Study on oxidation layer of size controlled Nickel nanoparticles

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Abstract

Research on morphology and structure of oxidation layer of Ni nanoparticles (NPs) is reported. Ni NPs were obtained by wet chemical solution method and their size controlled in the nickel nucleation step using a non-ionic surfactant. Particles were about 50nm in size and polycrystalline. Combining high-angle annular dark field (HAADF) and electron energy loss spectroscopy (EELS), the nickel oxide layer was identified as not continuous and with non homogenous thickness.

1. Introduction

Nanosized particles of ferromagnetic metals such as Fe, Co, and Ni are the focus of growing interest because of both the richness of their physical properties, and potential applications like catalysts, high density magnetic recording media, ferrofluids, and medical diagnostics [1]. Using magnetic nanobeads, magnetic separation of organic compounds, proteins, nucleic acids and other biomolecules and cells from complex reaction mixtures is becoming the most suitable solution for large production in bioindustrial purification and extraction processes [2-5].

Isolated Ni nanoparticles can be obtained by evaporation, and other techniques like sputtering, high energy ball milling, ion exchange,etc [6]. Most of the scientific studies converge on liquid-phase synthesis of the Ni nanoparticles [7]. The preparation of Ni nanoparticles exhibits two principal problems: the control of the size of the nanoparticles and the oxidation of their surface. The control of the average size of the

nanoparticles depends strongly on the parameters of the preparation method. However, because of the very high surface area to volume ratio, the nanoparticles have a high reactivity and can be easily environmentally degraded [6, 7]. This usually results in nanoparticles with a core-shell morphology where an antiferromagnetic oxide layer surrounds the ferromagnetic nanoparticles, which can yield misleading conclusions from the magnetic data.

In this work, Ni nanoparticles with diameters ranging from 45 to 55 nm were synthesized by conventional solution reduction process. The size control of the nanoparticles was allowed by the addition of a non-ionic surfactant as a surface agent. To avoid the magnetic aggregation, and assure monodispersed nickel nanoparticles, the Ni nanoparticles were surfacted in citric acid. The obtained nanoparticles were characterized by SEM. Citric acid was removed to observe shape and size of nickel oxidated NPs with High Resolution Transmission Electron Microscopy (HRTEM). The high-angle annular dark field (HAADF) combined with the electron energy loss were used to determine the morphology and structure of oxidation layer [8].

2. Materials and methods

2.1. Synthesis of controlled size Nickel Nanoparticles

Single core Nickel nanobeads were prepared by mixing hydrazine monohydrate (N_2H_4-H_2O) 2M, nickel (II) chloride hexahydrate ($NiCl_2.6H_2O$) 0.2M, and sodium hydroxide (NaOH) 8M in the molar proportion of 5:1:32. The pH value was about 11. The resulting solution was kept at 60ºC during one hour until a black powder was completed precipitated. Finally, the product was washed with distilled water and ethanol for several times, and then dried in a vacuum drying oven at room temperature. In order to control the size distribution of the nickel nanoparticles, the non-ionic surfactant triton Tx-100, was introduced in the reaction mixture at a molar concentration below its critical micelles concentration (CMC) and at a [Ni]/[Tx-100] molar ratio of 5 [7].

Citric Acid (CA) was used to stabilize the magnetic NPs, according to the method proposed by Campelj et al [9]. Approximately 3g of NPs were mixed with 65 mL of an aqueous solution of 2% CA (0.02 $mg \cdot mL^{-1}$). The pH value of the mixture was adjusted to 5 and then was raised to 10 using concentrated ammonia. The adsorption step of the CA was maintained at 80ºC and rigorously stirred for 60 min. The prepared suspension

was washed with distilled water and magnetically separated for several times to remove the excess of CA.

2.2 Characterization Methods

Scanning electron microscopy (SEM) imaging was performed with a FEI Nova 200 (FEG/SEM). TEM-EELS measurements were carried out using a JEOL 2010F field emission gun (S)TEM, working at 200 kV with GIF spectrometer.

