Pulsed Current Electrochemical Synthesis of Cadmium Sulfide Nanofibers

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This work describes electrosynthesis of cadmium sulfide. A cadmium sulfide/cadmium nanocomposite in nanofibers form was synthesized by using, cadmium chloride (0.2 M), sodium thiosulfate (0.02 M) as precursor by the pulsed current of 100 mA cm^{-2} with a frequency of 8 Hz at solution temperature of 50℃. Cd content of the samples can be decreased by using of higher synthesis temperature. A pure nanostructured cadmium sulfide can be synthesized at temperature of 150℃. The morphology and particle size of each synthesized sample were studied by SEM, TEM and XRD. The cadmium sulfide nanopowder synthesized in the optimum conditions has excellent uniform nanofibers with a diameter range of 80 to 100 nm (average diameter of 90 nm) and length of 5μm to 7 μm. The obtained results indicate that the pulsed current electrochemical method can be used as a confident and controllable method for the preparation of cadmium sulfide nanofibers. Based on XRD studies, the samples were contaminated with cadmium impurity, which impurity was decreased by increasing of synthesis temperature. At solution temperature of 150℃ (in electrohydrothermal bomb), cadmium sulfide was synthesized without any impurity of metallic cadmium.

1. INTRODUCTION

Much interest has been shown in cadmium sulfide (CdS) because of its important properties. The metal chalcoginides like CdS is important material due to its intrinsic properties of a narrow band gap, good chemical stability and ready preparation, and their technological applications, ranging from

microelectronics to non-linear optics, optoelectronics, catalysis, optical windows for solar cell and photo-electrochemistry [1-7].

Currently there has been a lot of interest to explore the optoelectronic applications of CdS semiconductor in areas such as photoelectrocatalysis, biology and communication. However, the optoelectronic properties of CdS nanomaterials are strongly influenced by their morphologies and structures. Therefore, it is very important to explore the simple and mild methods to achieve the controlled synthesis of inorganic semiconductor nanomaterials.

Cadmium sulfide is a well-known semiconductor that can be prepared by different chemical or physical methods. A number of methods have been developed to synthesize the CdS nanomaterials with different morphologies and structures such as nanocrystals, quasi-nanospheres, nanorods, nanowhiskers, nanowires, nanobelts and nanotubes.

In recent years, a large number of techniques have been developed to prepare nanoparticles. Among these techniques, precipitation in the reverse micellar system has been expected to be a useful methodology for the production of nanoparticles, such as CdS nanoparticles. Thus, the prepared nanoparticles need to be recovered from reverse micelles and immobilized onto stable supports, in order to be utilized as catalysts and photocatalysts essentially [8-15]. Penner and his group have studied the electrochemical/chemical (E/C) method to deposit CdS (and other semiconductor) nanocrystals and nanowires on highly oriented pyrrolytic graphite (HOPG) substrates [16–19]. E/C method for CdS preparation consists of two steps: (1) electrochemical deposition of Cd, and (2) annealing of Cd in H2S atmosphere to convert Cd into CdS. The advantage of E/C method is that good size monodispersity can be achieved over a range of particle diameters because the diameter of CdS nanocrystalsis determined by the diameter of Cd^0 precursor nanoparticles, and these electrochemically deposited metal pre- cursor particles possess a narrow size distribution [16].

One-dimensional (1D) semiconductor nanostructures have drawn intensive interest due to their fundamental research and potential applications in fabrication of nanoscale devices. CdS, one of the very important II–VI group semiconductors, plays an important role in optoelectronic devices such as lasers, light emitting diodes and solar cells. In recent years, considerable efforts have been made to synthesize CdS nanostructures by several methods such as electrochemical synthesis [20, 21], chemical synthesis [22], solvothermal route [23], thermal evaporation [24], chemical vapor deposition [25], vapor–liquid–solid growth [26] etc.

One way to make a nanowire (NW) is etching (dry and wet) process, by which variety of materials such as GaAs, Si, and rhenium [27–30] has been fabricated. Beside this, several approaches have been used for nanowire fabrication using chemical etching technique. Ling-Min et al. [31] have synthesized CdS/SiO2 nanowire arrays and CdS nanobelts by thermal evaporation of mixture of CdS and CdO powders with highly selective etching occurring on the silicon substrate surfaces. Maynor et al. [32] have created unique diameter-modulated GaN nanowires by reaction of the wires of different diameters with 1 M hydrochloric acid (HCl). Dongre and et al reported the synthesis of CdS nanowires by a simple chemical bath deposition process followed by chemical etching technique [33].

