

Surface analysis of nickel nanomaterials electrodeposited on graphite surface

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Pure Nickel (Ni) and Nickel–Palladium (Ni–Pd) alloy were electrodeposited on graphite surface via pulse electrolysis in dimethyl sulfoxide in form of rods and nanoparticles with a diameter of ~100–350 and ~10–35 nm, respectively. X-ray photoelectron spectroscopy (XPS) spectra of Ni 2p_{3/2} region for these nanomaterials suggests on their surface Ni²⁺ precursor while after Ar⁺ ion-etching metallic nickel starts to be dominated. Both Pd⁰ and Pd²⁺ for XPS spectra of Pd 3d_{5/2} and 3d_{3/2} were observed after electrodeposition. Scanning electron microscope-energy dispersive X-ray and XPS analysis confirmed electrodeposition of nickel nanomaterials in non-aqueous electrolyte. Using a lower concentration of Ni²⁺ precursor, nanoparticles with an average particle size of ~10–23 nm were prepared on a graphite surface.

1. Introduction: Nickel (Ni) deposition from an aqueous solution of Ni-salts is very well known during the past 50 years. However today new challenges of nickel preparation arise since its application is in demand for organic-based systems and their size required to be in nanolevel. These issues promote the synthesis of nickel nanomaterials in non-aqueous solutions. It is well known that preparation of nanomaterials very often influences their structure, and hence properties expected for future applications. Therefore, development and understanding of effective methods for their controlled synthesis are required. A promising approach to prepare micro or nanostructured metallic nickel stabilised on substrates is electrochemical deposition which gives a wide range of possibilities for deposits with a certain design (thin film, particles, rods, nets etc.), geometry and even chemical composition. From the technical point of view, pulse electrolysis in aprotic organic solvents might be very convenient [1–5]. Pulse electrolysis is considered as a sort of non-stationary electrodeposition of metals that influences nucleation process and particle growth. The nucleation/growth under pulse period causes depletion of electrolyte layer into metal ions close to the substrate/deposit interface. During the pause, due to diffusion, the ion concentration of deposited metal at the boundary layer becomes equal to that in the bulk of the electrolyte. Consequently, diffusion control is minimised and the formation of particles is operated mainly by the kinetic factor. The efficiency of pulse electrolysis was shown in combination with the medium of organic aprotic solvents, where their molecules are characterised by high electron-donor properties. The reaction environment can be expanded much wider than in water by using a solvent with weak acidity and/or basicity. This is the reason why dipolar aprotic solvents, which are either protophilic or protophobic, are used in a variety of ways in modern chemistry. Large molecules and ions are often difficult to dissolve in water unless they have hydrophilic site(s). Therefore, water is not suitable as a medium for reactions involving large hydrophobic molecules or ions. In contrast, most dipolar aprotic solvents are non-structured or only weakly structured and can dissolve many large hydrophobic molecules and ions. This is another major reason why dipolar aprotic solvents are often used instead of water.

The purpose of the work is to prepare pure Ni and Nickel–Palladium (Ni–Pd) alloy on graphite (G) surface using pulse electrolysis from a solution of NiCl₂ or NiCl₂ with PdCl₂ in

dimethyl sulfoxide (DMSO). Surface analysis of the deposits is made using Scanning electron microscope-energy dispersive X-ray (SEM-EDX) and X-ray photoelectron spectroscopies (XPSs).

