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Electrochemical synthesis of nickel nanoclusters by pulsed current method

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ABSTRACT

The main objective of this research is to prepare nickel nanoparticles with more porous structure by the pulsed current electrochemical method. In this method, there are some effective parameters including; pulse amplitude (current amount), pulse frequency, nickel salt concentration, ammonia concentration, structure director concentration, reduction agent concentration, and synthesis temperature, which were optimized by the "one at a time method". A nickel optimized nanopowder was synthesized by using nickel chloride (0.005M) as precursor, silver nitrate as a nucleation agent (at 0.5% mole of nickel salt in the starting solution), polyvinyl pyrrolidone (PVP) as structure director (with PVP/Ni=1.7g/g), ammonia (2 M), and hydrazine as reduction agent (with Hydrazine/Ni=16 g/g) by pulsed current of 58 mA.cm^{-2} with a frequency of 12 Hz. The morphology and particle size of each synthesized sample was studied by scanning electron microscopy (SEM). The obtained results showed that temperature has no considerable effect on the morphology and particle size of nickel nanopowder. The nickel nanopowder synthesized in optimum conditions has excellent uniform and a more porous structure including nanoclusters with a particle size of approximately 10-20 nm. The obtained results indicate that the pulsed current electrochemical method can be used as a confident and controllable method for the preparation of nickel nanoparticles.

KEYWORDS

Pulsed current;
Nanoclusters;
Nickel;
Electrochemical;
Nanopowder.

1. INTRODUCTION

Small metal particles in the nanometer range display different chemical and physical properties from bulk materials, and play an important role as a heterogeneous catalyst. The reactivity of the nanosized catalyst particle is associated with their high ratio of surface to bulk atoms[1,2]. The metal nanoparticles display unique properties that differ from the bulk substances, i.e.: a different heat capacity, vapor pressure, and melting point. Moreover, when decreasing the metal particle size sufficiently enough, there occurs a transition of the electronic state from a metallic to non-metallic one. Additionally, metal nanoparticles exhibit a large surface-to-volume ratio and an increased number of edges, corners and faces leading to altered catalytic activity and selectivity[3].

Nickel catalysts are widely used in chemical and petrochemical processes. Nickel is widely used as an alternative catalyst for the heterogeneous hydrogenation of vegetable oils in industrial processes (Raney Nickel). More recently it is used as a heterogeneous catalyst in a variety of organic syntheses, most commonly for hydrogenation reactions. Raney Nickel is produced when a block of nickel-aluminum alloy is treated with concentrated sodium hydroxide. This treatment, which is called "activation", dissolves most of the aluminum out of the alloy. The porous structure left behind has a large surface area, which gives a high catalytic activity. A typical catalyst is around 85% nickel by mass, which corresponds to approximately two atoms of nickel for every atom of aluminum. The aluminum which remains helps to preserve the pore structure of the overall catalyst. When the nickel powder is produced in a more porous structure, it is expected that the product does not need aluminum as a porosity maker. In the literature, there are many chemical methods proposed to obtain nickel nanoparticles[4,5]. Nickel nanowires are of particular interest to researches because they could be employed to increase magnetic storage density[6,7]. Stopic et al reported a high temperature process of spray pyrolysis in which submicron particles were produced by hydrogen reduction at temperatures of over 300^{0}C, it was however difficult to decrease the particle size down to the nanometer range with this technique[8]. Zhu et al reported a yield of about 90% after 12 hours of radiation for the production of nanocrystalline nickel powder from either aqueous solution or a poly solvent, such as ethylene glycol[9]. Kurihara et al synthesized nanosized nickel using hydrazine as the reducing agent at elevated temperatures[10]. Yu et al utilized a modified polyol process to synthesize nickel rods[11]. Chou et al synthesized nickel fibers from three different processes,the kinetics was investigated and it was noted that these processes could produce nickel fibers with a diameter of about 1-2μ[12]. Lee et al reported the formation of crystalline nickel fibers by chemical reduction in the presence of a magnetic field[13]. Takeshi synthesized nickel powder through the thermal decomposition of nickel oxalate[14]. Zubryckyj et al synthesized nickel powder by hydrogen reduction[15]. There are many other reports on the chemical synthesis methods of obtaining nickel powder[16,17,18,19].

