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Synthesis of Cobalt Nanorods by the Pulsed Current Electrochemical Method

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In this paper, cobalt nanorods were synthesized by the pulsed current electrochemical method on the stainless steel substrate in $CoSO_4$ solution which its pH adjusted to 3 with adding sulfuric acid. In order to obatin uniform morphology , narrowest size distribution and best composition of sample, the effect of experimental variables such as concentration of cobalt ion, type and concentration of additive, pH, bath temperature, pulse frequency and pulse height (current amount), have been investigated. The composition, morphology and structure were investigated using Energy scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction techniques (XRD). The obtained results revealed that the optimized experimental conditions were 10 mA cm^{-2} current density, 8 Hz pulse frequency, 0.2 M Co^{2+}, 0.4 M H_3BO_3, solution pH of 3, electrocrystallization temperature of 45 °C, 1.37 g/l PVP as structure director additive. The obtained results indicated that pulsed current electrochemical method can be used as a confident and controllable method for the preparation of the cobalt nanorods. The cobalt sample synthesized in the optimum conditions had uniform nanorods with average diameter of 35 nm and average length of 375 nm.

Keywords: Cobalt, nanorod, pulsed current, electrocrystallization, electrosynthesis

1. INTRODUCTION

Nanostructured materials have received increasing attention in various fields of science and technology [1-3]. A variety of physicochemical methods, including metal evaporation [4], spray pyrolysis [5], sol-gel [6] and electrochemical methods [7], have been used to produce nanometer-sized materials.

The electrochemical synthesis of nanoparticles has received a great deal of attention in the past several years. This is probably because electrosynthesisis a low cost and reaction condition that can be carried out under mild condition, and because the properties of the nanoparticles can be controlled by

several parameters, such as current density, applied potential, reaction temperature, and solution composition. In the recent years, a lot of nanostructures have been synthesized by the electrochemical methods, such as cyclic voltammetry [8-12], potentioastatic [13-18], galvanostatic [19-21], and pulse current [22-28] methods.

Compared with conventional galvanostatic method, pulse galvanostatic method is a modified, simple and controllable method. In the pulsed current, nanostructured materials can be synthesized on the electrode by controlling pulse variable such as pulse height (current density), pulse time, and relaxation time. There are many reports which show that the pulsed current electrosynthesis is more efficient than the direct current [22-26].

Cobalt nanoparticle is an attractive material, which has been used in variety of electrochemical and industrial applications, including its use as a positive electrode in rechargeable batteries [30-33], as increase in sensibility at medical photographic, as improvement anemic malady. Cobalt nanoparticles were previously synthesized by various methods such as hydrothermal, inverse micelle and etc. Based on the best our knowledge, there are a few reports about electrosynthesis of cobalt nanowires [29] by constant current method, but there is not any report about the elecxtrosynthesis of cobalt nanostructures by pulsed electrochemical methods.

In this work, we have tried to present a reliable method for the synthesis of cobalt nanorods. We have applied a pulsed current method for the direct synthesis of nanostructured metallic cobalt in cobalt ions solution in the presence of sodium sulfate as ionic strength adjuster and polyvinyl pyrrolidone (PVP) as structure director. A series of experiments were conducted to establish the optimum conditions for obtain uniform morphology, narrowest size distribution and best composition of metallic cobalt by the "one at a time" method. In the recent years, the sonochemical methods have been shown to be very promising in the preparation of a variety of materials with nanometer dimension. The ultrasonic of liquids results in acoustic cavitations, which caused the formation, growth, and implosive collapse of bubbles so, we investigated the effect of ultrasonic irradiation on the morphology and particle size of cobalt nanorods during its electrosynthesis process.

2. EXPERIMENTAL

2.1. Materials

Analytical grade sulfuric acid, nitric acid, sodium sulfate, cobalt (II) sulfate were purchased from Merck and were used without any purification. Saccharin and polyvinyl pyrrolidone (PVP) were obtained from Loba Chimie Co. (India). In all experiments, double-distilled water was used.

2.2. Instrumentals

The morphology and particles sizes of all samples were studied by a Philips scanning electron microscopy (XL30 model) and X-ray powder diffraction (Philips X'pert diffractometer) and Cu K_α radiation (λ = 0.15418 nm).. MPS-3010L model of a power source, made by the Taiwan Matrix

company was used for making a constant current. A home-made electrical pulse apparatus was applied to make the reproducible current pulses.

Figure 1 shows the used laboratory systems including power supply, pulse apparatus and electrochemical cell. The temperature of the synthesis solution was kept constant by water bath (Optima, Tokyo, Japan).

Figure 1. Laboratory systems used to syntheses the metallic cobalt nanorods including power supply, pulse maker apparatus and electrochemical cell.

2.3. Procedure

Before each deposition, the stainless steel electrodes were placed in the diluted HNO_3 for 30s and then rinsed with double-distillated water to remove any surface oxidized species in contact with air. Two stainless steel anodes were coupled with a stainless steel electrode as cathode of the electrochemical cell. The electrodes were put in the synthesis solution including 0.2 M Co^{2+}, 0.4 M H_3BO_3 as pH adjuster (pH = 3), electrocrystallization temperature of 45 °C, 1.37 g/l PVP as structure director additive. Different rates of the pulsed current were applied for reducing of the Co^{2+} ions on the surface of stainless steel cathode.