3. Results and discussion

3. 1. Influence of synthesis parameters on the size of nickel nanoparticles

In the classical model of LaMer and Dinegar, the process of synthesizing monodispersed particles occurs in two steps: (I) nucleation and (II) growth [4]. These two steps depend on the reactants and the parameters controlling the reaction. When nickel is added to hydrazine, a complex is formed. This complex is irreversibly reduced to metal by the addition of sodium hydroxide that catalyses the reduction action of hydrazine [7].

The reaction mechanism includes the formation of nickel hydroxide nanoparticles that upon dissolution, reduction, nucleation and growth result in Nickel NPs. The size of the formed NPs strongly depends on collision and coalescence rates of nickel nucleus during nucleation step. To achieve a better control of the size of the nanoparticles, the non-ionic surfactant Tx-100 (Triton) was chosen to prepare Ni nanoparticles. The polar heads of X-100 (Triton) adsorbed on Ni NPs can form a protective layer and act as inhibitor, which is in favour of the formation of the spherical NPs with homogeneous size. As shown in figure 1, the size of the Ni NPs were successfully controlled and homogeneous distribution of about 50 nm diameter size of the nanoparticles was obtained.

3. 2. Structural and morphological Characterization

The nanoparticles were found by HRTEM (figure 2) observations to effectively be about 50nm in size. The obtained Ni NPs were polycrystalline.

The presence of nickel oxide superficial layer was observed on nickel nanoparticles, as can be seen in figure 3, displaying HRTEM images and corresponding FFTs of Ni core

and NiO layer. Nickel oxide was confirmed by the elemental ratio between Ni and O observed in the EEL spectra [9]. The layer of nickel oxide was not continuous and the thickness was not homogenous.

In order to further characterize the NiO layer, EELS experiments were performed. A map of the Ni-NiO distribution in a Ni NP was obtained through multiple linear least-squares (MLLS) fitting of a spectrum image of a nickel nanoparticle, using two previously obtained reference spectra in the Ni and NiO regions of the sample (figure 4). MLLS fitting interprets each individual spectrum in the spectrum image as a linear combination of the reference spectra, and returns the fitting coefficients of this linear combination. The spatial distribution of the fitting coefficients can thus be interpreted as a mapping of the compounds to which the reference spectra correspond.
Spectrum image in figure 4 suggest a wrapping of the Ni interior by the nickel oxide phase.
MLLS analysis of the EELS spectrum image of a NP is given in figure 4. The MMLS fitting makes it possible to distinguish between the nickel core and the nickel oxide layer and confirm that the layer of nickel oxide was not continuous and the thickness was not homogenous

4. Conclusions

Monodispersed single core Ni nanobeads were successfully prepared. Magnetic single domain Ni nanoparticles with controlled size were prepared by using a wet chemical solution method. The control of the Ni nanoparticles size through controlling the nickel nucleation step was allowed using a non-ionic surfactant.
Nickel nanoparticles suffered superficial oxidation during the synthesis. The morphology and structure of nickel oxide layer was successfully studied by means of EELS. The nickel oxide shell was not continuous and the thickness was not homogenous.

5. Acknowledgments

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6. **References**

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7. Figure captions

Figure 1. SEM image of monodispersed nickel nanoparticles.

Figure 2. (a) Transmission electron micrograph of several Ni NPs and (b) High-resolution image of a polycrystalline Ni NP.

Figure 3. High-resolution image of the nickel oxide superficial layer of a Ni NP and corresponding FFTs of NiO and Ni.

Figure 4. (a) HAADF image of several nanoparticles. (b) EEL spectrum image from the indicated nanoparticle in (a). Reference spectra, (c) NiO and (d) Ni. (e) Composition map of the nickel nanoparticles (MLLS fitting of EEL spectrum image using reference spectra).

