

## Communication

# Synthesis of Graphite-Encapsulated Ni Micro- and Nanoparticles Using Liquid-Phase Arc Discharge

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**Abstract:** In this work, the synthesis of nickel particles encapsulated in a few-layer graphene shell was carried out using the method of electric arc discharge in the liquid phase, in various media: deionized water, alcohol, and toluene. Nickel and graphite were used as electrodes. The study was carried out to analyze how various liquids, acting as a cooling medium and a source of carbon, affect the formation of a protective shell around metal particles. Raman studies, analysis of X-ray diffraction data, and scanning electron microscopy confirmed the formation of spherical encapsulated nickel particles in all types of liquid media. It was found out that the use of toluene as a cooling medium increased the number of particles with a graphite shell and allowed obtaining micro- and nanoparticles covered with monolayer graphene. The absence of oxygen in the composition of toluene, in contrast with alcohol and especially water, prevents the oxidation of nickel particles during the synthesis. This fact, along with the initial basic hexagonal carbon structure of toluene, makes it a good medium for the formation of metal particles covered with a protecting graphite shell as a result of arc discharge in the liquid phase.

**Keywords:** micro- and nanoparticles; graphene encapsulation; X-ray diffraction; Raman spectroscopy; scanning electron microscopy



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## 1. Introduction

Since their discovery, catalysts have played a very important role in modern chemical, oil and gas and energy industries. Today, there is a wide range of catalysts known and used in production, including those based on noble metals (Pt, Pd, etc.), which demonstrate the importance of electronic properties for catalytic activity [1,2]. However, with the development of nanotechnology and the emergence of new possibilities for controlling the properties of materials, the issue of the creation of new and modified catalysts with high activity is a very urgent task. One of the ways to modify catalysts is to reduce their size, which leads to an increase in the specific surface area, chemical stability, and activity [3]. Recently, gold nanoparticles have been actively studied as efficient catalysts in oxidation and hydrogenation reactions [4]. As an alternative to nanoscale catalysts based on noble metals (Pt, Pd, Au, etc.), nanocatalysts based on transition metals (Fe, Ni, Co, etc.) are the most preferred as they demonstrate sufficiently high performance characteristics [4]. However, it should be noted that nanoparticles smaller than 100 nm in size are characterized by their increased reactivity, which not only promotes agglomeration [5] but also their reaction with oxygen even at room temperature [6]. One of the solutions to this problem is the stabilization by passivation of spherical metal nanoparticles with various inorganic oxides [7], carbons [8], and porous materials (zeolite, mesoporous silica, and

titanium dioxide) [9], which provides the encapsulated particles with increased stability and reusability, increased selectivity, strong metal–carrier interaction and the possibility of providing tandem catalysis [10]. The listed encapsulation materials have poor electrical conductivity, resulting in limited charge transfer between reactants and catalysts, thereby blocking the catalytic process. Therefore, research work is being actively carried out on the encapsulation of metal particles in various carbon nanostructured materials [11]. Coatings based on graphene are promising candidates for the role of a passivation layer due to their high electron mobility and chemical inertness to oxidizing gases [12]. Considering this fact, today, research is being carried out on the synthesis of metal particles encapsulated in a graphene layer, which are studied in the field of core-coating charge transfer and are used as an active nanocatalyst [13]. It was also shown [14] that three-dimensional graphene structures as encapsulating layers exhibit a large surface area, excellent mechanical strength, and fast heat and electron transfer. Graphene-based hybrid materials increase the rate of recombination of electron–hole pairs and reduce the band gap by adapting the valence and conduction bands, resulting in improved photocatalytic performance [15,16]. The structural characteristics of graphene-encapsulated nanomaterials contribute to a synergistic effect between the materials, improving electrochemical properties, which allows them to be integrated into powerful hybrid materials used in environmental and energy applications [17], as well as noninvasive bioimaging, photodynamic therapy, and the co-delivery of drugs and genes [18]. The work [19] demonstrates that graphene is a new two-dimensional support for the growth, assembly, and nucleation of metal and metal oxide nanoparticles, to create composite materials with fixed, encapsulated, wrapped, layered, and mixed structures. For the industrial production of such hybrid nanoparticles, there is potential for synthesis in solution in comparison with the CVD method [18]. In [20], synthesized highly stable graphene-encapsulated nickel nanoparticles have demonstrated excellent catalytic properties in the methanation reaction. Additionally, in [21], the researchers report the improvements in the magnetic properties of nickel particles encapsulated in a graphene structure, which can be used in studies of industrial reuse.