The effect of all parameters of the synthesis including $CoSO_4$ concentration, pH, type and concentration of additive, solution temperature, pulse frequency and pulsed current amplitude was optimized by a "one at a time" method.

3. RESULTS AND DISCUSSION

Cobalt nanostructures were directly synthesized by the pulsed current method on the stainless steel electrode in synthesis solution including 0.2 M Co^{2+}, solution pH of 3, electrocrystallization temperature of 45 °C, 1.37 g/l PVP as structure director additive. In the current study, a direct current with constant amplitude was supplied by a common power supply instrument. The output of the power supply system (DC current) was connected to a home-made pulse maker apparatus. The current output of the pulse system is a pulsed direct current as it is shown in Fig. 2.

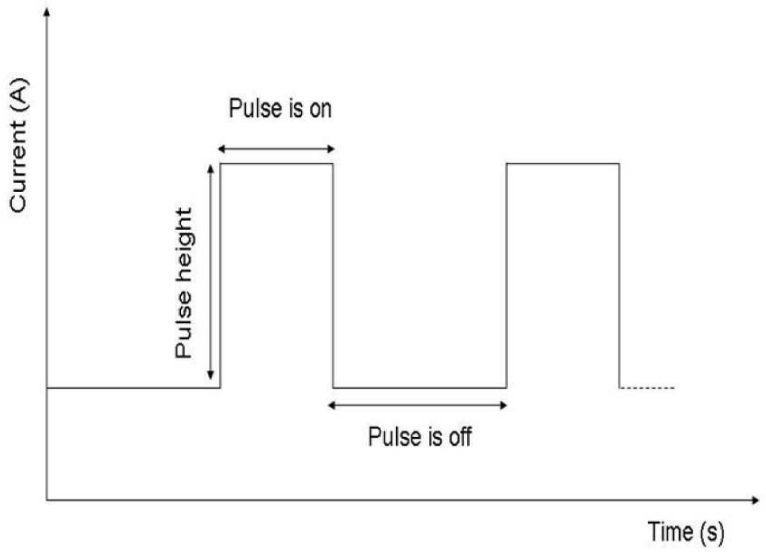

Figure 2. Used pulsed current diagram including pulse time, relaxation time and pulse height.

According to Fig. 2, there are 4 variable parameters for pulse system including pulse height, pulse time, relaxation time and pulse frequency. The results of our initial experiments indicated the desirability of relaxation time/pulse time ratio of 3 for majority of syntheses; therefore, the ratio of 3 was selected for further experiments. At a constant ratio of relaxation time to pulse time, a pulse system has 3 variable parameters including pulse height, pulse time and pulse frequency which they were optimized.

Hoshino and et al synthesized cobalt nanowires by constant current electrosynthesis method in cobalt ions solution including ammonia [29]. We tried to find an acidic solution for controllable synthesis of cobalt nanorods. Our initial studies showed that the mentioned propose can be achieved by using boric acid and a suitable synthesis additive such as saccharin and PVP. Therefore, in the present method, there are effective parameters including Co^{2+} concentration, type and concentration of synthesis additive, pH, temperature, pulse height, and pulse frequency which their amounts were optimized by the "one at a time" method.

3.1. Pulsed current amplitude optimization

The effect of pulse height (current amplitude) on the morphology and particles sizes of the synthesized cobalt nanoparticles was investigated. The pulse height was varied from10 mA.cm^{-2} to 300 mA.cm^{-2}, while the other parameters were kept constant (temperature of 25°C, pulse frequency of 8 Hz, 0.4 M boric acid, pH 3 and 1.37 g/l saccharine). The morphology and particle size of produced cobalt samples were studied by SEM. Figure 3 shows the SEM images of the obtained cobalt samples at different pulsed current amplitudes.