Electrochemical methods have been used as efficient and controllable techniques for the synthesis of different nanostructures [16, 34-40]. Nel and et al synthesized cadmium sulfide

nanostructures by using electrochemical deposition method [41]. They used constant current technique for electrosynthesis of cadmium sulfide nanostructures.

Based on our best knowledge, there is not any report about using of electrochemical pulse method for preparing of cadmium sulfide. In the present study, we report a simple way to synthesis cadmium sulfide nanofibers. Cadmium sulfide nanostructures were electrodeposited by applying a pulsed current technique from a cadmium chloride, sodium thiosulfate salts acidic solution containing hydrochloric acid. The synthesized samples were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD).

2. EXPERIMENTAL PART

2.1. Materials

All materials and reagents used in this work were of reagent grade and were produced in 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 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 [42]. The solution temperature was kept constant with usage of a water bath (Optima, Tokyo, Japan). A home-made electrohydrothermal bomb for high temperature and high pressure synthesizes,

A scanning electron microscope with EDX instrument from Philips Co. (XL30) was used for studying of morphology, particle size and surface analysis of the prepared iron nanopowders. X-ray diffraction (XRD) studies were performed by a Decker D8 instrument.

2.3. Procedure

Reagent grade cadmium sulfide and sodium thiosulfate was used as the precursors. The appropriate amounts of cadmium chloride (0.2 M) and sodium thiosulfate (0.02 M) were first dissolved in hydrochloric acid (pH= 2), which was then heated to the desired temperature. The obtained solution was used in the electrochemical synthesis cell with two platinum cylindrical electrodes as anode and cathode. The pulsed current of 100 mA cm^{-2} was applied for 2 h. After electrosynthesis, the obtained precipitate of cadmium sulfide/cadmium nanocomposie or cadmium sulfide was filtrated from the solution and, washed with water and ethanol. Finally, Washed yield was sonicated in ethanol for 1 h to obtain uniform nanofibers without any agglomerating and other physical adhesions. The sonicated cadmium sulfide was dried at room temperature in inert atmosphere. The morphology, dimension size, and structure of cadmium sulfide nanopowder were studied by SEM, TEM and XRD.

In this method, there are some effective parameters which include pulse amplitude (current amount or pulse height), pulse frequency, cadmium chloride and sodium thiosulfate concentrations, solution pH, and temperature of synthesis solution which were optimized by the "one at a time method".

3. RESULTS AND DISCUSSION

In this procedure, a pulsed current is exerted on the electrochemical solution containing two platinum cylindrical electrodes by the electrical pulse instrumentation. Experimental observations showed that the synthesized cadmium sulfide nanofibers do not stick to the electrode surface in this method. The synthesized particles immediately leave the electrode surface. Therefore, electrode surface is not completely covered by the synthesized particles. In this method, there are some effective parameters which include, pulse amplitude (current amount or pulse height), pulse frequency, cadmium chloride and sodium thiosulfate concentrations, solution pH, and temperature of synthesis solution which were optimized by the "one at a time" method.

Our previous studies showed that the pulsed current method is more effective than the simple constant voltage and simple constant current methods [43, 44] for the synthesis of nanomaterials. The pulsed current electrochemical method can be used as a confident and controllable method for the production of nanoparticles. In the pulsed current method, the current vs. time was applied as shown in Fig. 1.
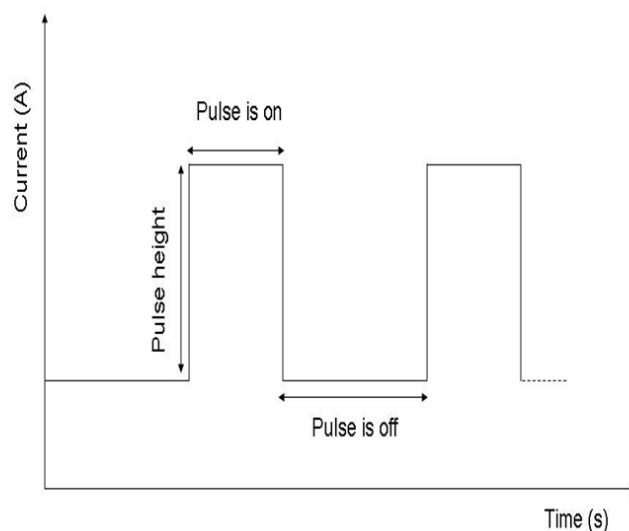