Thus, the production of metal particles encapsulated in a graphene shell is a hot topic for research.

The synthesis of graphene-coated metal particles is implemented using various methods. In the last decade, due to their practicality, solution methods are the most popular [22], although gas-phase synthesis methods are also widespread. Such methods include chemical vapor deposition (CVD) [23], spark [24], and arc discharge [25]. The transition metal encapsulation process was first described by Elliot et al. [26], who demonstrated the catalytic ability of Fe, Ni, and Co particles to grow a graphite shell on their surface.

In this work, the method of arc discharge in the liquid phase was used to obtain nickel particles encapsulated in a graphene shell [27]. This study was carried out with the aim of analyzing various liquids as a cooling medium and the main source of carbon for the formation of a protective shell around metal particles. Deionized (DI) water, alcohol, and toluene were used as the liquid medium. The advantage of the method used is the possibility of controlling the synthesis process and continuous refill of a cooling liquid medium, which, in the future, will make it easy to switch to the serial production of such nanostructures as catalytic materials.

## 2. Experimental Part

The synthesis of nickel particles encapsulated in a graphene shell (Ni@C) was carried out using the method of electric arc discharge in the liquid phase, in various media: in DI water, alcohol (ethanol)  $C_2H_5OH$  (96%), and toluene  $C_6H_5-CH_3$  (96%) for 60 min. DI water with a resistance of  $16.2\text{ M}\Omega\cdot\text{cm}$  was prepared on a Sartorius arium 611DI device. Figure 1 shows the experimental setup. The setup consists of a power source, a lower MPG-7 graphite rod as an anode with a diameter of 9 mm, and an upper movable nickel rod (99.6%) as a cathode with a diameter of 6 mm. The electrodes were completely immersed in a liquid medium; contact of the synthesized particles with air was excluded. Before

the experiment, the electrodes were treated with acetone, alcohol, and DI water and dried at room temperature. Pulsed arc discharge plasma is generated using the energy of capacitors (20  $\mu$ F) located in the power source. Synthesis was carried out in the voltage range of 80–100 V and current 1.2–3.6 A. The arc discharge was maintained by applying a pulsed voltage at a frequency of 64 Hz and a pulse width of  $\sim 0.5$   $\mu$ s. The duty cycle of particle synthesis was 1 h (more information about the voltage characteristics is provided in Figure S1 in the Supplementary Material). An electromagnetic vibrator (50 Hz) was used to increase the frequency of approach and separation of the electrodes. The soot formed during the synthesis is precipitated at the bottom of the reaction chamber. The resulting powder is filtered and dried in air at 120  $^{\circ}$ C for 2 h. Samples obtained using toluene were additionally annealed for 1 h in an SNOL muffle furnace in an argon atmosphere at 300  $^{\circ}$ C to remove the amorphous high-molecular carbonaceous compounds. The rate of the powder formation during the synthesis is 0.5 g per hour. Energy consumption at this rate is 0.46 kJs/g.