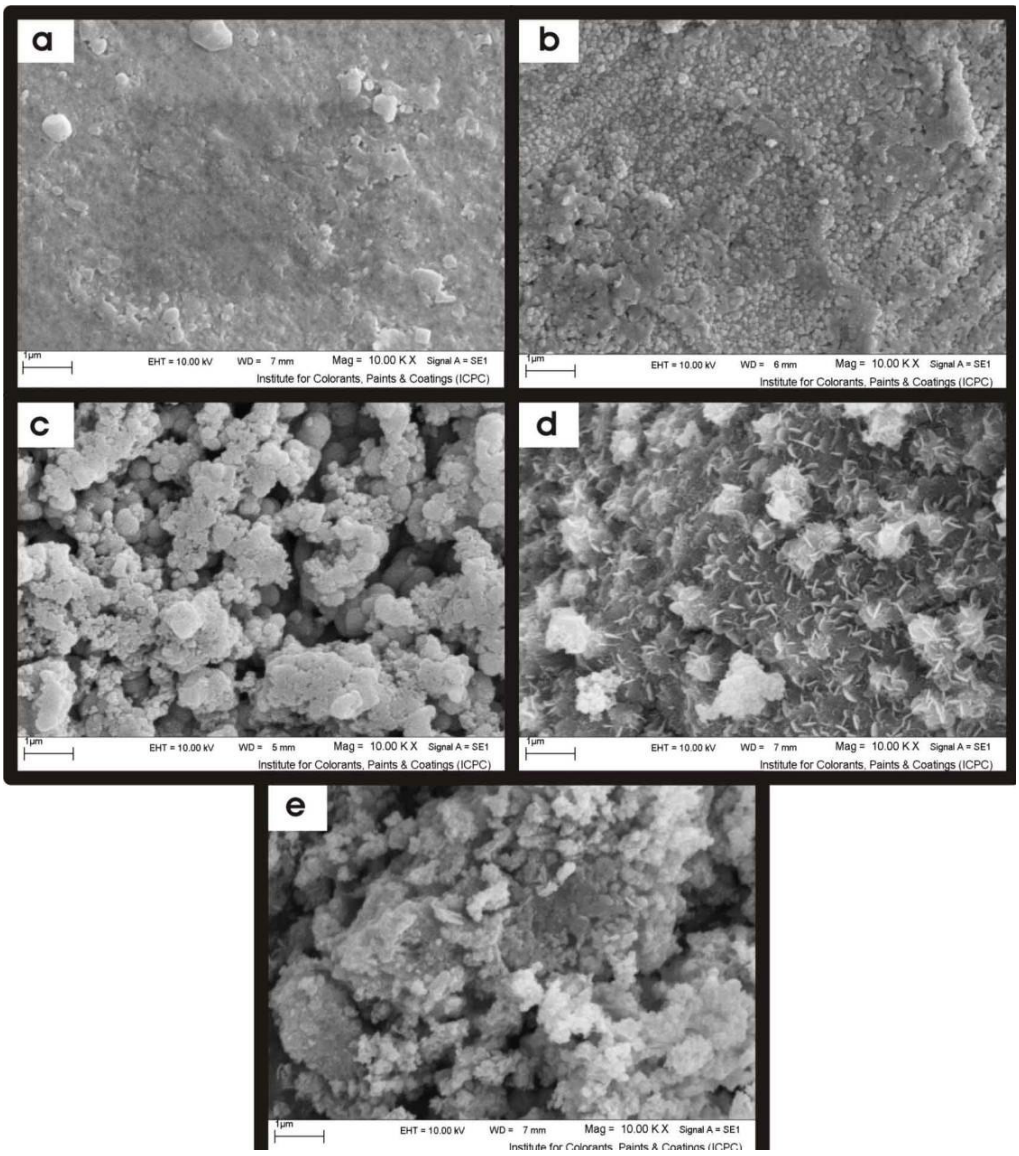

Figure 3. SEM images of cobalt samples synthesized at different pulsed current amplitudes; 10 mA.cm^{-2} (a), 80 mA.cm^{-2} (b), 150 mA cm^{-2} (c), 220 mA.cm^{-2} (d) and 300 mA cm^{-2} (e). The other experimental condition were kept.

As it is seen in Fig. 3, the pulse height (current amplitude) of 220 mA.cm^{-2} makes more uniform and smaller nanoparticles than the others. Large and agglomerated particles have been synthesized at lower pulse heights because, the nucleation rate is lower than particle growth rate. The more pulse heights (more than 220 mA.cm^{-2}) make very high synthesis rate thus the produced cobalt sample will be non uniform and agglomerated (Fig. 3e).

3.2. Optimization of pulse frequency

In the present method, each pulse cycle consists of one pulse time and one relaxation time (Fig. 2), and the pulse frequency (f) includes numbers of pulse cycles in the time unit (s). In the current work, the ratio of relaxation time to pulse time is kept constant of 3 therefore, the pulse time (t_{on}) and relaxation time (t_{off}) can be easily calculated from pulse frequency (1 and 2 equations):

$$t_{on(S)} = \frac{1}{4f} \quad (1)$$

$$t_{off(S)} = \frac{3}{4f} \quad (2)$$

In order to investigate the effect of pulse frequency on the morphology and particles size of the produced cobalt samples, the pulse frequency was varied from 0 to 16 Hz at temperature of 25°C, pulse frequency of 8 Hz, 0.4 M boric acid, pH 3, 1.37 g/l saccharine and pulse height of 220 mA.cm^{-2}.

Figure 4 shows the SEM images of cobalt samples of this experimental series. As it is seen from Fig. 4, at simple DC current (without pulse), cobalt particles make more agglomerations. At the absence of pulse, nucleation process and particle growth is continuously performed. At continuous reduction of Co^{2+} ions to cobalt atoms, particle growth and agglomeration rates are more than nucleation rate so that, the obtained sample including large and agglomerated balk particles. At frequency lower than 8 Hz, the synthesis condition is near to that's of without pulse. The nucleation rate is increased as the pulse frequency is increased, while the particle growth rate is decreased so that at the frequency of 8 Hz (Fig 4c), it can be seen that the nanoparticles are smaller and more uniform. The cobalt nanoparticles are changed to short nanorods when the pulsed frequency was increased from 0 to 8 Hz. At higher frequencies, the uniform nanorods are slowly transformed to large crystalline and agglomerated cobalt particles. This concept can be related to this fact that in the higher frequency, relaxation time between two subsequent current pulses is very short so that particle growth and agglomeration processes can be continuously occurred [34-37].