There are a few reports on the electrochemical deposition of nickel nanoparticles. Lisensky et al synthesized nickel nanowires by electrodeposition[20]. In the reported method by Lisensky et al, nickel nanowires are grown inside the pores of an alumina filter and then the filter is removed by etching, to yield magnetic nanowires.

Jin et al electrocrystallized nickel nanoparticles on a 4-nitroaniline (NA) radical monolayer-grafted on MWCNT through a molecular level design. The structure and nature of the Ni/NA/MWCNT was characterized by a field emission scanning electron microscope (FE-SEM), an X-ray diffraction (XRD) and an X-ray photoelectron spectroscopy (XPS). The results show that Ni nanoparticles were homogeneously electrodeposited on the surfaces of MWCNT[21].

Wang et al superimposed an external high parallel magnetic field into the co deposition process of Ni/nano-Al_2O_3 composites. It was found that the distribution of nanoparticles showed the network shape when superimposing a magnetic field, and the average size of the single network increased with increasing the current density. High concentration of nanoparticle could be obtained at low current density with a magnetic field, while a high current density was needed to realize that when without a magnetic field,the superimposed magnetic filed would improve the current efficiency. A possible mechanism on forming network shape was discussed[22].

In this experiment, a simple way to synthesis nickel nanoparticles was reported. Nickel nanoparticles were electrodeposited by applying a pulsed current technique from a nickel salt alkaline solution containing ammonia and polyvinyl pyrrolidone (PVP) as a structure director and colloid stabilizer.

2. EXPERIMENTAL

2.1. Materials

All materials and reagents used in these experiments were of reagent grade and were produced in the Loba Chemie Co. (India). Double-distilled water was used in all the experiments.

2.2. Instrumentals

A power source of the MPS-3010L model, made

Figure 1: Laboratory system used to synthesis the lead dioxide nanoparticles, including power supply, pulse maker apparatus, and electrochemical cell

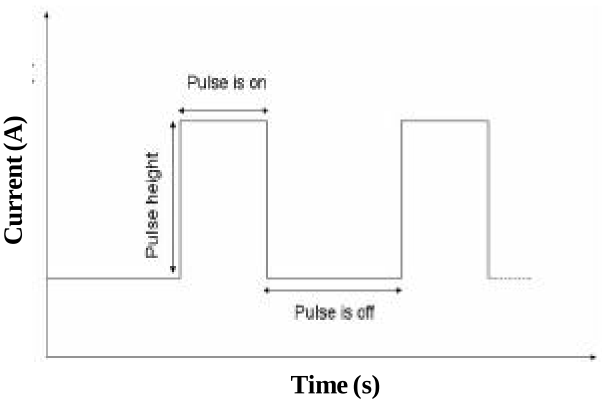

Figure 2: Used pulse diagram, including pulse time, relaxation time, and pulse height

by the Taiwan Matrix Company was used for producing the constant current. A home-made electrical pulse apparatus was applied to make the reproducible current pulses. Figure 1 shows the used laboratory systems, including the power supply, pulse apparatus, and electrochemical cell. The solution temperature was kept constant with usage of a water bath (Optima, Tokyo, Japan).

A scanning electron microscope from Philips Co. (XL30) was used for studying of morphology and particle size of the prepared nickel nanopowders. Energy-dispersive X-ray analyses (EDX) were performed by Philips 30 XL. X-ray diffraction (XRD) studies were performed by a Decker D8 instrument.

2.3. Procedure

Reagent grade nickel chloride hydrate ($NiCl_2 \cdot 6H_2O$) was used as the precursor for nickel synthesis and, silver nitrate ($AgNO_3$) was chosen as the source of Ag as a nucleation agent for nickel synthesis. The appropriate amounts of nickel chloride (0.005M) and $AgNO_3$ (at 0.5% mole of nickel in the starting solution) and PVP (PVP/Ni=1.7g/g) were first dissolved in water, which was then heated to the desired temperature for the reaction. The sufficient quantities of ammonia were quickly added into the above solution (final concentration is 2 M). The obtained solution was used in the electrochemical synthesis cell with two graphite electrodes as anodes and one stainless steel (316L) as a cathode. In theses cases, the precipitate was separated from the solution, washed with water and ethanol, and dried at room temperature. The morphology and dimension size of nickel nanoparticles were studied by scanning electron microscopy. At this method, there are effective parameters which include pulse amplitude (current amount or pulse height), pulse frequency, nickelsalt concentration, ammonia concentration, complex agent concentration, and temperature or synthesis solution which were optimized by a time method.

