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Pulsed Current Electrochemical Synthesis of Co_3O_4 Nanostructures

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This paper is going to describes pulse electrosynthesis of different types of nanostructures of cobalt oxide (Co_3O_4), and provides a detailed analysis of the various factors affecting the morphology, narrowest size distribution and yield. Used the"one at a time" method for investigating and optimized the best result by changing the amount of all experimental effect parameters such as concentration of lithium hydroxide and potassium chloride, type and concentration of additive, bath temperature, values of t_{on} and t o_{ff} and pulse height (current amount). The morphology and particle size of each synthesized sample were investigated by using Energy scanning electron microscopy (SEM), Transmission electron microscopy (TEM) and X-ray diffraction techniques (XRD). The optimum experimental conditions to synthesize cobalt oxide nanorods include lithium hydroxide (0.01 M), potassium chloride (0.1 M), pulsed current of 40 $mA.cm^{-2}$, pulse time(t_{on}) of 0.5 s, relaxation time (t_{off}) of 2 s and solution temperature of 25°C. Based on experimental results, the optimum sample includes pure and uniform cobalt oxide nanorodes with an average diameter of 30 nm and average length of 600 nm. The presence of glycerol (2 g l^{-1}) as agglomeration inhibitor and as structure directly additive in the synthesis solution makes to form uniform cobalt oxide nanoflakes with an average thickness of 25 nm. This approach can be used as efficient, inexpensive and environmentally friendly method for producing of Cobalt oxide nanoparticles.

Keywords: Pulsed current; Cobalt Oxide; Electrosynthesis; Nanorods; Nanoflakes

1. INTRODUCTION

Synthesis of nanoparticles materials is interesting because their wide applications in many sectors of the economy [1,2]. Materials on a scale of nano have different properties with bulk state, due to this fact, researcher are trying to synthesize nanomaterials in different methods [3]. Controlling of size and morphology is an important key in developing nanomaterials and much effort has been attempted for improving these aims. Metal oxides have been greatly applied as a transporter and

support for a different kind of industrial catalysts at high and low temperatures because of extended surface, chemically and thermal stability properties. Cobalt oxide nanoparticles are considering for numerous applications in catalysts [4], adsorbents [5,6], composite materials [7,8], and ceramics [9-11]. Cobalt oxides are particularly interesting due to their prodigious physical and chemical properties, which make its assuring materials widely used in rechargeable Li-ion batteries [12,13], gas sensing [14], catalysis [15], ionic exchanges [16] and others. Cobalt oxide (Co_3O_4) is one of the famous p-type semiconductor magnetic which has a meandering band gap of 1.5 eV[17]. Li et al [18] reported that Co_3O_4 nanomaterial in all types of tube, particles and rods are suitable to use as the anode materials of lithium-ion batteries. Spinel Co3O4 is approved to be the most thermodynamically stable phases of cobalt oxide in atmospheric air below 1164 K, while over this temperature Co3O4 is decomposed into CoO [19]. Structurally, Co_3O_4 with a cell constant of a = 8.0722 A is an important transition-metal oxide and be linked with the regular spinel crystal form depend on a cubic closely-packed formation of oxide ions, in which Co^{2+} ions take place the tetrahedral 8a sites and Co^{3+} ions infuse the octahedral 16d sites [20].

Several methods have been devised in order to prepare cobalt oxide nanoparticles, including powder immobilization [21], chemical vapor deposition [22], sonication [23], thermal salt decomposition [24], sol–gel [25] and electrodeposition [26, 27]. Jana et al. [28] synthesized Co_3O_4 nanoparticles with narrow sizes by the decomposition of Co (II) fatty acid salts at 320 °C. Feng et al. [29] advised a nitrate salt-mediated method for preparation Co_3O_4 nanocubes and the particle sizes were controlled by getting on time. He et al. [30] synthesized Co_3O_4 nanocrystals by controlling the solubility of the product by using appropriate amounts of cobalt nitrate and sodium dodecyl benzenesulfonate in organic solvent of n-octanol. Dong et al. [31] prepared Co_3O_4 nanoparticles by operating ammonia and Co $(CH_3COO)_2 \cdot 4H_2O$ as initial reagents; the incompatible mean size of Co_3O_4 samples was picked up by modifying the ethanol value in the mixed solvent (ethanol and water) and optimizing of the initial concentrations of starting materials. Zou et al. [32] obtained Co_3O_4 nanoparticles through a facile wet chemical oxidation path at normal temperature and pressure by applying 1-n-butyl-3- methylimidazolium hydroxide as an ionic liquid. In all of the mentioned synthesis methods, there are operating difficulty and many other disadvantage in the synthetic route

In thisd study, for the first time, the experimental conditions for the synthesis of Co_3O_4 nanostructures are evaluated. In the literature, there is no report about using this method for preparation of Cobalt oxide nanoparticles. Three most advantages of this method over the other regular methods is the high purity, narrower in size of particle, and short time of formation. This method uses well defined terms to create nanoparticles by size controlling and structure without the need for chemical precursors or heat treatments. [34-39]. It is mentionable that pure Co_3O_4 cannot be synthesized easily by a simple chemical route since this approach typically produces a mixture of CoO and Co3O4. The purpose of this report is to controllably synthesis of cobalt oxide nanomaterials with special morphology by simple method. The resultant Co_3O_4 was consistently analyzed by XRD, SEM, and TEM techniques.

2. EXPERIMENTAL

2.1. Materials

Analytical grade lithium hydroxide, nitric acid and potassium chloride were purchased from Merck. Metallic cobalt was purchased from BDH Company. Saccharin, glycerol, Triton, Cetyl trimethyl ammonium bromide (CTAB), and polyvinyl pyrrolidone (PVP) were obtained from Merck Co. (Germanydouble-distilled water was used in all experiments.