3.3. Effect of synthesis temperature

Among the synthesis parameters, solution temperature had more effect on the phase composition of the produced cobalt samples. Therefore, four samples were synthesized at different

temperatures. The prepared samples were characterized by SEM. Figure 5 shows the SEM images of the cobalt samples which synthesized at 20, 45, 75 and 95 °C. When the electrosynthesis was performed at temperature lower than 45 °C, the reaction rate was very slow and also, the prepared sample was amorphous and agglomerated. At temperatures higher than 45 °C, the synthesis rate is fast, but the prepared samples showed that the higher temperature causes more agglomeration and amorphous percent of samples is increased because, at high reaction rate, nucleation and particle growth processes are not controllable.

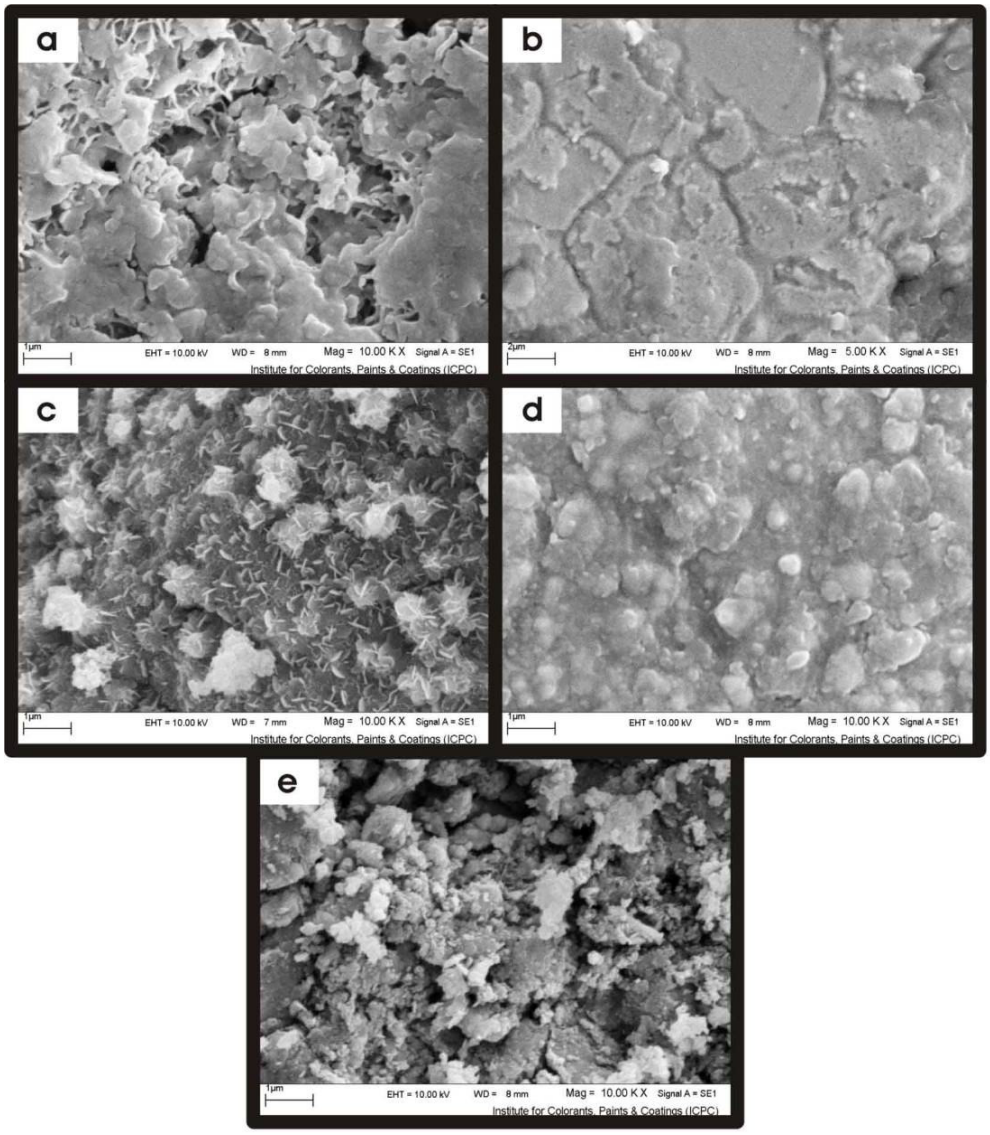

Figure 4. SEM images of cobalt samples synthesized at different pulse frequencies; simple constant current without pulse (a), 4 Hz (b), 8 Hz (c), 12 Hz (d) and 16 Hz (e). The other experimental conditions were fixed (pulsed current amplitude of 220 mA.cm^{-2}, temperature of 25°C, pulse frequency of 8 Hz, 0.4 M boric acid, pH 3 and 1.37 g/l saccharine).