3. RESULTS AND DISCUSSION

In this procedure, a pulse current is exerted on the electrochemical solution containing a stainless steel (316L) cathode and two graphite anodes by the electrical pulse instrumentation. In this method, there are some effective parameters which include, pulse amplitude (current amount or pulse height), pulse frequency, nickel salt concentration, ammonia concentration, complex agent concentration, and temperature or synthesis solution which were optimized by the "one at a time" method.

In the pulsed current method, the current vs. time was applied as shown in figure 2. As shown in figure 2, the used current pulse has 4 variable parameters: pulse height (current amplitude), pulse time, relaxation time, and pulse frequency. Our initial studies show that the relaxation time/pulse time ratio of 3 is suitable and optimum most of the synthesizes, thus the ratio of 3 was selected for later studies. At constant ratio of relaxation time to pulse time, a pulse system has 3 variable parameters: pulse height, pulse time, and pulse frequency. The effect of all effective parameters was optimized by the "one at a time" method.

3.1. Pulse frequency optimization

Our initial studies showed that the pulse current method is more effective than the simple constant volt-

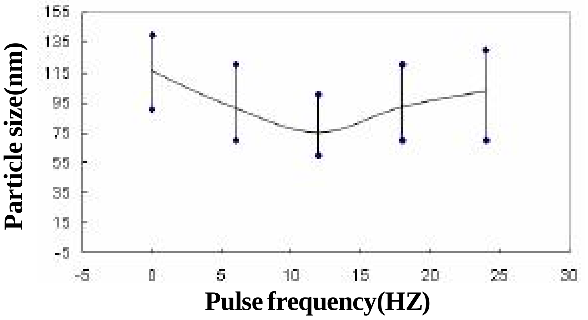

Figure 3: Effect of the pulse frequency on the average and range of nickel nanoparticles size

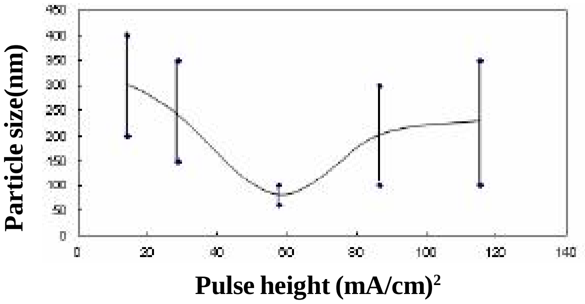

Figure 4: Effect of the pulse height (current density) on the average and range of nickel nanoparticles size

age and simple constant current methods. The pulsed current electrochemical method can be used as a confident and controllable method for the production of nanoparticles. Figure 2 shows the used pulse diagram. As it is seen from figure 2, each current pulse contains an “on” time (pulse time) and an “off” time (relaxation time), so that the pulse frequency can be related to the sum of current pulses which can be applied in to the system at one unit of time. At constant ratio of relaxation time/pulse time (which is equal to 3), any variation in pulse frequency makes a new pulse and relaxation time.

In order to investigate the effect of pulse frequency on particle size, the pulse frequency was varied from 0 to 24 Hz. The SEM results showed that at a frequency of 12Hz, the synthesized nickel nanopowder is more uniform, it has smaller particles and more porous, exceptional nanostructures. The variation of average particle size and the range of particles sizes vs. pulse frequency, based on the SEM data, are illustrated in figure 3. As shown in the diagram, increasing pulse frequency from 0 to 12 Hz not only causes a considerable decrease in the average particle size (from 115 nm to 75 nm), but also produces a decrease in the particle size range (from the range of 85-145nm to 60-100nm). For the pulse frequency of 12 Hz, the “on” and “off” durations were 20 ms and 60 ms, respectively. Applying the synthesis current in pulse form decreases the nuclear growth, thus the uniform and smaller particles are synthesized. At higher pulse frequencies (more than 12 Hz), the relaxation time between two successive pulses is very short so that the new synthesis cycle (according to the new pulse) starts before the finishing of the previous synthesis cycle (according to the previous pulse). It should be mentioned that the nuclear growth has little hindrance time with respect to pulse time (reduction of nickel). At lower frequencies, the rate of the nuclear growth is more than the nuclear production rate.