2.2. Instrumentals

Philips scanning electron Microscopy (XL30 model), transmission electron microscopy (TEM, Philips, Model EM-208) and X-ray powder diffraction (Philips X'pert diffractometer) and Cu K_α radiation ($\lambda = 0.15418$ nm) have used for studying of the morphology and the estimate of particle size of all of the samples. A pulse electrolyzer apparatus (BTE 04, Iran) was applied to obtain the reportable current pulses.

2.3. Procedure

2.3.1. Electrode preparation

In order to prepare of cobalt electrodes, we melted pure Cobalt in 1500 ºC and was cast in a wax mould. The structure and dimensions of the electrode which obtained by the casting method is shown in Fig.1.

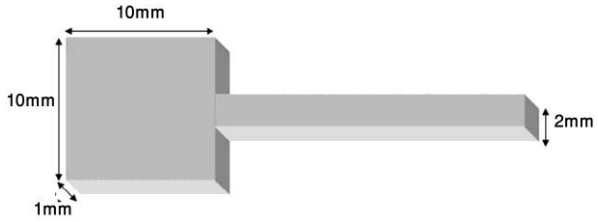

Figure 1. Scheme and dimensions of the casted electrode

2.3.2. Cobalt oxide synthesis

First of all, the cobalt electrodes were put in the diluted HNO_3 for 30s, then rinsed it with double-distillate water to remove any surface oxidized species in contact with air. We used two anodes out of cobalt that were coupled with other cobalt electrode as the cathode of the electrochemical cell. The electrodes were put in the synthesis solution.in a typical synthesis, an aqueous solution of 0.01 M, Li OH was prepared adding 0.1 M KCl as supporting electrolyte, electrocrystallization temperature of

25 °C, 1 $g.l^{-1}$ glycerol as structure director additive. Pulsed current in different rates were applied for the direct anodic oxidizing of cobalt electrode.

"One at a time" method was used to investigate of the effect of all affecting parameters on the synthesis. LiOH and KCl concentrations, type and concentration of additive, solution temperature, pulse time (t_{on}), relaxation time (t_{off}), and pulsed current amplitude were the affecting parameters in synthesis.

3. RESULTS AND DISCUSSION

Co_3O_4 nanostructures were directly synthesized by the pulsed current method on the cobalt electrode in synthesis solution including 0.01 M Li OH and 0.1M KCl, solution temperature of 25 °C, 1 g l^{-1} glycerol as structure director additive, t_{on}=0.5 s and t_{off}= 2 s and t_{off}/t_{on}=4. Pulsed current was supplied by the BTE 04 pulse maker apparatus as it is shown in Fig. 2.

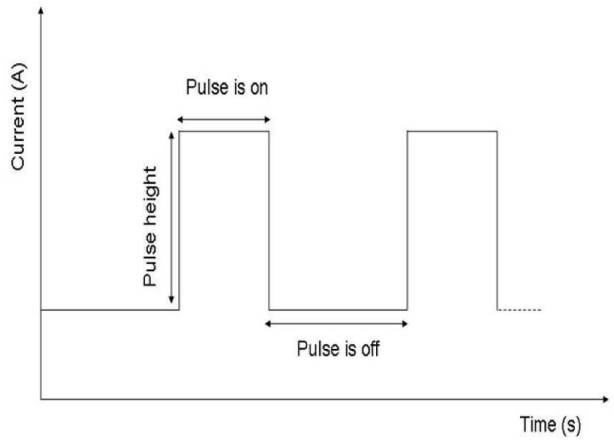

Figure 2. Pulsed current diagram; pulse parameters including pulse time (t_{on}), relaxation time (to_{ff}) and pulse height (current amplitude) are shown on the diagram.

According to Fig. 2, there are 4 variable parameters for a pulse system, including pulse height, Pulse time, relaxation time and pulse time/relaxation time ratio.

During the electrochemical synthesis of cobalt oxide, the following reactions are performed:

On the anode surface:

$Co \longrightarrow Co^{2+} + 2\ e^-$

$Co \longrightarrow Co^{3+} + 3e^-$

On the cathode surface:

$2H_2O + 2\ e^- \longrightarrow H_2 + 2\ OH^-$

Overall reaction:

$3\ Co + 8\ OH^- \longrightarrow Co_3O_4 + 4\ H_2O + 8\ e^-$

In this work, the effect of each effective parameter was investigated and optimized by "one at a time method".

3.1. The effect of t_{off}/t_{on}

In a first set of experiment, the effect of t_{off}/t_{on} ratio was investigated on the particle size of the synthesized Cobalt oxide. The importance of this parameter was noted in some previous reports [34,35]. For this part of experiments for investigating the best amount of t_{off}/t_{on}; six synthesis was carried out at different value of t_{off}/t_{on} while the other parameters were kept constant. Figure 3 shows the SEM images of the prepared samples at different ratios of t_{off}/t_{on} . The ratio of t_{off}/t_{on} changes mechanism, particle growth and agglomeration rates of yield formation. As Fig. 3 shows, the ratio of t_{off}/t_{on} is a strong parameter which can affect on the morphology and particle size of nanoparticles synthesized. An increase in the ratio of t_{off}/t_{on} was observed when the amount of this parameter increasing from 1 to 4; uniformatiy in prepared particles increase too. At a higher ratio than 4, nanorods are converted to non-uniform particles. At a higher ratio of t_{off}/t_{on} (more than 4), the relaxation time between two successive pulses is very long, so that the nanoparticles synthesized have redecorated and get out of their morphology. The obtained results are consistent with previously reports [34,35].

