 nm (Table 1).

The growth of Ag nanoparticles on the nickel surface begins with the galvanic displacement of Ni(0) surface metal atoms by Ag(I) complexes. This spontaneous reaction occurs due to three main conditions: Ni atoms are metallic on the surface, surface ligands are labile, Ag(I) complexes can adsorb and react on Ni. Although these conditions are usually matched in aqueous medium, organic solvent implies the use of ligands/surfactants and soluble Ag complexes while Ni metallic surface should be freshly synthesized since further etching, mainly promoted by aqueous species, does not apply in a conventional manner. Herein, the synthesis benefits from the organometallic Ni precursor which keeps the surface metallic. The long chain amines, used as ligands, are also well-known for their equilibrium with free species,^{28,29} leading to available reducing surface state (Ni metal atoms) for the oxidative addition of Ag(I).

As pointed in the introduction, GRR reaction has already been observed for several metals and leads to the formation of a core/shell, hollow, or Janus geometry. The present study reports a rare case where the pristine nanocrystals are nicely faceted and the nucleation and overgrowth occur on specific locations of the nanocrystal surface.

The reaction is mainly governed by the chemical potential of Ni on the surface and the dynamic exchange of amine ligands to provide reaction sites. The first factor, thermodynamic by nature, varies with the exposed crystallographic facet and the defects density. The vertices and edges are therefore highly reactive, followed by the 200 facets and the 111 ones. As observed from TEM, the silver nucleates almost exclusively (95%) on the vertices of the pyramidal particles while this case accounts for 53% of the cubes (Table 1).

The second aspect drives the nucleation on vertices and edges: these surfaces display a depletion of ligand density due to the loose packing and steric hindrance. Therefore, the rapid exchange of amine ligands with free ligands available from the solution

(oleylamine) promotes the Ni reactivity and the galvanic displacement. Oleylamine ligand can even be considered as a transfer agent for Ag(I) from the solution to the nanocrystal surface. A similar result has been observed for tip induced growth of Au on Co nanorods.³⁰

Tip enhanced GRR growth of Ag occurs in highly defective surface states. HRTEM study of pristine Ni nanocrystals has shown the single crystalline character. In the bimetallic nanocrystal, Ag single crystals grow on top of Ni without a clear relationship between the two lattices. Ag does not grow epitaxially at the Ni/Ag interface on pyramidal or cubic shapes. The large lattice mismatch and very small interface can explain this growth habit together with the presence of ligands. The long chain amines decreases the surface energy of the two metals and induces the formation of quasi-spherical Ag particles as already observed during the aging of Cu@Ag nanoparticles.³¹

The particles exhibit interesting electronic properties with an intense plasmon resonance observed for all samples. The particles display a superparamagnetic behavior with a large magnetic moment at low temperature: $86 \text{ Am}^2/g_{\text{Ni}}$ for 8/1 atomic ratio compared to $58 \text{ Am}^2/g_{\text{Ni}}$ for bulk Ni (Table 2). The magnetic moment decreases with a further increase of Ag ($55 \text{ Am}^2/g_{\text{Ni}}$ for 2/1 ratio). The temperature dependence of the susceptibility remains very close to the pristine Ni behavior above 20 K. Below this temperature, the zero-field cooled curve shows a second maximum related to a new magnetic phase. Ag, as most of the 4d or 5d metals, is known to be magnetically polarizable as a result of a slight change in the lattice parameter or at the interface with a ferromagnetic metal, besides the well-known case of 3d-5d alloys like FePt.³² This induced magnetization has been observed for Ru,³³ Rh,³⁴ and Au in colloidal nanocrystals³⁵ or calculated for very small clusters of Au or Ag.³⁶ The increase in magnetization observed on the Ni/Ag samples cannot be explained by the presence of a NiO shell which should decrease the magnetization. Therefore, the most plausible explanation lies in the magnetic polarization of Ag which would be promoted by the small size of Ag tips together with the interface of ferromagnetic Ni, as already observed on Pt in Ni/Pt multilayers.³⁷ In the present case, the effect is particularly large with 48% increase of the magnetic moment at low temperature. The origin of this phenomenon is under investigation.

CONCLUSIONS

We have investigated the tip-enhanced growth of Ag nanocrystals on pyramidal and cubic Ni nanocrystals synthesized from organometallic route. The nonaqueous galvanic displacement leads to the selective nucleation on the tips of the Ni nanocrystals as a result of the metallic surface of pristine Ni nanocrystals, the use of soft alkylamine ligands and the slow kinetics of the nonaqueous GRR. The bimetallic nanocrystals retain their initial shape with the formation of crystalline Ag almost exclusively on the vertices of the pyramids while Ag tips equally nucleate on the vertices and edges of Ni cubes. The two metals do not interdiffuse and Ag tips display a strong plasmon resonance. The bimetallic particles exhibit very high magnetic moment with a maximum spontaneous magnetization almost 50% above Ni bulk value suggesting the magnetic polarization of Ni/Ag interface.

AUTHOR INFORMATION

Corresponding Author

*E-mail: david.zitoun@biu.ac.il

Notes

The authors declare no competing financial interest.

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