3.2. Optimization of pulsed current amplitude

In order to investigate the effect of a pulse current amplitude (pulse height) on the morphology and particle size, the pulse which height varied from 14 to 115 mA/cm^2 was exerted on the electrochemical solution while the other parameters were kept constant. The morphology and particle size of each nickel powder yield was studied by SEM. Five different current amplitudes were used in this series of optimization experiments. Figure 4 shows the effect of pulse height on the average particle size and the range of nickel particles sizes. As shown in figure 4, as the pulse height increases from 14 to 58 mA.cm^{-2}the range and average particle size decreases. This result can be related to this fact that in the electrochemical pulse system, nuclearation rate increases making the pulse height increase, which therefore causes a decrease in that particle size. At higher current amplitudes, particle growth rate and agglomeration rate is higher than the nuclearation rate. This fact cases to increase the range and the average particle size of the synthesized nickel powder. Based on the obtained information derived from figure 4, the pulse height (current amplitude) of 58 mA.cm^{-2} was selected as the optimum current for the synthesis of uniform nickel nanopowder.

3.3. Temperature optimization

For investigation of the synthesis temperature effect on the morphology and particle size of nickel nanopowder, four synthesizes were carried out at temperatures of 0, 25, 45 and 100^{0}C. Figure 5 shows the morphology and particle size of the nickel nanopowder

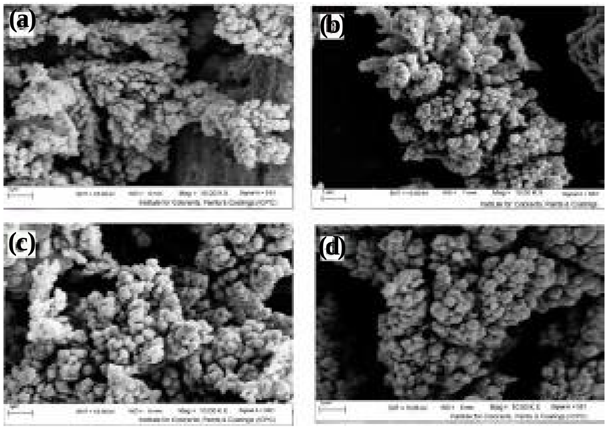

Figure 5: SEM images of nickel nanopowder samples which were synthesized at temperatures of 0⁰C (a), 25⁰C (b), 45 ⁰C (c) and 100⁰C (d)

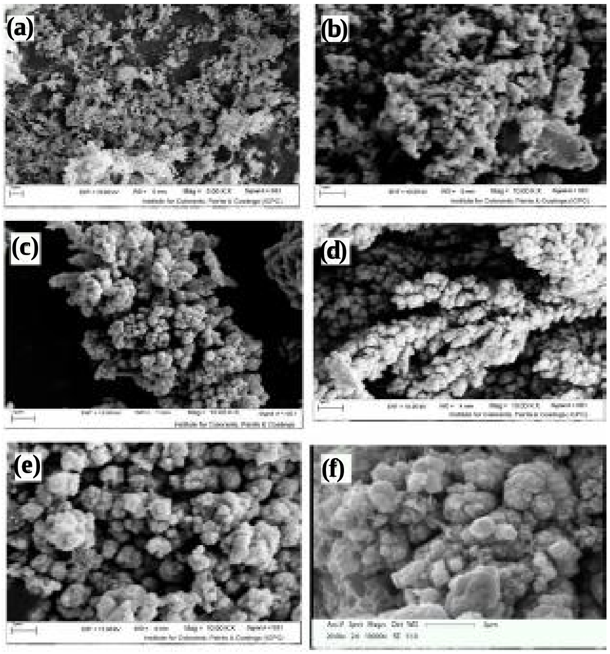

Figure 6: SEM images of nickel nanopowder samples which were synthesized at nickel chloride initial concentration of 0.005 M (a), 0.01 M (b), 0.02 M (c), 0.03 M (d), 0.04 M (e), and 0.08 M (f)

samples synthesized at different solution temperatures. As seen in figure 5, solution temperature does not have any considerable effect on the morphology and particle size of the nickel nanopowder. Nevertheless, as the solution temperature increases from 0 to 25⁰C, the synthesis rate of nickel nanopowder also increases. At higher temperatures, there is a high rate of ammonia evaporation from the solution thus causing a decrease in the synthesis rate. At the temperature of 25⁰C, the synthesis rate and solution stability is optimum.