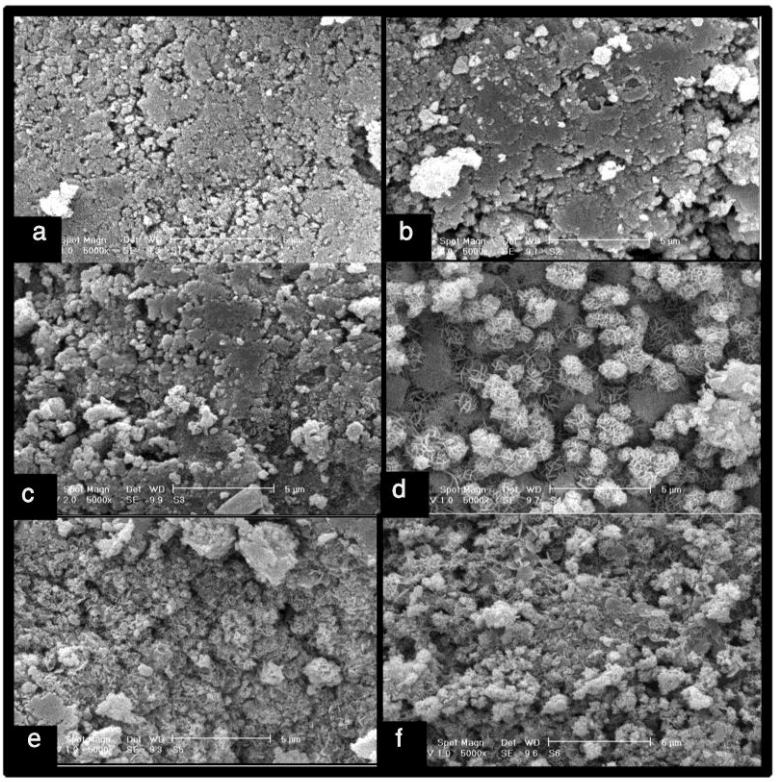

Figure 3. SEM images of the six cobalt oxide samples synthesized under different amounts of t_{off}/t_{on} ratios: 0 (a), 0.5 (b), 1 (c), 2 (d), 3 (e) and 4 (f).

3.2. The amount of t_{on} and t_{off}

In pulsed current method, the t_{on} and t_{off} values for materials are different and depends on the kinetics of nucleation and growth of compounds[35,36]. To investigate the effects of amounts of t_{on} and t_{off}, six synthesis was carried out at different amounts of t_{on} and t_{off} (according Table 1) and were studied by SEM (Fig. 4). The SEM images of Fig. 4 shows that the amount of t_{on} and t_{off} can be changed the morphology and particle size of the final product.

Table. Different values of t_{on} and t_{off} were used in the experiments

Sample	t_{on} (s)	t_{off} (s)
a	0.1	0.4
c	0.2	0.8
c	0.5	2
d	0.75	3
e	1	4
f	2	8

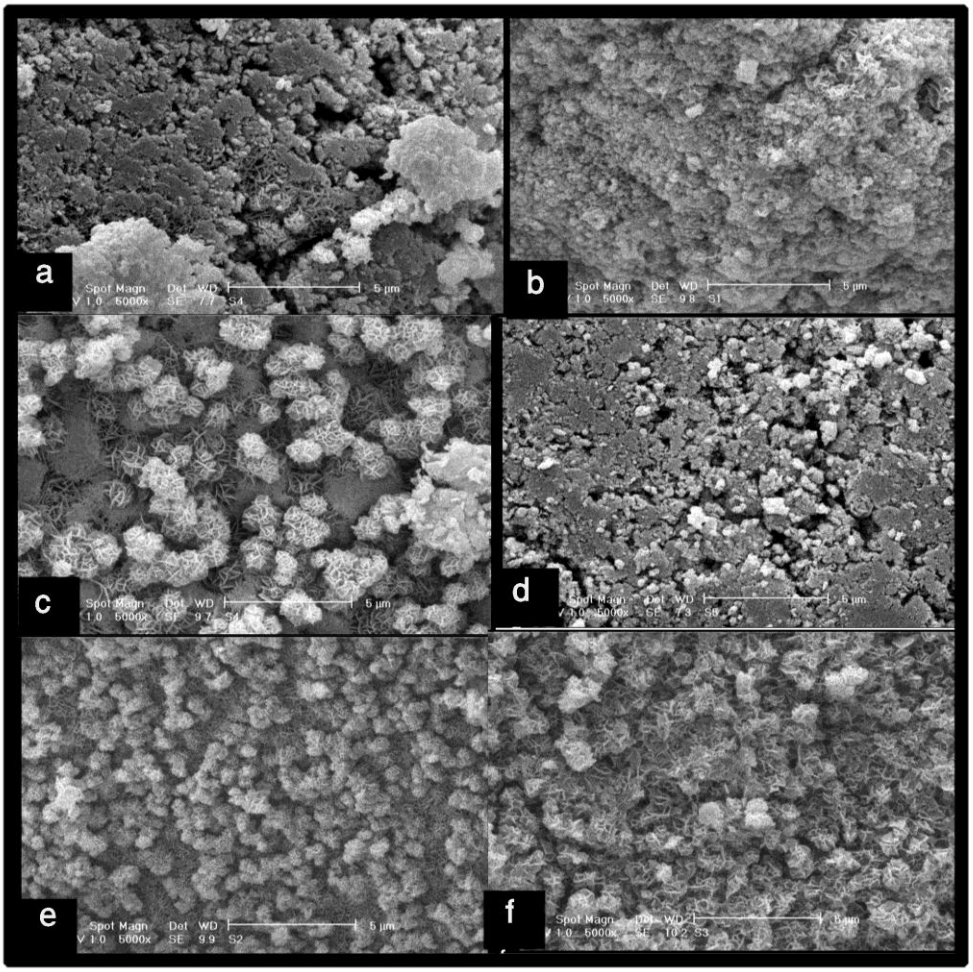

Figure 4. SEM images of cobalt oxide samples were synthesized at different amounts of t_{on} and off according to Table 1.