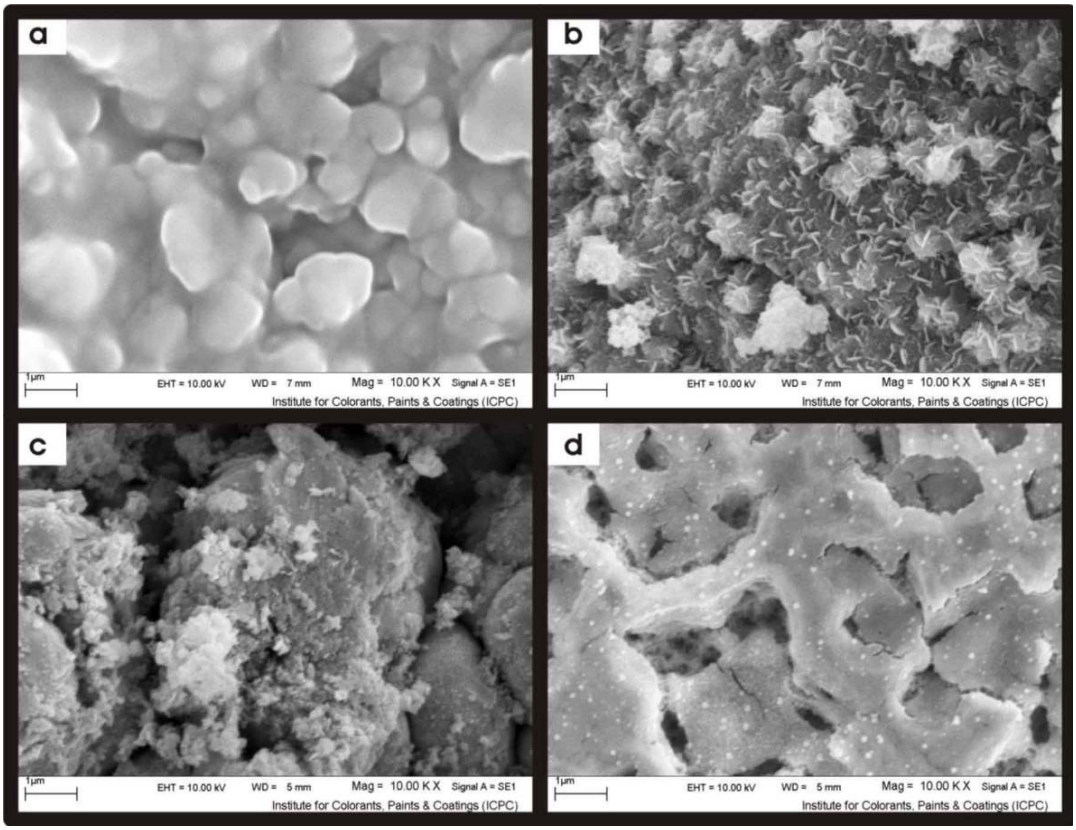

Figure 5. SEM images of cobalt samples synthesized at temperatures of 20 ºC (a), 45 ºC (b), 70 ºC (c) and 95 ºC (d); the other experiment conditions were kept constant.

Three sample synthesized at 20, 45 and 70 °C were also analyzed by XRD. Figure 6 shows the XRD patterns of these samples. As it can be seen in Fig. 6, the solution temperature has important role in composition and phase controlling of the synthesized sample. At 45 °C and lower, pure metallic cobalt can be synthesized. At high temperature (70 ° and more), cobalt will be formed in oxide forms such CoO, Co_2O_3 and CoO_2. Based on XRD results, the metallic cobalt content of samples is decreased when the synthesis temperature is increased from 45 °C up to 70 °C and more. Combining of SEM and XRD results for temperature studies shows that the sample synthesized at 45 °C has uniform morphology, small particles and composition without any impurity.

3.4. Effect of solution pH

At acidic media, hydrogen ions interfered at reduction of cobalt (II) ions. Therefore, it can be expected that pH of synthesis solution is a must important factor on the cobalt electrocrystallization. For this propose, four samples were synthesized at pHs of 1.5, 3, 4 and 5. Figure 7 shows the SEM images of the synthesized samples. The obtained results shows that solution pH of 3 is suitable to synthesize uniform cobalt nanorods. At lower pH (1.5), H^+ reduction was considerable so that the

cobalt sample was completed agglomerated. At higher pHs (4 and 5), reduction rate of Co^{2+} ions were fast so the obtained samples were agglomerated without any nanorod.