2. Experimental

2.1. Electrochemical deposition of pure Ni and Ni–Pd: Pure Ni was deposited in (CH₃)₂SO (99%, Alfa Aesar) solution with 0.1 M NiCl₂ (98%, Sigma Aldrich) at 35°C in a three-electrode thermostated glass electrolyser with a volume of 50 cm³. The solution of 0.05 M Bu₄NClO₄ (99.0%, Sigma Aldrich) in DMSO was used as supporting electrolyte for higher electroconductivity. The surface of G (99.9995%, Alfa Aesar) tablet ($S = 2.9 \times 10^{-4}$ cm²) was used as the working cathode surface. Before every experiment the G surface was mechanically polished using 3; 1 and 0.3 µm microfinishing films. After that, the electrode surface was ultrasonicated with distilled water and *i*PrOH and then dried in argon flow. Prior to electrolysis, the electrode surface was rinsed with DMSO. In this electrochemical system platinum plate ($S = 2.0 \times 10^{-4}$ cm²) was used as a counter electrode. All the experimental potential values were referred to as Ag/AgCl in saturated KCl solution. IPC-Pro-200 potentiostat was used for electrolysis in pulse mode. The potential pulses were arranged in a rectangular shape with a pulse duration of (τ_{on}) 6 and pause period (τ_{off}) of 300 ms as in [4]. On account of applied potential value (–1.5), V versus SCE, 800 pulse cycles were used to predict ~0.004 mA·h amount of electricity. The obtained deposits, being kept on the substrate, were washed sequentially with DMSO and *i*PrOH. Finally, the deposits were dried in argon flow at 40°C.

Using 0.1 M NiCl₂ together with 0.01 M PdCl₂ (99%, Sigma Aldrich) at the same electrochemical deposition procedure, Ni–Pd alloy was prepared. At lower concentration of Ni²⁺ precursor (0.01 M NiCl₂ in DMSO) electrochemical deposition of pure Ni carried out in two steps: (i) 20 ‘pulse cycles’ at –2.6 V versus SCE; and (ii) cycling at –1.3 V versus SCE with different cycle numbers (20, 80 and 160). The working electrodes were kept in the electrolyte when the electrochemical deposition was switched to another potential value. Finally, the G surface of the working electrodes was washed and dried at the same procedure.

2.2. SEM-EDX observation: Morphology and chemical composition of pure Ni and Ni–Pd alloy were studied by EDX spectroscopy