To get more information on the optimum amount and effect of ton and t_{off} on the morghologhy, seven experiments were carried out in different value while the other parameter were kept constant. As expected, this parameter play important role in particles size and morphology. By increasing of the amount of it $_{off}$ from 0.4 to 2 s uniformity was increased. By getting bigger amount of t_{off} from 2 to 8 was observed that the regular nanorods steadily converted to large crystalline. The obtained results probably confirmed the fact that describes in short relaxation time, there is not enough time for terminating the cycles. Them could cause the new synthesis cycle (according to the new pulse) starts before the ending of the previous synthesis cycle (according to the previous pulse). In these series of experiments the amount of other were set according temperature of 25ºC, t_{off}/t_{on} of 4, pulsed current of 41 mA.cm^{-2}, lithium hydroxide and potassium chloride concentration respectively 0.01, 0.1 M.

3.3. Pulsed current amplitude

As previous reports shows [34-38], the current density is the main factor in the electrochemical synthesis and depends on the nature of synthesized material.

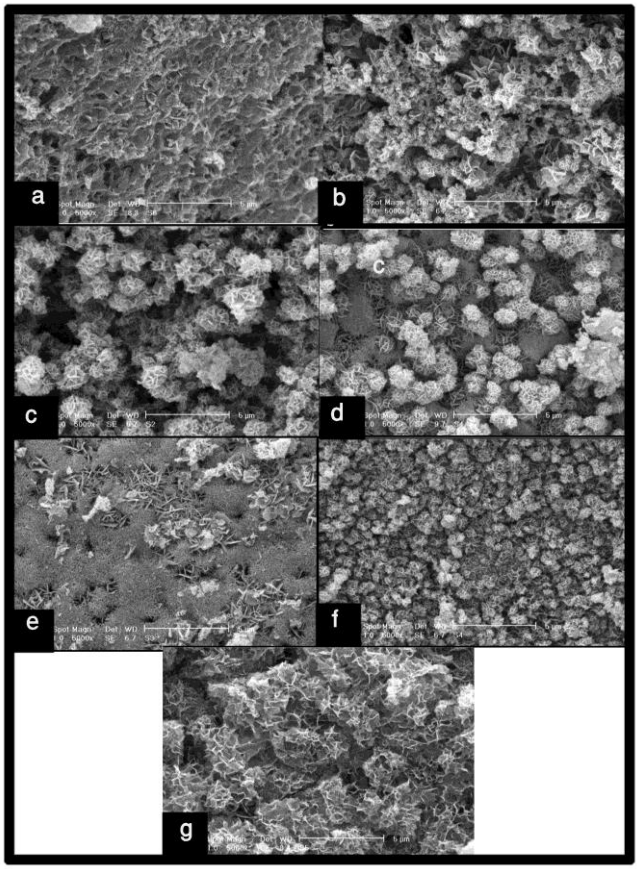

Figure 5. SEM images of different cobalt oxide samples which synthesized at different current densities; a (5 mA.cm^{-2}), b (20 mA.cm^{-2}), c (30 mA.cm^{-2}), d (40 mA.cm^{-2}), e (85 mA.cm^{-2}), f (125 mA.cm^{-2}) and f (210 mA.cm^{-2}).

In order to get more information about the influence of pulse current range (pulse altitude or current density) on the morphology and particle size, the pulse height was applied from 4 to 208 $mA.cm^{-2}$ .As always the other parameters were kept constant to explore the effect of pulse current (temperature of 25ºC, t_{off}/t_{on} of 4, t_{on} of 0.5 s and t_{off} of 2 s, 0.01 M lithium hydroxide and 0.1 M potassium chloride). The results summarized in Figure 5.

As it is seen in Fig. 5, uniformity in nanoparticles observes in the pulse height (current amplitude) of 401 $mA.cm^{-2}$. At lower pulse heights amorphous and agglomerated particles have been synthesized. It is happening when the nucleation rate goes down relative to particle growth rate. The use of elevated currents altitude causes to drop conformity and get larger particle sizes. The result obtained definitely are related to the fact that the claims in the electrochemical pulse system, particle blooming and cluster rates increase as the pulse height increases.