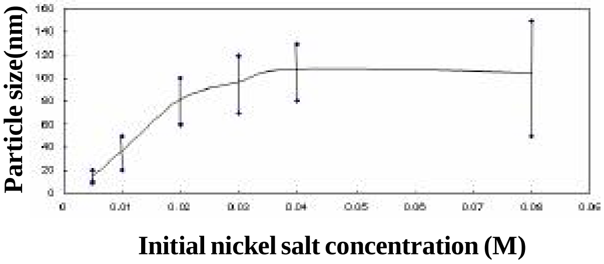

Figure 7: Effect of the initial nickel salt concentration on the average and range of nickel particles size

3.4. Optimization of the initial nickel chloride concentration

The effect of the initial nickel chloride concentration on the particle size and morphology of nickel nanopowder was investigated by varying the nickel salt concentration from 0.005 M to 0.08 M. Figure 6 shows the SEM images of the synthesized nickel nanopowder samples at different concentrations of nickel chloride. As it is seen in figure 6, the lower concentrations of nickel salts create a uniform structure and the smallest particle size for the final nickel nanopowder. For more clarification, the average effect of the initial nickel chloride concentration and ranges of the samples' particle sizes are shown in figure 7. As Figure 7 shows, as the initial concentration of nickel chloride in the synthesis solution decreases from 0.08 M to 0.005 M, the average particle size of nickel nanopowder also decreases from 100 nm to 15 nm. In addition to the particle size itself, the range of particle sizes also decrease from 50-100nm to 10-20nm. The obtained results can probably be related to the reduction of particle growth and the agglomeration rate at lower concentrations. At initial nickel chloride concentrations which are lower than 0.005 M, the amount of nickel nanoparticle precipitation is very low, thus it can not be filtered and collected therefore The initial concentration of 0.005 M was selected for the optimization of other parameters.

3.5. Optimization of NH_3 concentration

The reduction of nickel ions by the chemical agents or using the electrochemical method should only be carried out in the basic media of ammonia[19-21]. Therefore, the concentration of NH_3 (as a complex and basic agent) was varied from 0-19 M at a temperature of 25⁰C, 12Hz frequency, 58 mA/cm^2 pulse current and a nickel

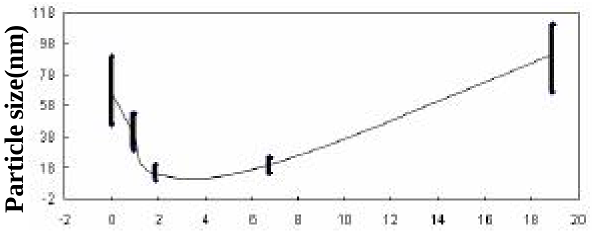

Figure 8: Effect of the initial ammonia concentration on the average and range of nickel particles size

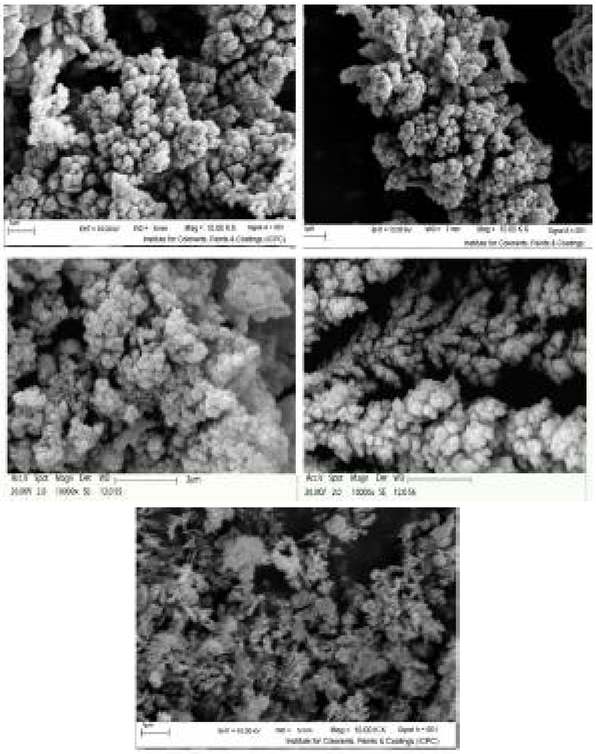

Figure 9: Final SEM images of the obtained nickel nanopowder at the different optimization steps: (a) optimized pulse frequency, (b) optimized current amplitude, (c)optimized solution temperature, (d) optimized initial concentration of nickel salt, and optimized initial concentration of ammonia