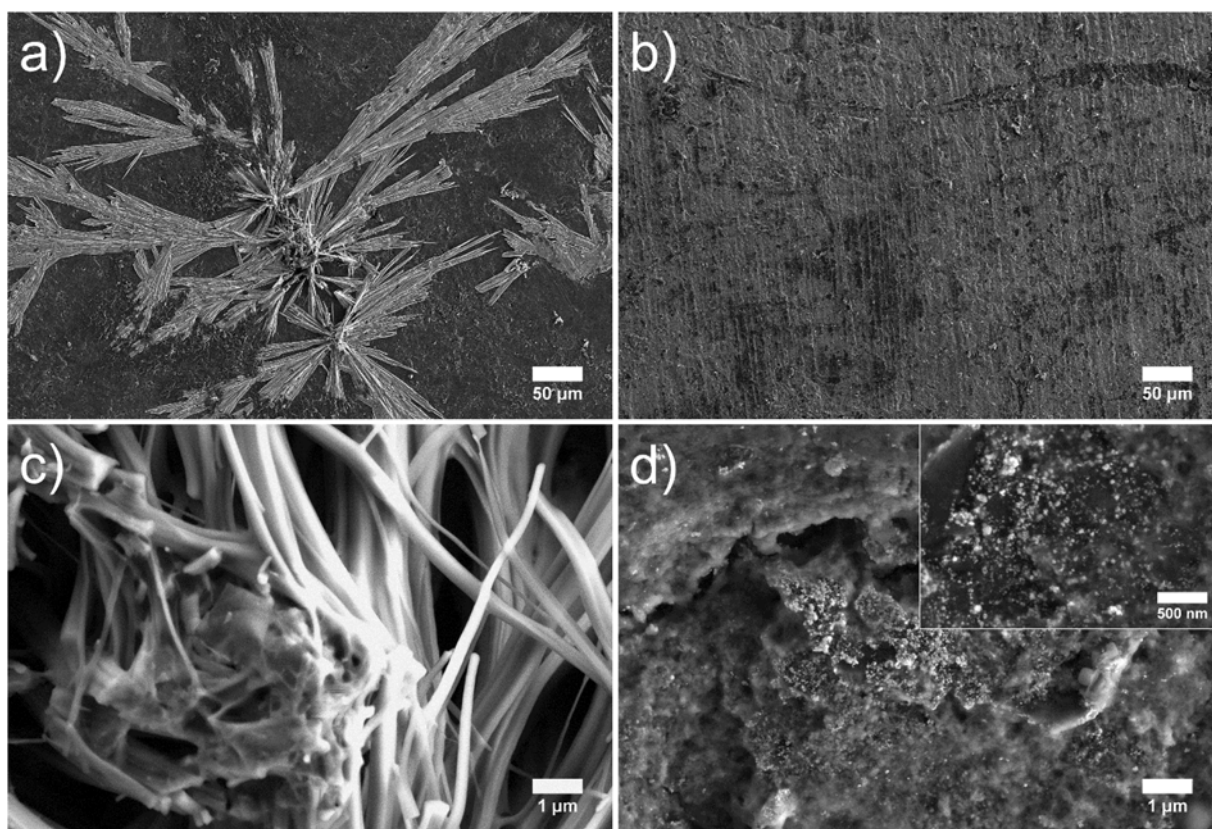


Fig. 1 SEM images

a, c Ni rods showing the formation of dendritic branches

b, d Ni-Pd alloy showing nanoparticles on the graphite surfaces

in a Zeiss Merlin SEM equipped with an X-Max 80 mm² Silicon Drift Detector. The SEM operates with a Schottky Field Emission Gun and a secondary electron detector. The samples were mounted on a standard aluminium stub using bi-adhesive carbon tape. All data were obtained using an acceleration voltage of 5 kV.

2.3. Surface analysis by XPS: XPS was conducted using an Ulvac-Phi Quantera II spectrometer which uses monochromatic Al K α radiation. Energy scale was calibrated against reference samples of Au, Ag and Cu, according to ISO 15472 [6]. XPS spectra of pure Ni and Ni-Pd alloy deposited on G were attained on the sample surfaces as well as after sputter-etching for 1 min using 500 eV Ar⁺ ions to remove ≈ 1 –2 nm of material. The Ar⁺ ion-etched area was $\approx 1 \times 1$ mm and the analysis area had a diameter of ≈ 100 μ m. XPS survey spectra, as well as details of the selected core level were acquired in both cases. Chemical composition was calculated from the survey spectra using standard sensitivity factors, provided by the instrument manufacturer.

3. Results and discussion: SEM observations indicate that pure Ni deposited in form of rods nucleated at a certain point and grew up forming dendrite branches while Ni-Pd alloy resembled aggregates made of nanoparticles (Fig. 1). Nickel dendrites rods are stretched out till ~ 500 μ m, cover G surface in all directions (Fig. 1*a*) and interlaced with each other to form a porous microstructure (Fig. 1*c*). Deposition of Ni-Pd alloy looks like amorphous coating with precursors dissolved in DMSO (Fig. 1*b*) but at higher magnification (Fig. 1*d*) ~ 10 –35 nm nanoparticles, often combined in aggregates, are clearly visible. EDX analysis shows carbon signal from G as well as nickel or nickel and palladium with residual chlorine and sulphur for the pure Ni or Ni-Pd alloy, respectively, (Fig. 2 and 3). SEM-EDX suggests that in both