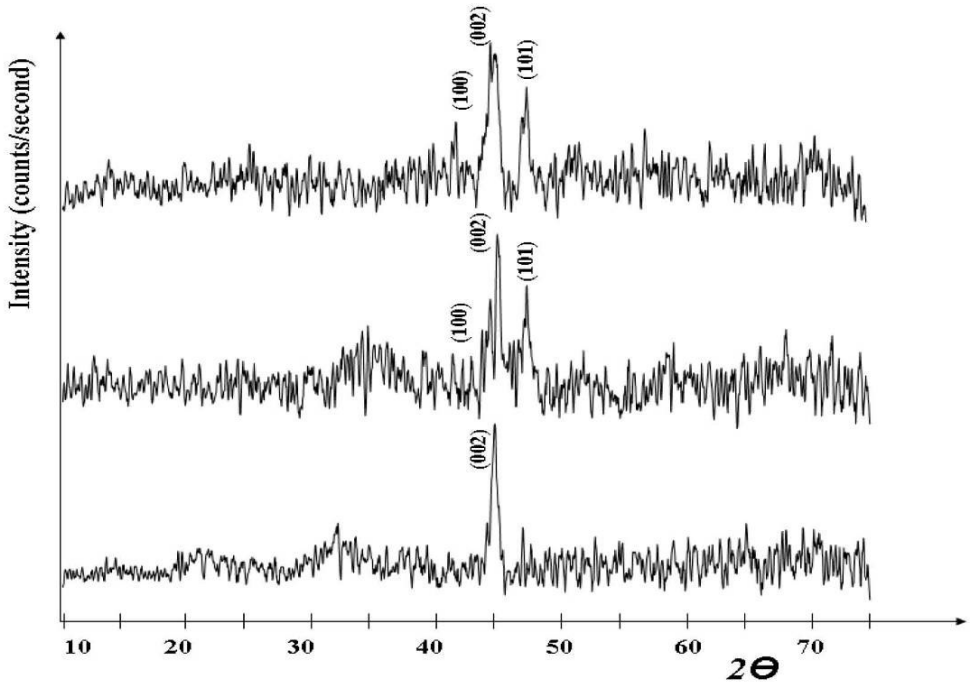

Figure 6. XRD patterns for the samples which synthesized at different temperature of 20 ºC (a), 45 ºC (b) and 70 ºC (c).

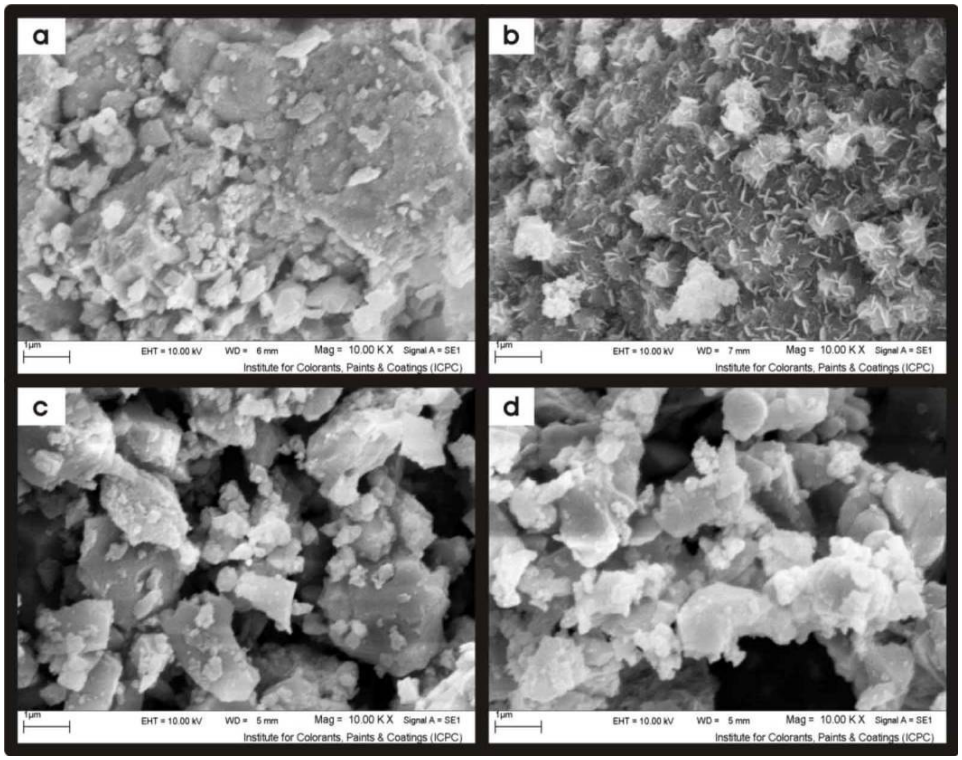

Figure 7. SEM images of samples which synthesized at different pHs 1.5 (a), 3 (b), 4 (c) and 5 (d).

3.5. Effect of cobalt ion concentration

To investigate the effect of cobalt ion concentration, three samples were synthesized at 0.05, 0.2 and 0.5 M Co^{2+} and were studied by SEM (Fig. 8). The SEM images of Fig. 8 shows that Co^{2+} concentration can be changed the morphology and particle size of final product. At lower concentrations, it is expected that the nucleation rate is low so that formation of large particles is acceptable. Fig. 8a shows that cobalt was electrodeposited as nanoflakes in 0.05 M Co^{2+} solution. Because of high particle growth and agglomeration rates, the synthesized sample will be non-porous (Fig. 8c) at higher concentrations.