chloride concentration of 0.005 M. SEM Images showed that with the increase of the ammonia concentration from 0-2 M, the samples acquired uniform nanostructures and, with the greater increase of the ammonia concentration from 2-19 M, the uniform nanocluster structures converted to simple nanoparticles. Figure 8 shows the average effect of ammonia concentration and the range of particles sizes. As demonstrated in figure 8, at the increase of the ammonia concentration from 0-2 M, the average range of the samples' particle sizes decrease. At lower and higher concentrations of ammonia, the nickel powder lacks a stable, regular structure. This result can probably be related to the unsuitable ratio of nucleation and nuclear growth.

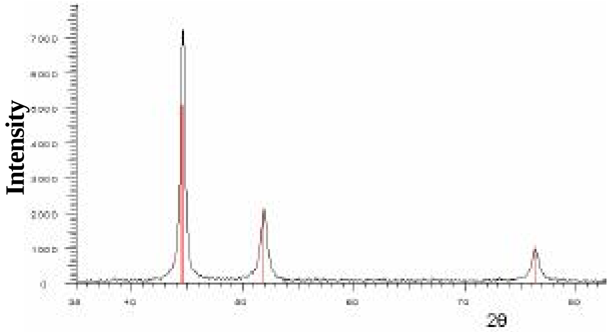

Figure 10: XRD patterns for the optimized nickel nano powder sample

3.6. The effect of the structure director agent

The effect of the three different structure director and colloid stabilizer agents (glycerol, PVA and PVP)[23] was studied on the morphology and particle size of the nanostructured nickel. SEM studies show that the PVP has the best role in stabilizing the colloid and controlling the nanostructured nickel particle growth. As it has been previously reported[20,23], PVP can be used as an effective structure director agent and colloid stabilizer for chemical and electrochemical synthesis. The experimental results showed that the previously used PVP concentration (PVP/Ni=1.7g/g) is the suitable value to obtain an excellent uniform nanostructured nickel in nanopowder form.

3.7. Optimized nickel nanoclusters

The excellent uniform nanoclusters of nickel in nanopowder form can be synthesized at the optimum conditions as followings:

1. Pulse frequency of 12 Hz
2. Pulse height (current amplitude) of 58 mA.cm^{-2}
3. Synthesis solution temperature of 25^{0}C
4. Initial nickel ion concentration of 0.005 M in chloride salt form
5. Ammonia (complex and basic agent) concentration of 2 M
6. PVP (structure director agent) with the weight ratio of PVP/Ni=1.7g/g

When a synthesis is carried out under the above-mentioned conditions, needle-shaped nickel nanoclusters can be obtained in powder form. Figure 5 shows the final SEM images of the obtained nickel powder samples for the optimization of the effective parameters (sections 3.1 to 3.6). In figure 9, for each effective parameter (pulse frequency, pulse height, temperature, initial concentration of nickel ion, and ammonia concentration) the final SEM image of the sample which synthesized in the optimum value of the proposed parameter has been presented. As observed in figure 9, in the duration of the optimization steps, the morphology and particle size of the synthesized nickel change from simple particles to perfect uniform needle-shaped nanoclusters.

Figure 10 shows the XRD patterns for the optimized nickel sample. At it is seen in figure 6, there is only metallic nickel in the synthesized sample. The calculation of particle sizes using Scherrer's formula suggested the particle sizes to be about 17 nm. This result is well supported by scanning electron microscopy.

4. CONCLUSION

The experimental results indicate which pulse current electrochemical method can be used as a confident and controllable method for the preparation of needle-shaped nickel nanoclusters. When a synthesis is carried out under a pulse frequency of 12 Hz, a pulse height (current amplitude) of 58 $mA.cm^{-2}$, a synthesis solution temperature of 25^0C, an initial nickel ion concentration of 0.005 M in chloride salt form, an ammonia (complex and basic agent) concentration of 2 M and a PVP (structure director agent) with a weight ratio of PVP/Ni=1.7g/g, nickel nanopowder can be obtained in the perfect uniform structures in nanocluster form with an average particle size of 10 to 20nm.

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