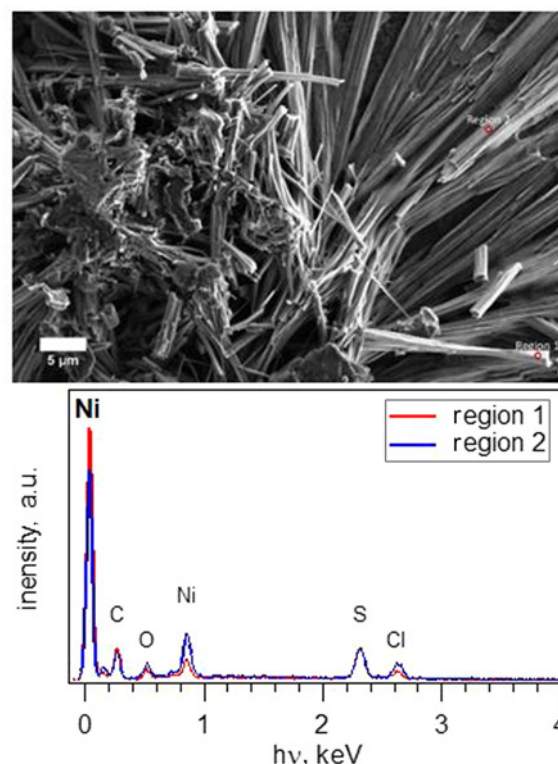


Fig. 2 SEM images with magnification of 5000 and EDX analysis for pure Ni deposited on graphite

Since the nickel nanomaterials yielded ‘micro or nanoislands’ their survey XPS spectra read signal from both G and deposits. Besides the nickel, palladium and carbon peaks, oxygen was the major component identified by XPS (Fig. 4). This fact indicates that after electrodeposition in aprotic organic electrolyte surface of the samples might be easily oxidised in air. Additionally,

Ni rods		
Ni 2p_{3/2}	856.4 eV	853.2 eV

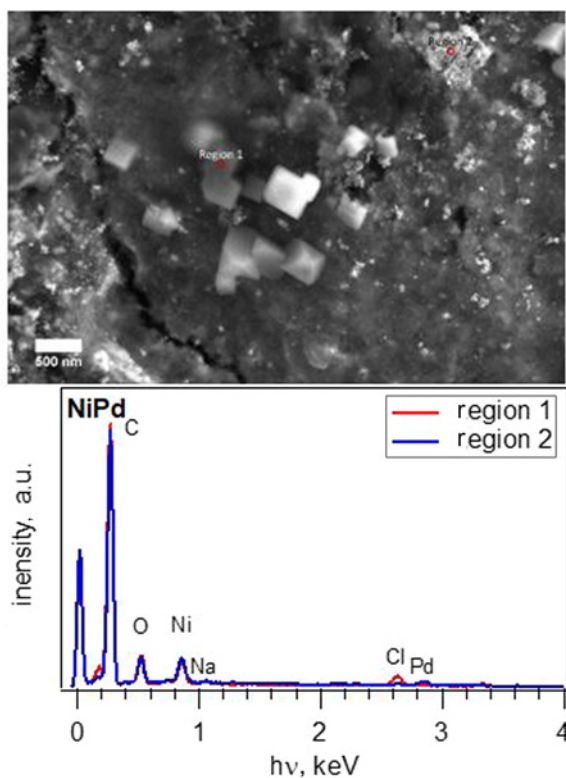


Fig. 3 SEM images with magnification of 50000 and EDX analysis for Ni-Pd alloy deposited on graphite