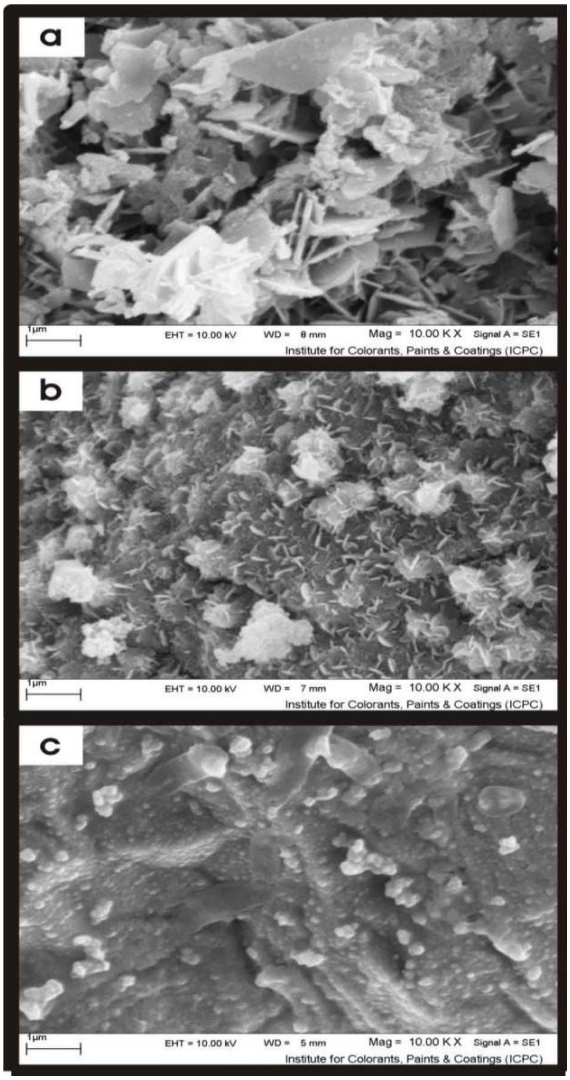

Figure 8. SEM images of samples which synthesized at different concentrations of cobalt (II) sulfate; 0.05 M (a), 0.2 M (b) and 0.5 M (c).

3.6. Effect of synthesis additive

Based on the previous reports, some compounds such as sodium dodecyl sulfate (SDS), cetyltrimethyl ammonium bromide (CTAB), glycerol, saccharin, polyvinyl pyrrolidone (PVP) have been used as structure director to obtain more uniform nanostructures in nano-scale synthesizes. Our initial studies showed that saccharine and PVP are suitable for the electrocrystallization of metallic cobalt in acidic media. The obtained results showed that PVP are more efficient to obtain smaller and more uniform cobalt nanorods (Fig. 9). PVP acts as an efficient complex agent to control the reduction kinetics [35].

Figure 10 shows the effect different concentrations of PVP on the morphology and particles sizes of cobalt. As Fig. 10 shows, uniform cobalt nanorods can be obtained at 1.37 g/l PVP. At this value, PVP concentration is suitable to form a suitable complex with cobalt ions to control reduction kinetics.

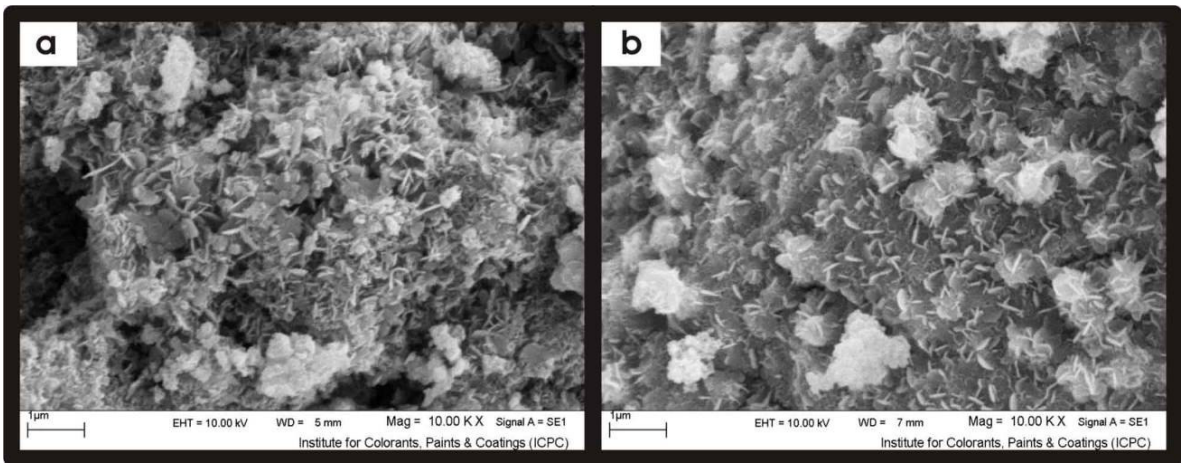

Figure 9. SEM images of samples which synthesized in the presence of PVP (a) and saccharine (b). The 1.37 g/l concentration of each additive was used.

The sample synthesized in optimum conditions was studied by TEM. Figure 11 shows two TEM images of the sample in two different magnifications. Based on SEM images, XRD pattern (according to debye-Scherer equation) and TEM images, the optimum sample includes uniform nanorods with average diameter of 35 nm and average length of 375 nm.

3.7. Effect of ultrasonic irradiation

Ultrasonic irradiation can be change the morphology, phase composition and particles sizes of samples. In this study, effect of ultrasonication during electrosynthesis of cobalt nanorods was investigated. Figure 12 compares the morphology and particles sizes of two cobalt samples which one was synthesized in the presence of ultrasonication and another synthesized without ultrasonication. As

Fig. 12 shows, Ultrasonication causes to reduce the diameter of nanorods and increase their lengths. The ultrasonic waves can be change the particle growth mechanism.