Figure 1. Scheme of the used pulse diagram, including pulse time, relaxation time, and pulse height
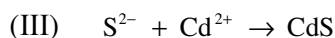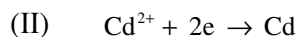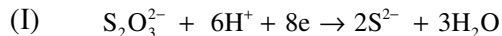
As it can be seen in Fig. 1, the used current pulse has 4 variable parameters: pulse height (current amplitude), pulse time, relaxation time, and pulse frequency. Our initial studies show that the relaxation time/pulse time ratio of 3 is suitable and optimum to obtain a suitable synthesis, thus the ratio 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. Each current pulse contains a "t_{on}" time (pulse time) and a "t_{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 time unit (1 s). At constant ratio of relaxation time/pulse time (which is equal to 3), any variation in pulse frequency makes new pulse and relaxation times.

The pulse time and pulse frequency are two dependent parameters. The pulse time is decreased as the pulse frequency is increased and, it can be calculated from equation 1:

$$(\text{eq. 1}) \qquad t_{on} = \frac{1}{f} \times K$$

In equation 1, t_{on}, f and K are pulse time, pulse frequency and pulse ratio (ratio of pulse time to relaxation time), respectively. With respect to the above mentioned equation, in optimization process, pulse time will be optimized when the pulse frequency is optimized without need to separate step.

At electrochemical synthesis of cadmium sulfide, the following reactions are performed:

$$(\text{I}) \qquad S_2O_3^{2-} + 6H^+ + 8e \rightarrow 2S^{2-} + 3H_2O$$

$$(\text{II}) \qquad Cd^{2+} + 2e \rightarrow Cd$$

$$(\text{III}) \qquad S^{2-} + Cd^{2+} \rightarrow CdS$$

The reactions of I and II are performed on the cathode surface and depend on pulse specifications, thiosulfate ion concentration, pH and temperature. When reaction I and II can be performed together, the final product contains cadmium sulfide/cadmium nanocomposite. Rate constants of reaction I and II depend on the synthesis temperature with different coefficients. The 3rd reaction is a chemical reaction and is performed in the solution. The kinetic and mechanism of the last reaction is strongly depends on cadmium ion concentration, production rate of sulfide ion and solution temperature. Based on the mentioned reactions, morphology and particle size of cadmium sulfide should be depends on all the mentioned parameters.

In this work, the effect of each effective parameter was optimized by "one at a time method". Table 1 shows synthesis conditions of all the optimization experiments. In this Table, all optimization experiments of each parameter were blocked and optimized amount was underlined.

Table 1. Synthesis conditions of optimization experiments

Sample	Pulse height (mA cm^{-2})	Sodium thiosulfate concentration (M)	Cadmium Chloride (M)	pH	Pulse frequency (Hz)	Temperature (°C)
1	**25**	0.02	0.2	2	6	50
2	**100**	0.02	0.2	2	6	50
3	**250**	0.02	0.2	2	6	50
4	**400**	0.02	0.2	2	6	50
5	**550**	0.02	0.2	2	6	50
6	**750**	0.02	0.2	2	6	50
8	250	**0.02**	0.2	2	6	50
9	250	**0.05**	0.2	2	6	50
10	250	**0.1**	0.2	2	6	50
11	250	**0.21**	0.2	2	6	50
12	250	**047**	0.2	2	6	50
13	250	**0.6**	0.2	2	6	50
14	250	0.02	**0.02**	2	6	50
15	250	0.02	**0.09**	2	6	50
16	250	0.02	**0.2**	2	6	50
17	250	0.02	**0.33**	2	6	50
18	250	0.02	**0.47**	2	6	50
19	250	0.02	**0.6**	2	6	50
20	250	0.02	0.2	**2**	6	50
21	250	0.02	0.2	**3.5**	6	50
22	250	0.02	0.2	**5.5**	6	50
23	250	0.02	0.2	2	**0**	50
24	250	0.02	0.2	2	**5**	50
25	250	0.02	0.2	2	**6**	50
26	250	0.02	0.2	2	**8**	50
27	250	0.02	0.2	2	**12**	50
28	250	0.02	0.2	2	**18**	50
29	250	0.02	0.2	2	**24**	50
30	250	0.02	0.2	2	6	**0**
31	250	0.02	0.2	2	6	**25**
32	250	0.02	0.2	2	6	**50**
33	250	0.02	0.2	2	6	**75**
34	250	0.02	0.2	2	6	**95**
35	250	0.02	0.2	2	6	**125**
36	250	0.02	0.2	2	6	**150**