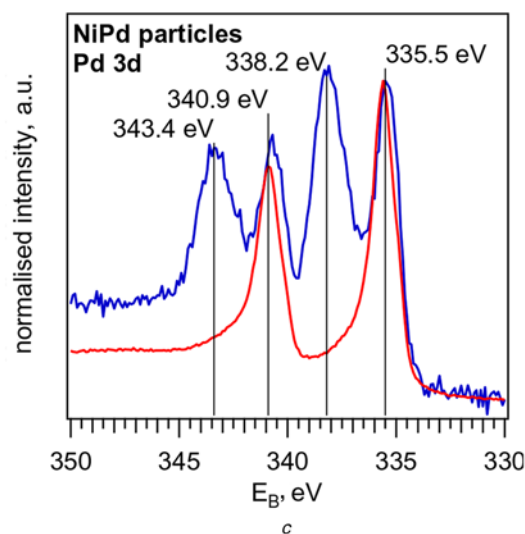
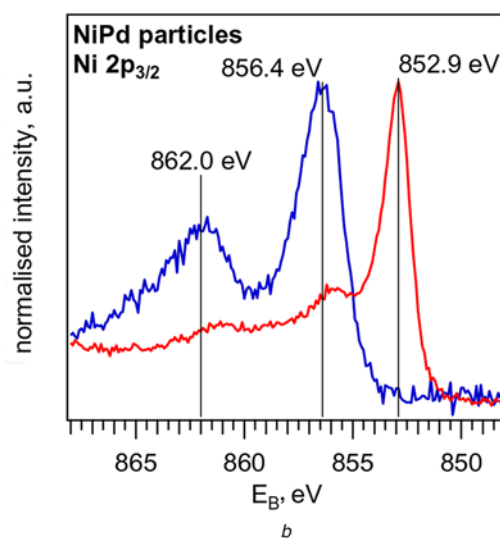
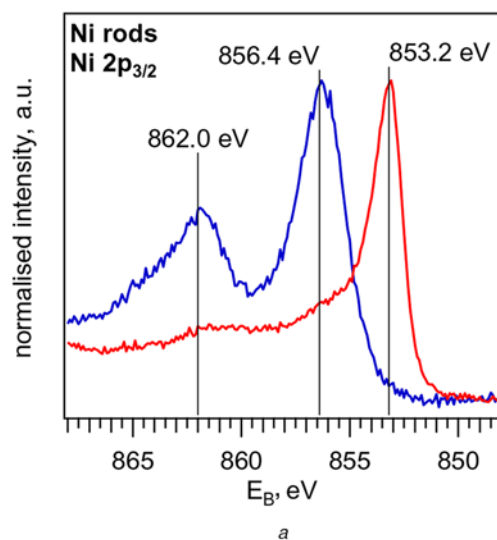


Fig. 5 Photoelectron core level spectra of
a Electrodeposited Ni rods
b, c Ni-Pd alloy nanoparticles of the sample surfaces (blue) and after Ar⁺ ion-etching (red)

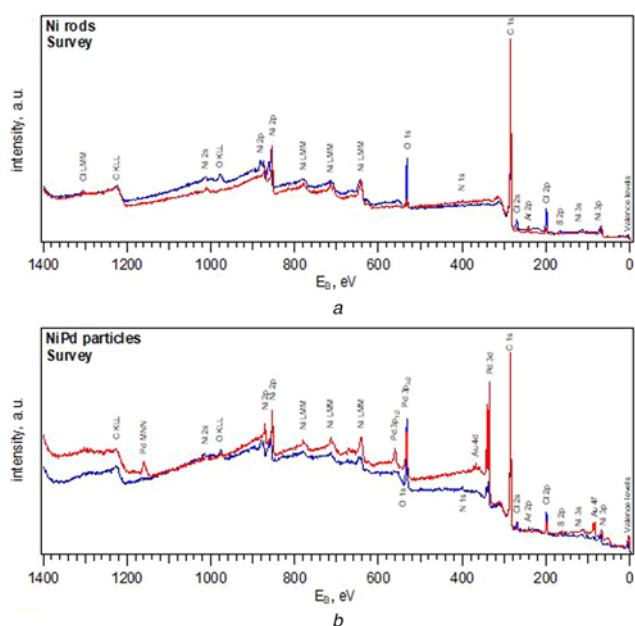


Fig. 4 Survey spectra of the sample surfaces (blue) and after ion-etching (red)