3.4. Temperature studies

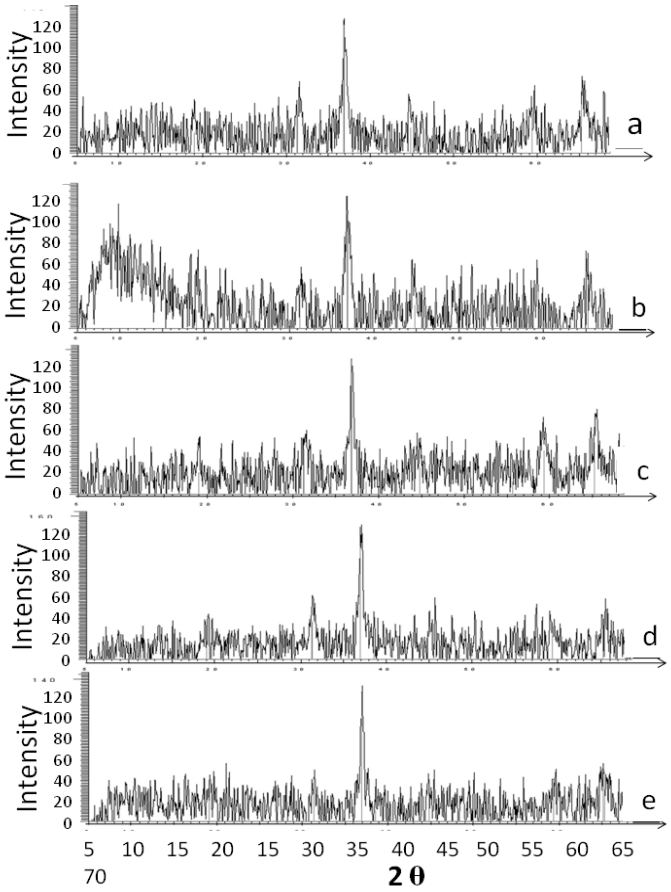

Figure 6. XRD patterns of cobalt oxide samples were synthesized at different solution temperatures; a (0 ºC), b (25 ºC), c (45 ºC), d (75 ºC) and e (95 ºC).

Temperature is one of the key important factors in the synthesis of nanoparticles. In order to investigate the influence of heating and cooling process in the synthesis of cobalt oxide nanoparticles, the solution temperature was cooled by ice-bath to 0 ºC or heated. Five synthesizes were carried out at temperatures of 0, 25, 45, 75 and 95 ºC while other parameters were kept constant (pulsed current of

40 mA.cm^{-2}, t_{off}/t_{on} of 4, t_{on} of 0.5 s and t_{off} of 2 s, 0.01 M lithium hydroxide and 0.1 M potassium chloride).

Table 2. Particle sizes of the cobalt oxide samples were calculated based on XRD data

Sample	2 θ (ºC)	Particle size (nm)
a	35	25
b	35	23
c	35	35
d	35	45
e	35	30

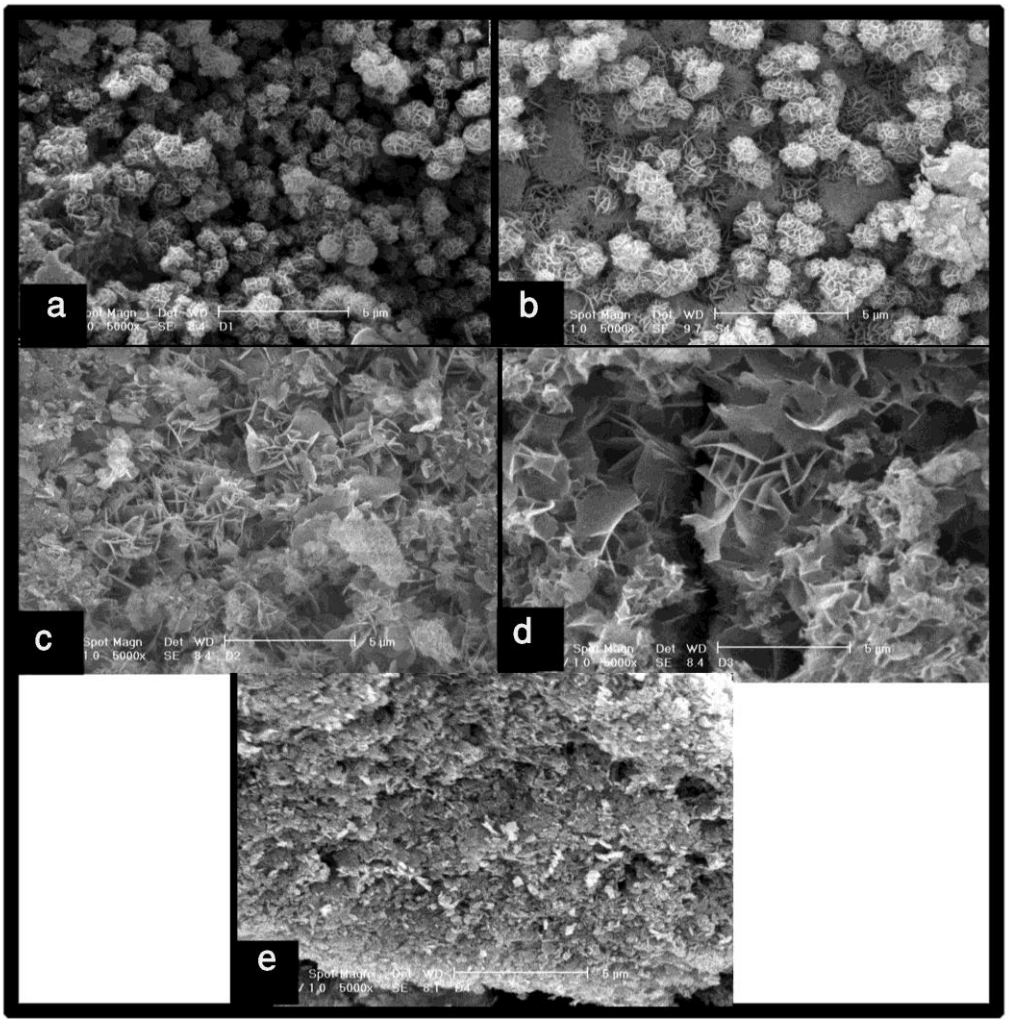

Figure 7. SEM images of different cobalt oxide samples were synthesized at temperatures of (0 ºC), b (25 ºC), c (45 ºC), d (75 ºC) and (95 ºC).

The X-ray powder diffraction pattern of nanoparticles product is shown in Figure 6. As it is obvious from XRD patterns shown in Fig. 6, only Co_3O_4 nanoparticles can be formed at different

temperatures. The average crystallite size was determined from the full width at half maxima (FWHM) of the maximum peak using Debye-Scherrer formula. The calculated data were shown in Table 2.