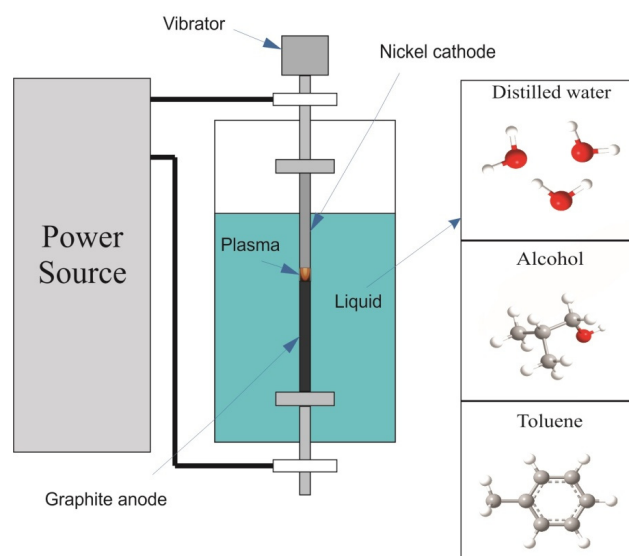


**Figure 1.** Experimental setup of arc discharge in liquid phase.

The morphological properties of the synthesized samples were studied using a Quanta 3D 200i scanning electron microscope (SEM). The structural properties of the samples were investigated based on X-ray diffraction and Raman scattering (RS) analyzes. XRD analysis was performed using a Rigaku MiniFlex 600 X-ray spectrometer with copper radiation ( $\text{CuK}\alpha$ ). The acquisition modes are as follows: X-ray tube voltage of 40 kV, tube current of 15 mA, and goniometer movement step  $2\theta = 0.02^{\circ}$ . The phase analysis was performed using the PCPDFWIN program with the PDF-2 diffraction data base. Raman analysis was carried out using a Raman spectrometer Solver Spectrum, NT-MDT. The spectra were recorded in the range from 0 to 3250  $\text{cm}^{-1}$ . The excitation source was a laser with a wavelength  $\lambda = 473$  nm. The diameter of a laser spot on the sample was  $\sim 2$   $\mu$ m.

### 3. Results

Figure 2 shows the results of SEM analysis of the nickel particles encapsulated in the multilayered graphene shell (Ni@C) synthesized using the method of electric arc discharge in various liquid media: DI water, ethanol, and toluene. The results of SEM analysis show that the particles synthesized in DI water (Figure 2a–c) had a diameter ranging from 80 nm to 15  $\mu$ m, mostly spherical-shaped and partial coverage with a multilayered graphene shell (Figure 2c). In addition to metal particles, the sample also contains individual carbon flakes. When alcohol was used as the liquid medium (Figure 2d–f), the nickel spherical particles were completely covered with a multilayered graphene shell. The particle sizes also varied from 70 nm to 12  $\mu$ m. The complete encapsulation of metal particles by a

multilayered graphene shell can be explained by the presence of an additional source of carbon in a liquid medium (in alcohol). The results of SEM analysis of samples synthesized in toluene are shown in Figure 2g–i. The SEM image (Figure 2i) shows that all Ni particles were completely covered by carbon shells with wrinkles typical of multilayered graphene and graphite, which was also observed in the works of other authors [25]. Particle sizes varied from 80 nm to 25  $\mu\text{m}$ . The typical elemental composition of particles synthesized in toluene was determined using energy-dispersive X-ray spectroscopy (EDS) and is shown in Figure S2 in the Supplementary Material.