3.1. Pulse height

In order to investigate the effect of pulse current amplitude (pulse height or current density) on the morphology and particle size, the pulse height varied from 25 to 750 mA cm^{-2} was exerted on the electrochemical solution while the other parameters were kept constant (See Table 1). Figure 2 shows the effect of pulse height (current density) on the morphology and particle size of yield cadmium sulfide/cadmium nanocomposite.
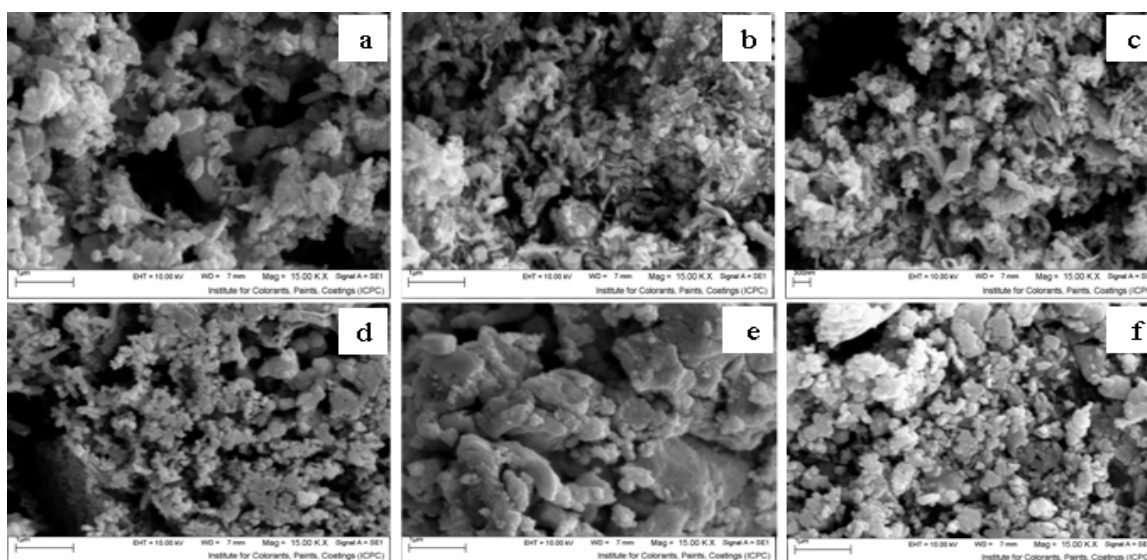
Figure 2. Effect of pulse height (current density) on the on morphology and particle size of cadmium sulfide: (a) 25, (b) 100, (c) 250, (d) 400, (e) 550 and (f) 750 mA cm^{-2}.