Therefore, SEM was performed to research the morphology and particle size of the samples prepared at different temperatures for choosing an ideal temperature worth. The cobalt oxide nanoparticles morphology that was examined by SEM is shown in Figure 7. The SEM images (Figure 7) revealed that 25ºC is the most optimum temperature to yield the smallest size and most uniform particles. The results showed that at temperature of 25ºC, rate of growing and nucleation are satisfactory for initiating more uniform particles. Based upon the acquired data from Figs 7, the temperature of 25ºC is the peak for the synthesis of the uniform nanostructures and the XRD patterns confirmed this result.

3.5. Lithium hydroxide concentration

To get more information about the role and the optimum amount of concentration of lithium hydroxide on the morphology of cobalt oxide nanoparticles synthesized, the effect of this parameter was investigated while the other parameter were kept constant. In this phase, lithium hydroxide concentrations fluctuated from 0.001 to 0.1 M. Each procured sample was studied by SEM to investigate the morphology and particle size. In 0.001 M hydroxide ion, the average diameter of the cobalt oxide nanorods is smaller than those of 0.01 M but, the synthesis rate is slow and the sample precipitation is low.

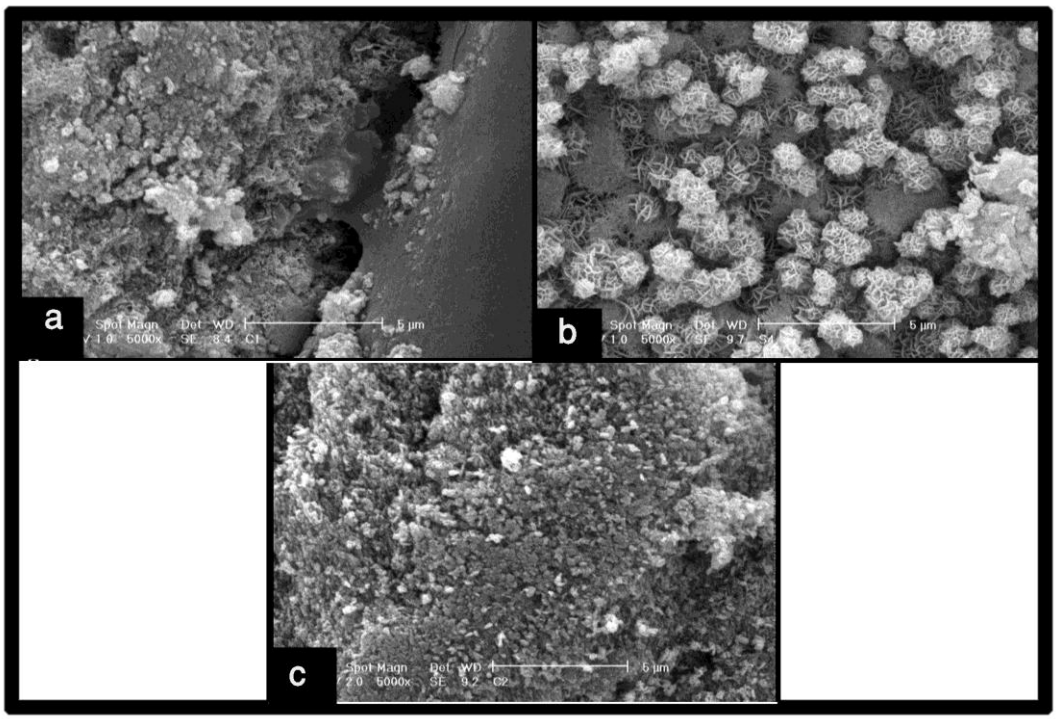

Figure 8. SEM images of three cobalt oxide samples were synthesized in different concentrations of lithium hydroxide; a (0.001 M), b (0.01 M) and c (0.1 M)

By using a higher concentration of hydroxide ion, the nucleation rate is strongly increased so that, crustal growth is not completed, cobalt oxide nanorods are not formed, and the precipitated sample consisting smaller nanoparticles. Based the mentioned facts, 0.01 M hydroxide can be used in future synthesis to prepare uniform cobalt oxide nanorods. Figure 8 shows comparative samples that synthesized in different amount of Lithium hydroxide and constant amount of other parameters (pulsed current of 41 $mA.cm^{-2}$, temperature of 25ºC, t_{off}/t_{on} of 4, t_{on} of 0.5 s and t_{off} of 2 s and 0.1 M potassium chloride).

3.6. Potassium chloride concentration

By using potassium chloride, which acts as supporting electrolyte, Co3O4 nanopartocles were obtained. In the direction of investigating the effect of potassium chloride concentration, this parameter was swinged from 0.01 to 1 M and the amounts of other parameter were kept constant. SEM was used to probe the morphology and particle size of each sample. As it can be seen in Fig. 9. According to Fig.9, the potassium chloride as ionic strength adjusting agent can change the crystal growth mechanism and change finally the sample morphology. In all three samples, cobalt oxide nanorods can be seen, but the 0.1 M potassium chloride makes more uniform nanorods.