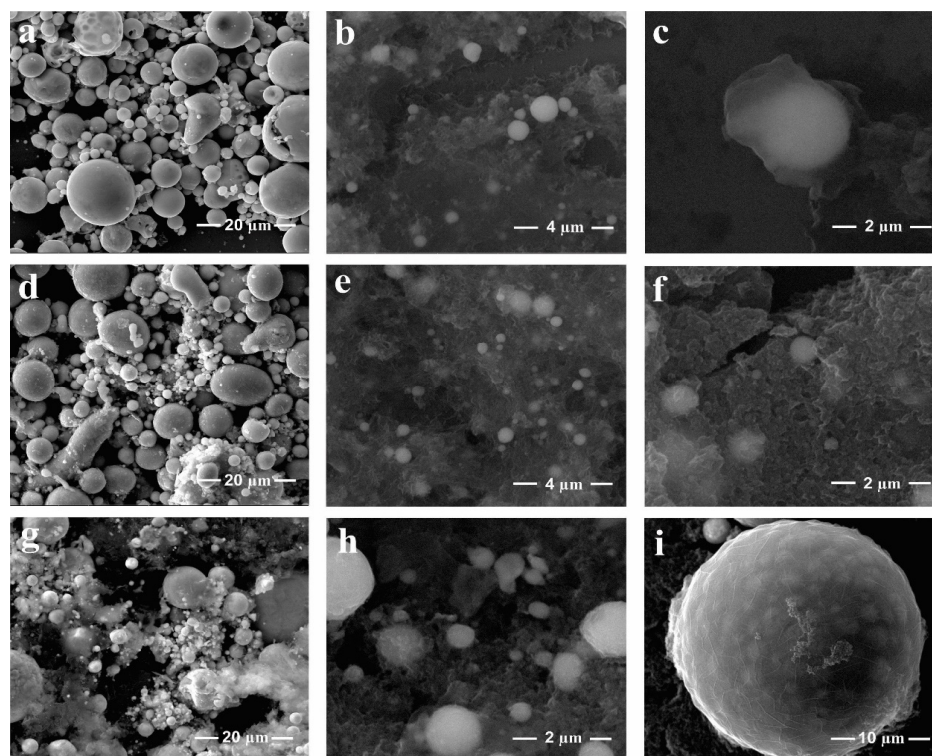


**Figure 2.** SEM micrographs of nickel particles synthesized in DI water (a–c), alcohol (d–f) and toluene (g–i).

To analyze the structural properties of the samples obtained, Raman spectroscopy studies were carried out. Figure 3 shows the Raman spectra of particles obtained in three different liquids (DI water, alcohol, and toluene). The Raman spectra of all three samples were very similar and showed the main peaks characteristic of graphite structures: D, G, D', and 2D [28]. The D band is associated with defects in  $\text{sp}^2$  structures. Peak G is an inherent mode of graphitic materials. The shoulder D' corresponds to the breaking of the symmetry of an  $\text{sp}^2$  crystal of finite size and is characteristic of free bonds (vacancies) in  $\text{sp}^2$  carbon materials. The 2D peak is the second order of the D-mode, which indicates the long-range order in the structure. A slight overlapping of the G and D peaks indicates the presence of an amorphous carbon phase in the samples.

A detailed analysis of the Raman spectra is presented in Table S1. The level of imperfection can be estimated from the  $I(\text{D})/I(\text{G})$  ratio, which in this case is equal to 0.58 (synthesis in DI water), 0.23 (synthesis in alcohol), and 0.4 (synthesis in toluene). The high intensity and low FWHM (full widths at half maximum) value of the G peak band indicate that the amount of graphitized and well-organized carbon exceeds the amount of amorphous and disordered carbon in the samples. The relative intensity of the 2D peak is usually used to estimate the number of graphene layers [29], the peak ratio  $I(2\text{D})/I(\text{G}) \sim 2\text{--}3$  for monolayer graphene,  $2 > I(2\text{D})/I(\text{G}) > 1$  for two-layer graphene, and  $I(2\text{D})/I(\text{G}) < 1$  for multilayer [30]. In the samples synthesized in DI water and alcohol, the  $I(2\text{D})/I(\text{G})$  ratio was 0.25 and 0.23, respectively, which corresponds to multilayer graphene or graphite. In the samples synthesized in toluene, the  $I(2\text{D})/I(\text{G})$  value was 2.29, which indicates the

presence of monolayer graphene. In addition, the degree of crystallinity of carbon materials is estimated from the FWHM of the G peak. Thus, the number of defects in the carbon shell for the samples synthesized in DI water was higher than that in the case of alcohol and toluene media (see Table S1).