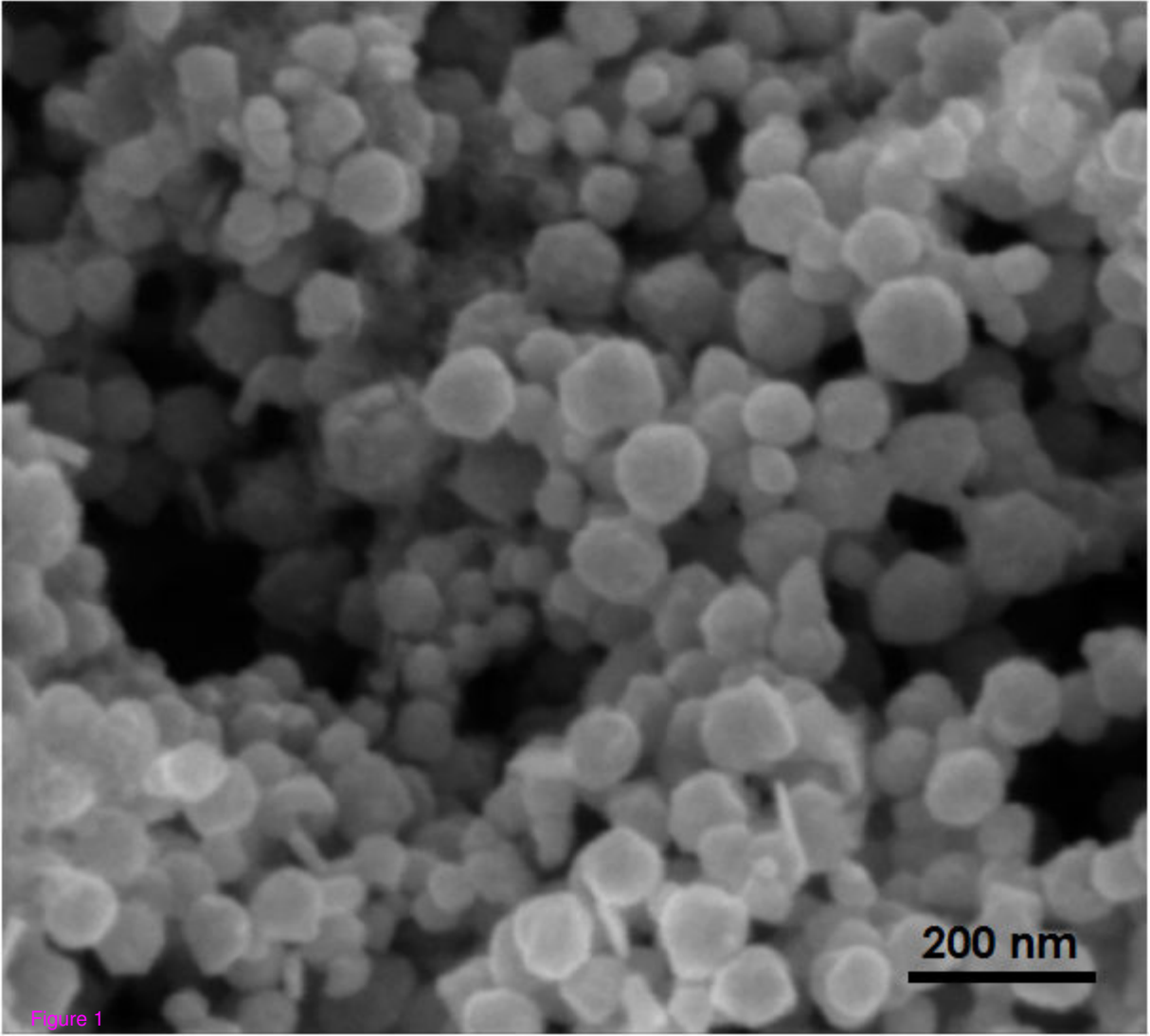


Figure 1