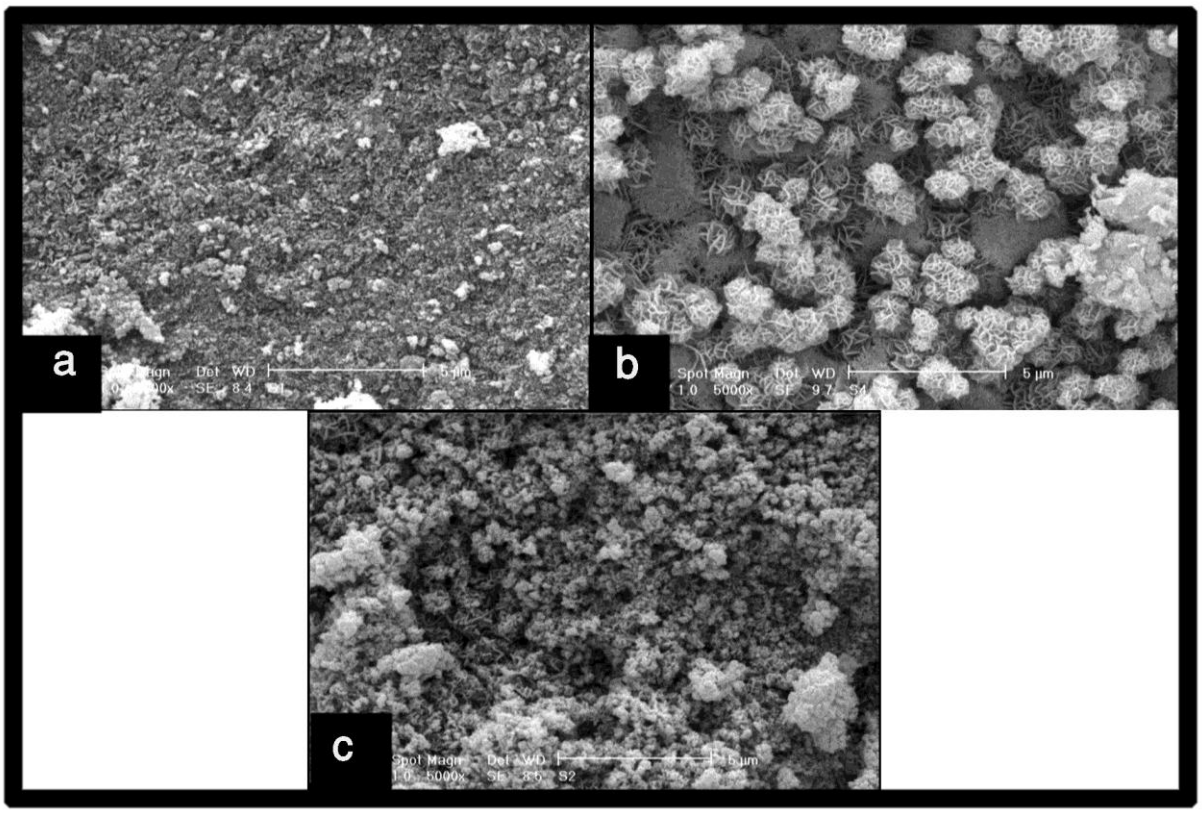

Figure 9. SEM images of three cobalt oxide samples which prepared in 0.01, 0.1 and 1 M potassium chloride.

Based on the presented data, the optimum conditions to synthesize uniform cobalt oxide nanorods including lithium hydroxide (0.01 M), potassium chloride (0.1 M), pulsed current of 40 $mA.cm^{-2}$, pulse time(t_{on}) of 0.5 s, relaxation time (t_{off}) of 2 s and solution temperature of 25°C. The synthesized sample in the above mentioned state was investigated by TEM image. Figure 10 shows the TEM image of the cobalt oxide nanorods. TEM images show that the sample includes nanorods with a normally thickness of 30 mm and length close to 1000 nM .

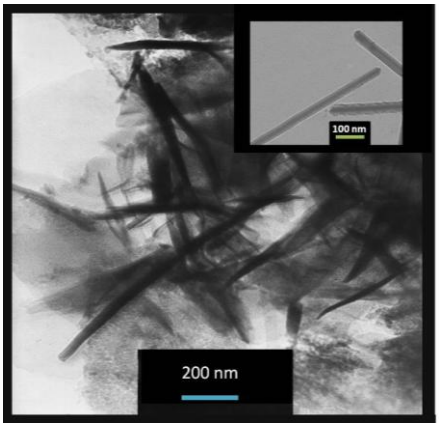

Figure 10. TEM of cobalt oxide nanorods

3.7. Effect of synthesis additive

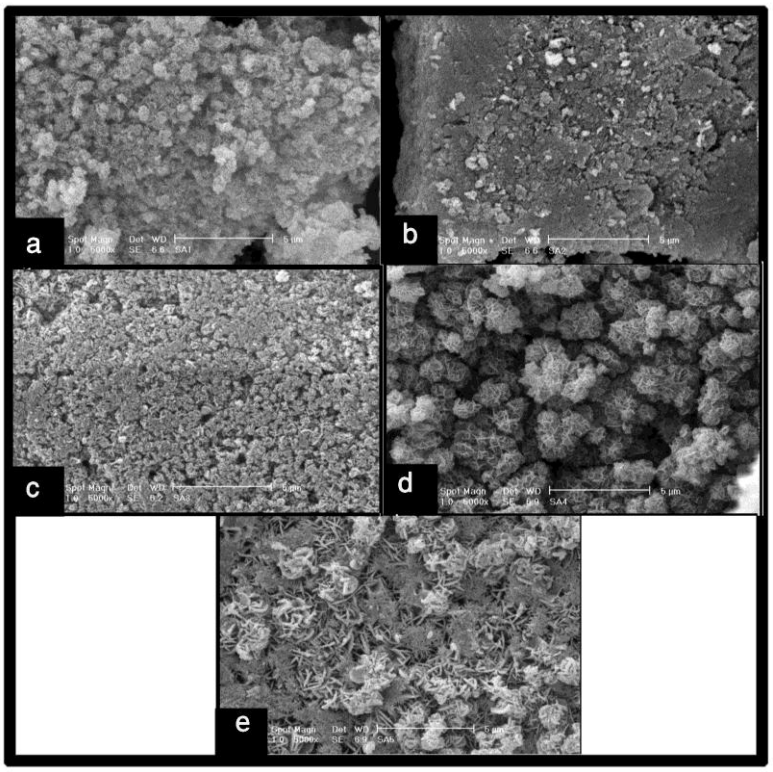

Figure 11. SEM images of cobalt oxide samples were synthesized in the presence of 2 $g.L^{-1}$ CTAB (a), PVP (b), Triton (c), SDS (d) and Glycerol (e).