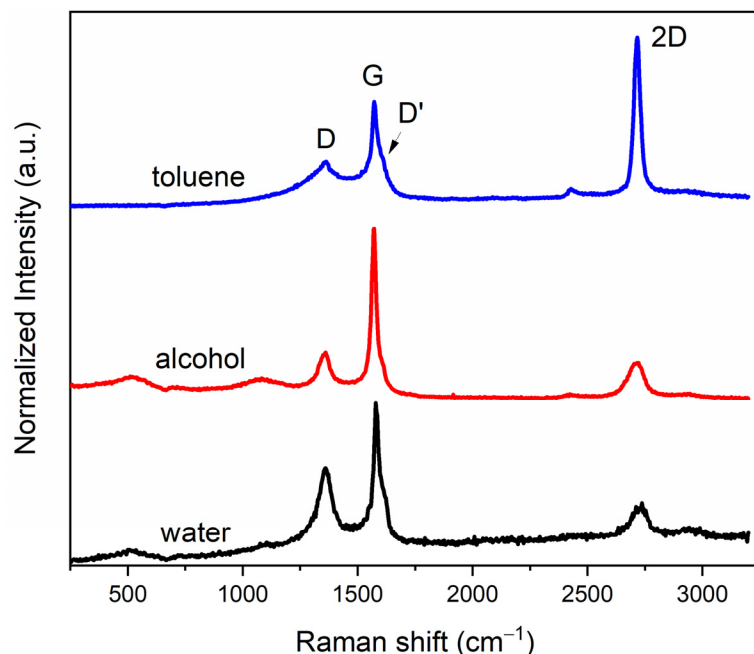


**Figure 3.** Raman spectra of nanoparticles obtained in three different liquids (water, alcohol, and toluene).

It is important to note that the Raman spectra of samples synthesized in DI water and alcohol show additional broad bands at about 500 and 1100  $\text{cm}^{-1}$  corresponding to nickel oxide. This can be explained by the possible partial/surface oxidation of nickel particles with the formation of  $\text{NiO}_x$  during synthesis due to oxygen contained in water and alcohol. There are no peaks of nickel oxide in the spectrum of samples synthesized in toluene, which is explained by the absence of oxygen in the synthesis medium, while the complete encapsulation of particles in the multilayered graphene shell protects the metal from oxidation in air after the synthesis.

The X-ray patterns of the samples obtained in various liquid media are shown in Figure 4. The spectra of the samples synthesized in DI water and alcohol showed a sharp peak at  $2\theta = 26.50$ , which corresponded to the C(002) plane of the graphite crystal structure. The samples obtained in toluene had a different trend in this region. The C(002) diffraction line in this case looked wider and less intensive than the peak of the samples obtained in water and alcohol. This corresponded to the structure located between the crystalline and amorphous phases [31] and it is a typical pattern for graphene nanosheets, the presence of which was also confirmed through Raman analysis.

In addition to these carbon peaks, the XRD spectra of the samples obtained in DI water showed peaks at  $2\theta = 44.50$ ,  $51.90$ , and  $76.50$ , which are characteristic of the (111), (200), and (220) planes of the face-centered cubic structure of nickel [32]. In the case of samples obtained in alcohol and toluene media, these peaks were manifested with a relatively lower intensity, and with a pronounced additional peak at  $58.60$ , which indicates the appearance of the nickel carbide structure [33]. It should be noted that for the samples synthesized in the medium of DI water and alcohol, a peak at an angle of  $37.50$  corresponding to nickel oxide was also noticeable (JCPDS Card No: 22-1189). Thus, the data of XRD analysis were in good agreement with the results of Raman spectroscopy.