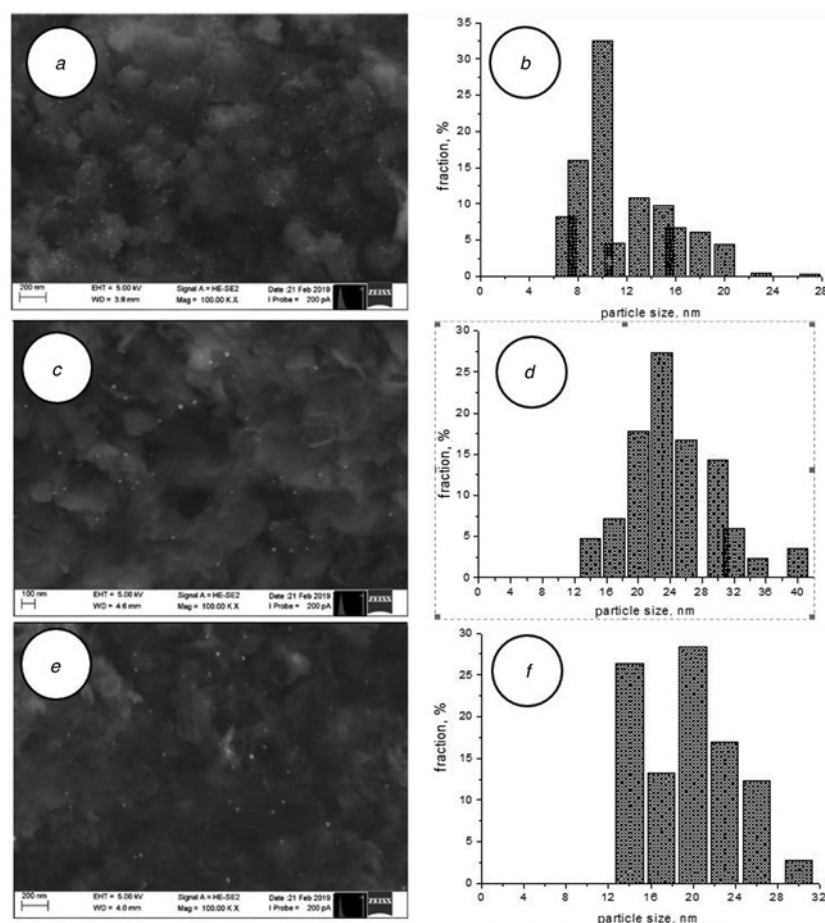


Fig. 6 SEM images for Ni deposits obtained by pulse electrolysis after 20 pulse cycles at -2.6 V vs SCE and after that 20 (a), 80 (b) and 160 (c) pulse cycles at -1.3 V vs SCE. Corresponding fractions of deposited nanoparticles versus their diameter are shown in (d) (e) and (f)

very low XPS signal for Ar is also observed for the Ar^+ ion-etching samples.

Detail XPS spectra of the Ni $2p_{3/2}$ and Pd $3d$ regions are shown in Fig. 5, blue curves for spectra attained at the sample surface after electrodeposition and red curves – after additional Ar^+ ion-etching. The shown Ni $2p$ region only contains one of the spin-orbit-splitting doublets ($2p_{3/2}$), but the Pd $3d$ contains both doublets ($3d_{5/2}$ and $3d_{3/2}$) and thus each chemical surrounding will give two contributions in the region. The Ni $2p$ surface spectra (blue curves Figs. 5a and b) of both samples exhibit the main peak at a binding energy of 856.4 eV, and a satellite XPS peak at 862.0 eV. These contributions could be attributed to Ni_2O_3 [7], or NiCl_2 [8]. The uncommon nature of this oxide suggests that presence of NiCl_2 makes it reasonable to assign these XPS peaks to NiCl_2 precursor. No signature of Ni^0 is observed at the surface after electrodeposition. Also the Pd $3d$ region (blue curve Fig. 5c) of Ni–Pd alloy suggests contributions (at 338.2 and 343.4 eV) of PdCl_2 in the same manner where XPS peak positions match PdO_2 [7] and PdCl_2 [9]. However, in contrast to the Ni $2p$ region, the metallic contribution of Pd^0 (335.5 and 340.9 eV) [7] can be observed clearly. The assignment to chlorides is further strengthened by the concentration as estimated from the survey spectra (Fig. 4), which show that chlorine and metal concentrations are of the same order of magnitude. This suggests a strong physical adsorption of precursor molecules on the rough G surface and even on nickel deposit. XPS spectra were obtained from the sample surface after electrochemical deposition (blue curves), and after Ar^+ ion-etching (red curves).