As it was shown in Fig. 2, the current density of 100 mA cm^{-2} is a suitable amount to synthesis a powder including more uniform nanostructures. Use of higher currents causes to decrease uniformity and increase particles sizes. This result can be related to this fact that in the electrochemical pulse system, particle growth and agglomeration rates increase as the pulse height increases [42]. At lower current density (25 mA cm^{-2}), particle growth rate is more than nucleation rate so that, a sample is obtained with large particles.
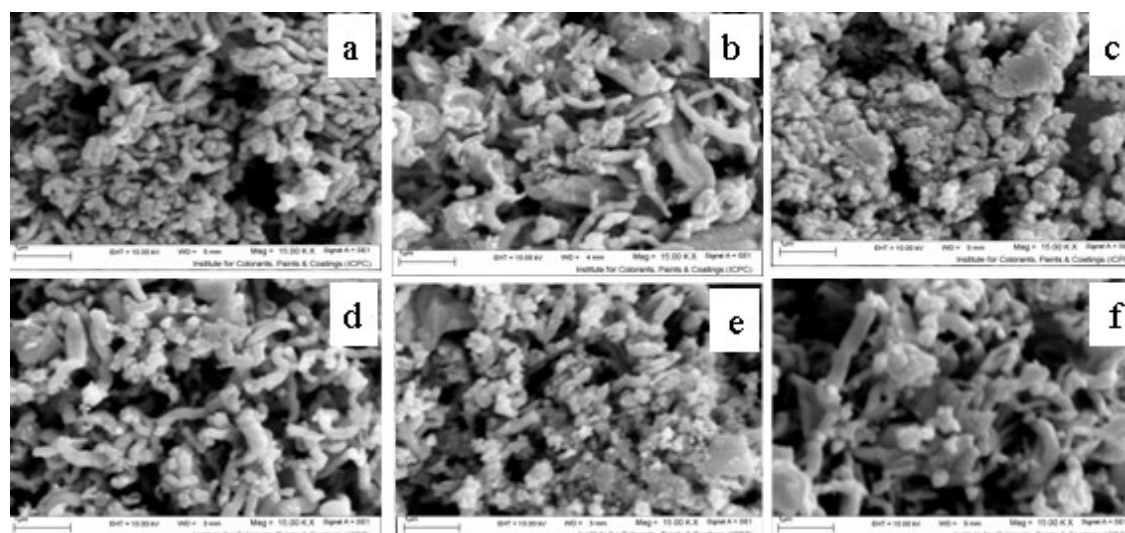

Figure 3. SEM images of the samples which synthesized at different concentrations of sodium thiosulfate: (a) 0.02, (b) 0.05, (c) 0.1, (d) 0.21(e) 0.47 and (f) 0.6 M.

3.2. Thiosulfate ion concentration

In order to investigate the effect of thiosulfate ion concentration, this parameter was varied from 0.02 to 0.6 M. The SEM images of the synthesized samples were shown in Fig. 3. As Fig. 3 shows, the lower concentration makes more uniform and smaller fibers. Particle growth and agglomeration rates are decreased by decreasing of thiosulfate concentration.

It should be mentioned that thiosulfate concentration lower than 0.02 M can not use because at lower concentrations, the amount of the product is very low so that, it can not be filtrated and collected.

3.3. Cadmium chloride concentration

In this step, cadmium chloride concentration was varied from 0.02 to 0.6 M while other parameters were kept (Table 1). Each obtained sample was studied by SEM to investigate morphology and particle size. As Fig. 4 shows, simple nanoparticles in the lowest concentration (0.02 M) change to nanofibers in 0.2 M. This phenomenon can be related to this fact that the kinetic and mechanism of cadmium sulfide/cadmium nanocomposite formation are strongly depend on cadmium ion concentration. At higher concentrations (more than 0.2 M), uniformity of the samples is decreased and, particle growth is increased. Based on the obtained results, much uniform nanofibers of cadmium sulfide/cadmium nanocomposite can be synthesized at 0.2 M cadmium chloride.

Figure 4. SEM images of the samples which synthesized at different concentrations of cadmium chloride: (a) 0.02, (b) 0.09, (c) 0.2, (d) 0.0.33, (e) 0.47 and (f) 0.6 M.