Normally to avoid agglomeration and get better results have to apply the surfactants through or afterward the synthesis. A number of approaches have been created to cover nanoparticles. In situ and after synthesis coatings are two famous methods. Within in situ method, during the process, the synthesized nanoparticles are covered. Therefore, the particle development can be controlled [40]. The after synthesis covering technique contain of conjoining the surfactant molecules onto the sample particles once synthesized [41,42].

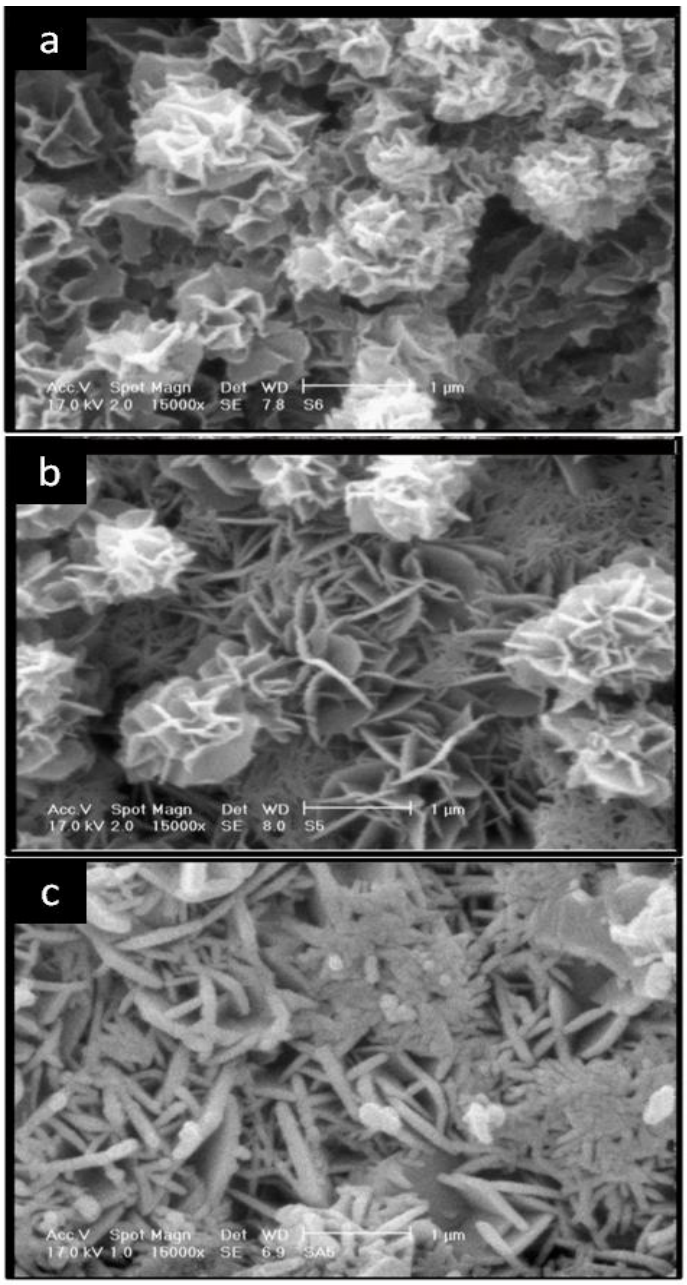

Figure 12. SEM images of Co_3O_4 samples were synthesized in the presence of glycerol with different concentrations of 1 (a), 2 (b) and 3 $g.l^{-1}$ (c).

Based on the previous reports, some cationic, anionic and nonionic surfactant such as sodium dodecyl sulfate (SDS), cetyltrimethyl ammonium bromide (CTAB), glycerol, saccharin, polyvinyl

pyrrolidone (PVP) have been operated as structure directly to obtain more uniform nanostructures. According to our initial studies, except PVP other surfactants were acceptable for the electro-crystallization of cobalt oxide nanoparticles. SEM images of all samples synthesized in the presence of different additives were shown in Fig. 10. The obtained results showed that glycerol are more efficient to obtain smaller and more uniform cobalt nanorods (Fig. 11). Glycerol acts not only as an agglomeration inhibitor, but also acts as an efficient complex agent to control the anodic oxidation kinetics of cobalt [43].

To investigate the effect of additive concentration, three synthesis was done in the presence of glycerol with concentrations of 1, 2 and 3 $g.L^{-1}$. Figure 12 shows the SEM images of three cobalt oxide samples were synthesized in the different concentration of glycerol as an agglomeration inhibitor and as an effective structure director. As Fig. 12 shows, glycerol with an initial amount of 2 $g.l^{-1}$ acts as a suitable additive to synthesize uniform Co_3O_4 nanoflakes. At this value, the number of glycerol molecules is enough to control the particle growth direction and to prevent the agglomeration of the formed nanoflakes.

4. CONCLUSIONS

Aim of this research was to study pulsed current electrochemical method as a confident and controllable technique for the electrosynthesis of different nanostructures of Co_3O_4 such as nanoparticles, nanorods and nanoflakes. Changing of synthesis conditions can easily change the morphology and particle size of the synthesis product. The presence of glycerol as an agglomeration inhibitor and also as a structure director of crystal growth makes to grow the cobalt oxide in nanoflakes form.

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