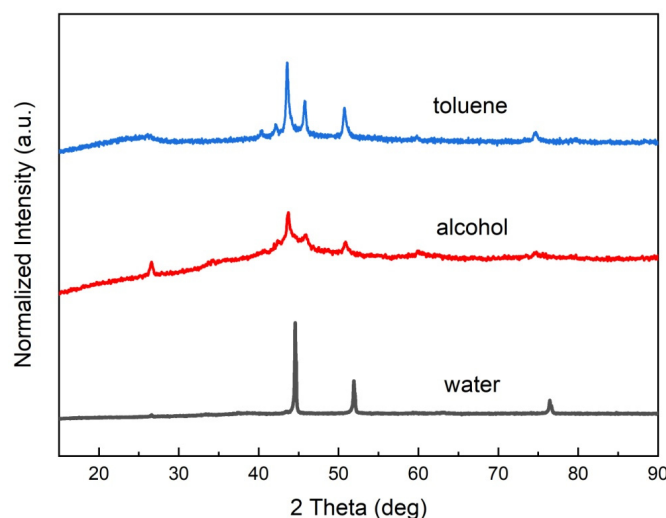


**Figure 4.** XRD patterns of encapsulated nickel particles obtained in three different liquids.

From the results of SEM, Raman, and XRD analyses, it can be concluded that the toluene medium allows synthesizing oxide-free nickel particles well-encapsulated in a graphene shell.

For further detailed analysis, the samples synthesized in toluene were annealed in an inert argon atmosphere at a temperature of 300 °C to remove the residual amorphous carbonaceous component and nickel carbide phase [34]. The X-ray pattern and Raman spectrum of encapsulated nickel particles obtained in toluene before and after annealing are shown in Figure 5. The Raman spectrum after the annealing process showed clearly defined G and 2D peaks without an amorphous component. The peak ratio  $I(D)/I(G)$  and FWHM of the G peak were significantly reduced to 0.08 and 22, respectively. This trend indicates a decrease in defects in the samples after the annealing process. The peak ratio  $I(2D)/I(G)$  after the annealing process was 1.01, which corresponds to two-layer graphene. The XRD spectra showed no nickel carbide peaks after the annealing process, with the main characteristic nickel and graphene peaks preserved. Thus, the transformation of a monolayer to bilayered graphene after annealing in an inert atmosphere can possibly be explained by the precipitation of carbon being in the nickel carbide phase on the surface of the metal particle.

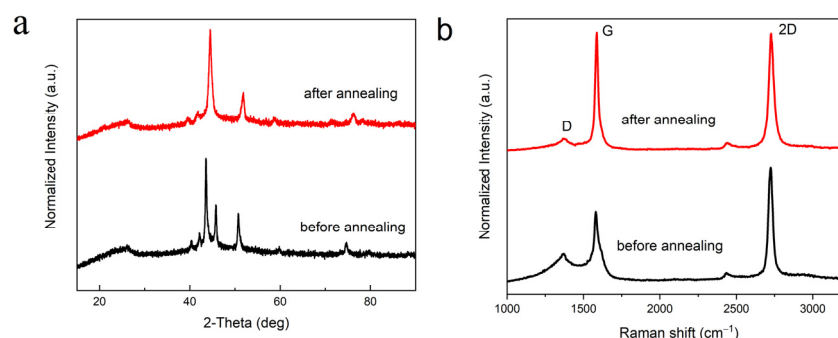


**Figure 5.** XRD patterns (a) and Raman spectra (b) of encapsulated nickel particles obtained in toluene before and after annealing.

#### 4. Discussion

The mechanism of graphene encapsulation of Fe, Ni, and Co nanocrystals was first proposed by Elliott in [26]. This method consists of two stages: phase separation and catalysis. At the initial stage, the arc discharge column transforms the graphite and metal electrodes into a gaseous state; then, leaving the plasma region, the carbon and metal vapors rapidly cool and aggregate into liquid-like particles. Upon further cooling, carbon