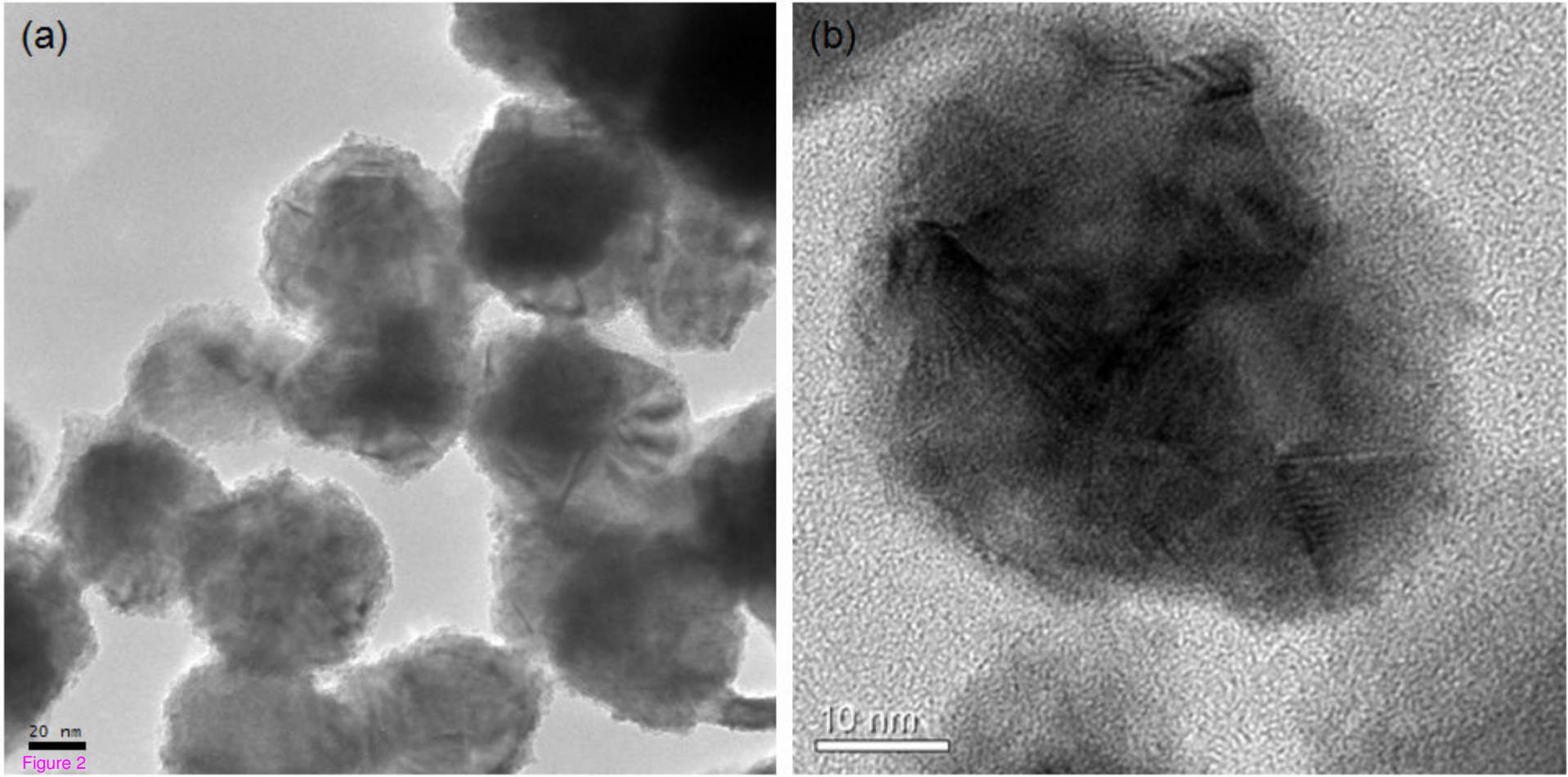
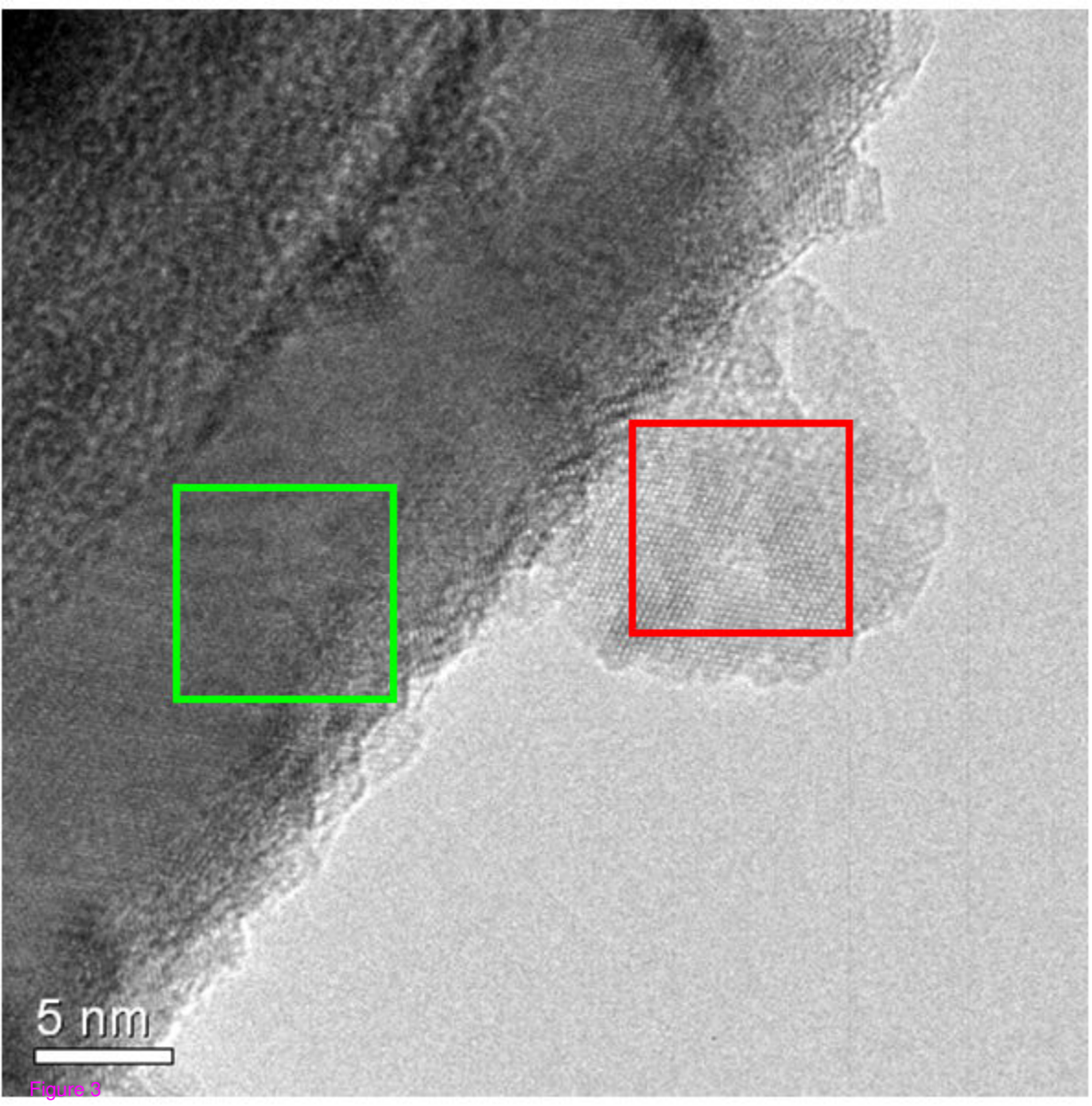
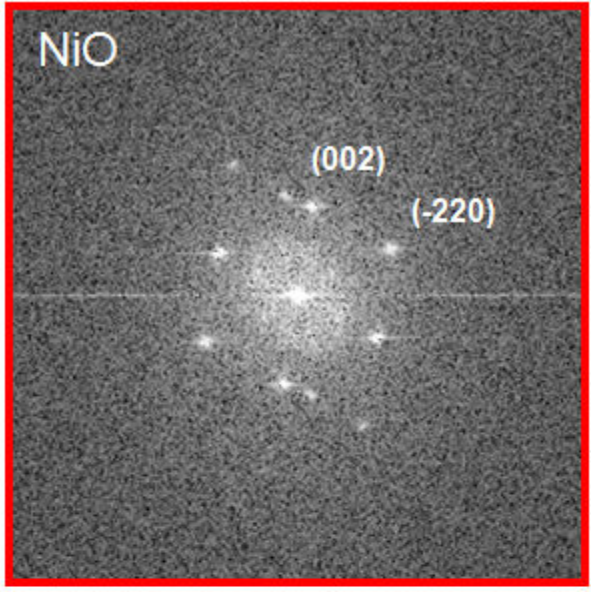