After Ar^+ ion-etching the metal core levels change significantly (red curves in Fig. 5). Only with minor contributions of NiCl_2 and PdCl_2 both the Ni $2p_{3/2}$ and Pd $3d_{5/2}$ regions are dominated by the Ni^0 (852.9–853.2 eV) and Pd^0 (335.5 and 340.9 eV) signals. The

asymmetric line-shape with continuous tailing towards higher binding energy of these peaks clearly shows the metallic state of nickel and palladium. The XPS peak for Ni $2p_{3/2}$ shows a slight difference in position between the deposited pure Ni (853.2 eV) and Ni–Pd alloy (852.9 eV) (red curves Figs. 5a and b) meaning the difference between Ni metal and its alloy with Pd [10]. At the same time both these experimental values obtained for nickel nanomaterials are slightly shifted (*ca.* +0.5 eV) compared to their corresponding bulk materials [7, 10]. The positive shifts are well known for nanoparticles or low surface coverage metal deposits on carbon or insulating substrates [11–13].

Using one order lower concentration for Ni^{2+} precursor (0.01 M NiCl_2) nanoparticles were prepared on G surface (see supplementary Fig. 6a–c). Calculations indicate appearance of deposits with average particle size of ~ 10 –23 nm (Fig. 6d–f) that was difficult to analyze by EDX. However experimentally it was confirmed that only 20 pulse cycles at -2.6 V vs SCE for cluster nucleation and after that 20 pulse cycles at -1.3 V vs SCE for clusters growth were enough to form particles with average particle size of ~ 10 nm (Fig. 6d). Moreover, higher cycle number for clusters growth resulted in bigger particle size but their particle density was lower (Fig. 6e–f). Similar dependence was recently found for deposition of Pd nanoparticles and explained as a competition between nucleation and growth processes [14].

4. Conclusions: SEM-EDX observation shows Ni rods (diameter ~ 100 –350 nm) and Ni–Pd alloy nanoparticles (diameter ~ 10 –35 nm) prepared on graphite surface via pulse electrolysis in DMSO. XPS spectra of Ni $2p_{3/2}$ region for these nanomaterials suggests on Ni^{2+} species at their surface meaning strong physical adsorption of NiCl_2 molecules on graphite and nickel deposit.

Both Pd⁰ and Pd²⁺ for XPS spectra of Pd 3d_{5/2} and 3d_{3/2} were observed after electrodeposition. After additional Ar⁺ ion-etching, the Ni 2p_{3/2} and Pd 3d_{5/2} regions are dominated by the Ni⁰ (852.9–853.2 eV) and Pd⁰ (335.5 and 340.9 eV) signals and their asymmetric line-shape with continuous tailing towards higher binding energy confirms the metallic state of nickel and palladium. Surface analysis suggests on preparation of pure Ni and Ni–Pd alloy at nanolevel and stronger adsorption of the precursors on nickel deposit than palladium after electrodeposition. Experimentally it was confirmed that only 20 pulse cycles at –2.6 V versus SCE for cluster nucleation and after that 20 pulse cycles at –1.3 V versus SCE for clusters growth were enough to form particles with an average particle size of ~10 nm from 0.01 M NiCl₂ solution in DMSO. The proposed method of nickel nanomaterials preparation might be recommended to fabricate an effective catalyst with a certain shape and size for organic syntheses developed in a non-aqueous medium.

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