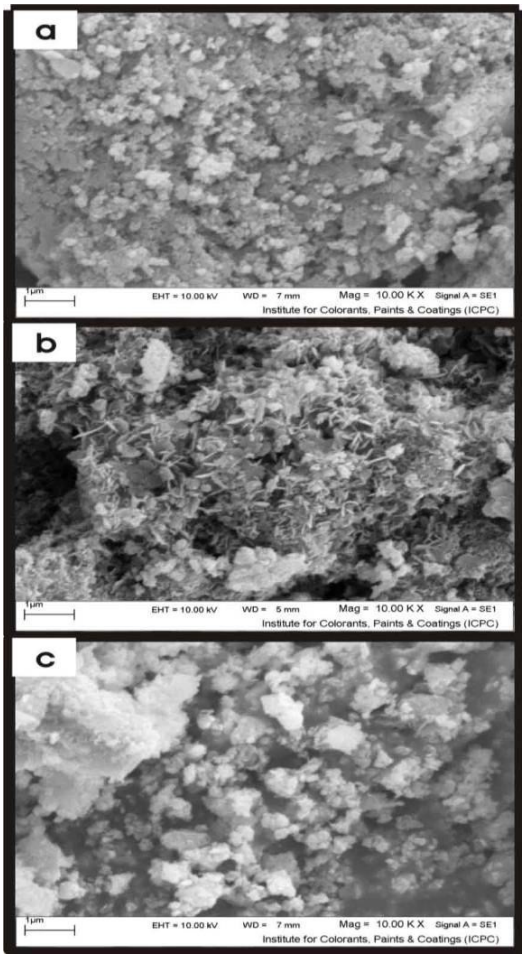

Figure 10. SEM images of samples which synthesized in different concentrations of PVP; 0.69 g/l (a), 1.37 g/l (b) and 2.67 g/l (c).

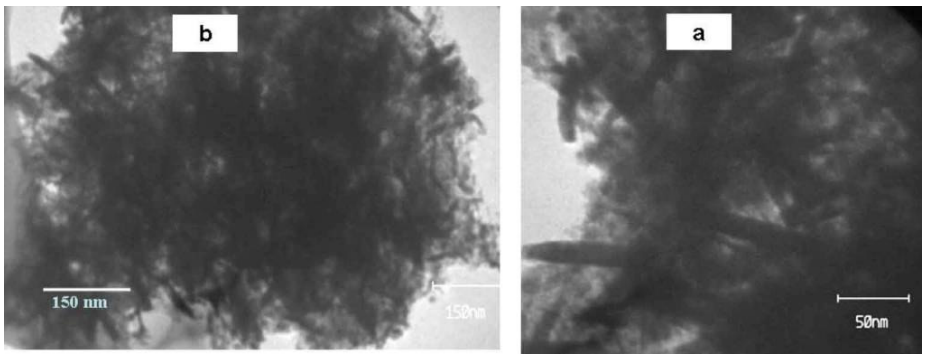

Figure 11. TEM images of sample which synthesized in the optimum conditions in two magnifications. The optimum conditions including pulsed current amplitude of 220 mA.cm^{-2}, temperature of 45°C, pulse frequency of 8 Hz, 0.4 M boric acid, pH 3 and 1.37 g/l PVA and with ultrasonic irradiation during electrodeposition.

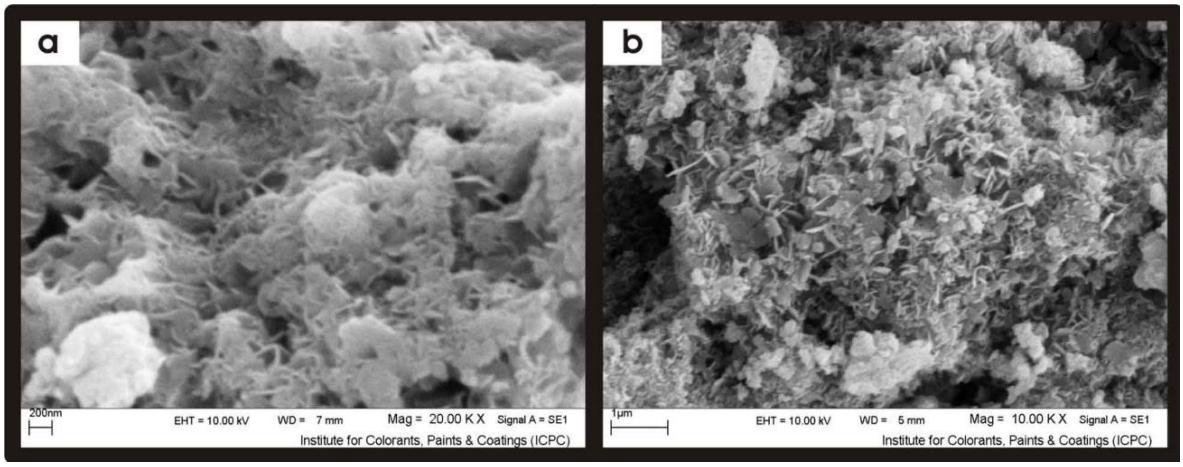

Figure 12. SEM images of samples which synthesized in the presence of ultrasonic irradiation (a) and without ultrasonication (b).

4. CONCLUSIONS

Results indicated which pulsed current electrochemical method could be used as a confident and controllable method for preparation of cobalt nanorods. Metalic cobalt is formed on the stainless steel electrode from a acidic cobalt sulfate solution by use of pulsed current electrochemical method. Pulse time, relaxation time, pulse height, synthesis temperature, pH, structure additive and ultrasonic irradiation are the most important parameters affecting the morphology, particles sizes and phase compositions of cathodic products.

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