Figure 2





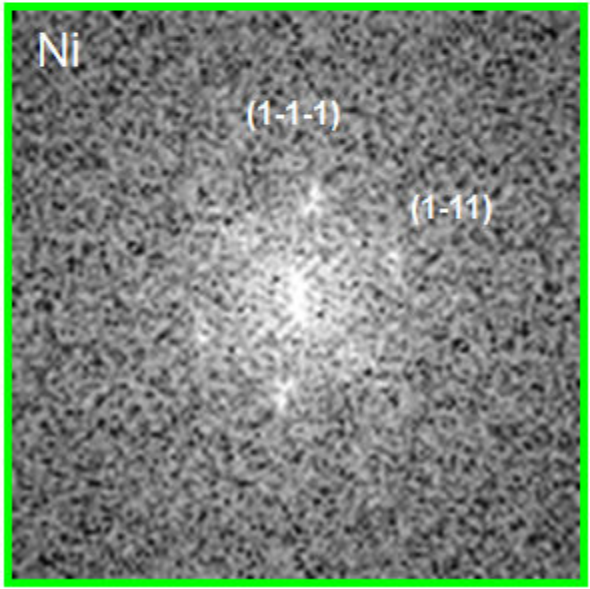


Figura 3

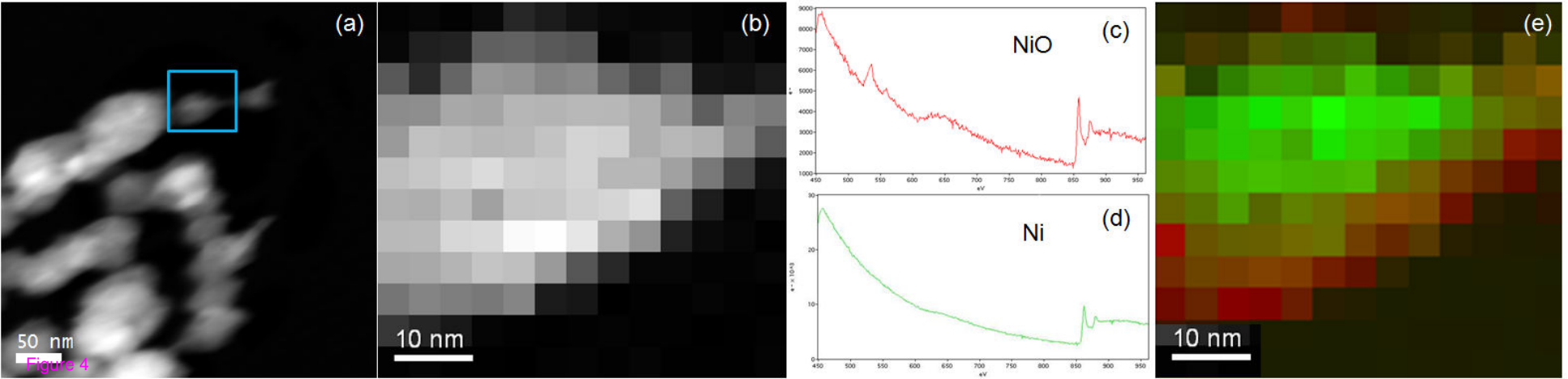


Figure 4