particles crystallize into graphite, then agglomerate with metal particles and cover the metal core. This process occurs until the encapsulating layer of graphite is cold and thick enough to prevent the coalescence of metal particles. The second stage is characterized by the ability of transition metals (Fe, Ni, and Co) to catalyze the growth of a graphite structure from amorphous carbon on its surface. However, Elliott notes that the second stage is only ancillary to the first one metal. In [25], a third stage was proposed, which is possible when carbon vapor is added from the outside, that is, from the working chamber or vessel into the hot coalescence zone. The authors considered cyclohexane, which is capable of forming amorphous carbon on the surface of nanoparticles, and benzene, which forms a graphite shell, as additional sources of carbon. Benzene, due to the stable structure of aromatic rings, can directly condense into crystalline graphite through phenyl radical molecules at higher temperatures. Moreover, it was shown in [30,35] that benzene vapor forms a graphene layer on the surface of a catalytic metal at 1099.85 °C, making it possible to use benzene to form nanosized carbon materials in an arc discharge system. In our method, DI water, alcohol, and toluene were used as a cooling liquid (Figure 3). Toluene, like benzene, has an aromatic ring structure and a greater amount of carbon than alcohol. A detailed analysis of the decomposition of toluene at high temperatures was demonstrated in [36,37]. In our experiments, analysis of the SEM and XRD data confirmed the formation of spherical encapsulated nickel particles in all types of liquid media, which is consistent with the Elliott's theory [30]. By synthesizing nickel particles in toluene [38], it is also possible to obtain carbon nanotubes and nanohorns [39]. In [40], it was shown for the first time that the use of low-voltage power supplies and a decrease in the energy of the capacitor leads to the formation of graphene fibers. However, in our case, the Raman spectra showed the presence of more graphite and graphene layers in the encapsulated particles synthesized in alcohol and toluene, demonstrating the importance of an additional carbon source in the cooling medium. Although the three-stage model for obtaining encapsulated particles agrees with theoretical models and experimental data, more research is needed to describe the mechanism of encapsulation more accurately.

## 5. Conclusions

In this work, the arc discharge method in liquid phase was used to synthesize spherical nickel particles encapsulated in a multilayered and monolayered graphene shell. The samples obtained in different liquid media were characterized using SEM, Raman, and XRD methods. Analysis of the XRD and Raman data demonstrated the presence of the NiO<sub>x</sub> oxide phase in the samples synthesized in water and alcohol, which was not observed in the case of using the toluene medium. This is explained by the absence of oxygen in the structure of toluene and the complete encapsulation of nickel particles by carbon, which prevents the surface oxidation of the samples. A large amount of carbon in the composition of toluene promotes the formation of metastable nickel carbide, which disappears during heat treatment. Thus, the use of toluene as a cooling medium in the arc discharge method makes it possible not only to synthesize high-quality metal particles but also to form a protective thin graphene layer on the surface of nickel particles, which can provide better catalytic performance.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/en16031450/s1>, Figure S1: Current source for the synthesis of arc discharge particles in the liquid phase (a) and typical V characteristic during arc discharge (b); Figure S2. EDX microanalysis nickel particles synthesized in toluene; Figure S3. SEM micrographs of nickel particles synthesized in distilled water (a), alcohol (b) and toluene (c); Table S1: Detailed analysis of the Raman spectra of carbon-encapsulated Ni particles synthesized in water, alcohol and toluene.

**Author Contributions:** Conceptualization, M.T.G. and Y.Y.; data curation, M.N.U., A.S.Z. and R.R.N.; formal analysis, M.T.G. and Y.Y.; investigation, M.N.U., A.S.Z., N.Y.A., R.R.N., Y.Y. and M.B.A.; methodology, M.N.U., A.S.Z., R.R.N., Y.Y., S.A.O., D.S., A.Z. and M.T.G.; resources, M.T.G.; supervision, M.T.G.; visualization, M.N.U., A.S.Z., R.R.N., Y.Y. and B.Y.K.; writing—original draft, M.T.G., A.S.Z., R.R.N. and Y.Y.; writing—review and editing, Y.Y. and M.T.G. All authors have read and agreed to the published version of the manuscript.

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**Data Availability Statement:** The data presented in this study are available on request from the corresponding author.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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