3.4. pH

Based on the reaction 1, synthesis of cadmium sulfide and cadmium sulfide/cadmium nanocomposite is strongly depends on solution pH so, this parameter was varied from 0 to 10. At lower pH than 2, thiosulfate anions are protonated and they can not electrochemically reduce to sulfide ions. At higher solution pH than 5.5, cadmium ions precipitate as cadmium hydroxide. Cadmium sulfide only synthesizes at pH range of 2 to 5.5. Figure 5 shows the SEM images of the samples synthesized at different pHs. As it can be seen in Fig. 5, uniform nanofibers of cadmium sulfide are only seen in pH 2. The solution pH controls mechanism of product formation so that it can change the morphology and particle size of final product. XRD patterns showed that the samples synthesized at higher pH (5.5) contain cadmium hydroxide.
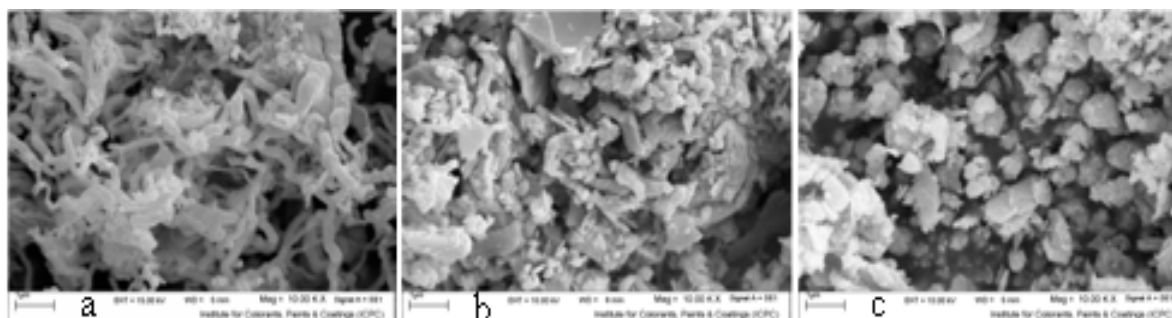
Figure 5. SEM images of the samples which synthesized at different pH of initial synthesis solutions: (a) 2, (b) 3.5 and (c) 5.5.
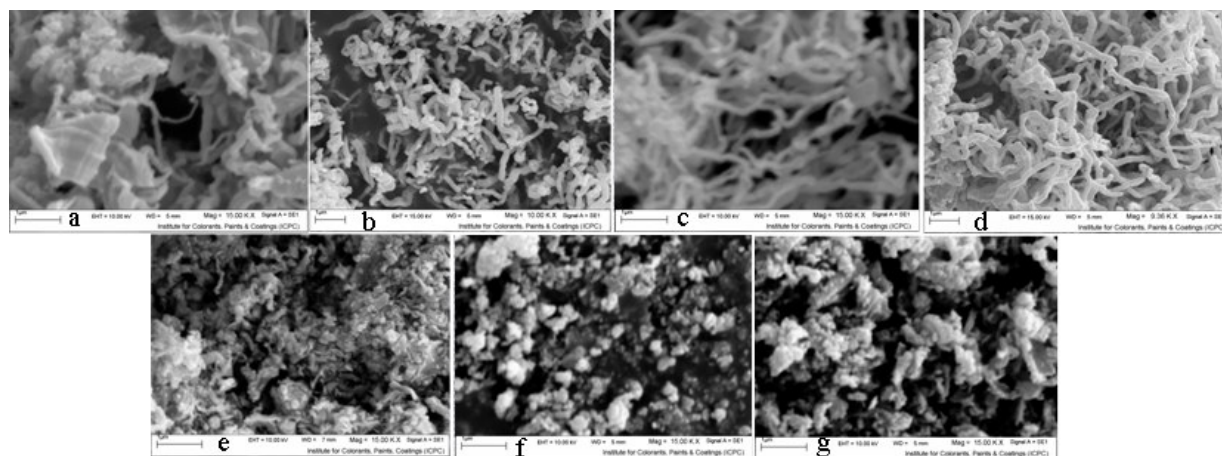
Figure 6. SEM images of the samples which synthesized at different pulse frequency: (a) without pulse, (b) 5 Hz, (c) 6 Hz, (d) 8 Hz, (e) 12 Hz, (f) 18 Hz and (g) 24 Hz.

3.5. Pulse frequency

Seven synthesizes were carried out at different pulse frequencies to investigate the effect of this parameter on the morphology and particle size of samples. Figure 6 shows the SEM images of the

samples synthesized at different pulse frequencies. The pulse frequency changes mechanism, particle growth and agglomeration rates of yield formation.

As Fig. 6 shows, the pulse frequency is a strong parameter which can affect on the morphology and particle size of the yield. Uniformity of the samples is increases by increasing of pulse frequency from 0 to 8 Hz. At higher frequencies, nanofibers are converted to non-uniform particles. Applying the synthesis current in pulse form decreases the nuclear growth also controls mechanism of product formation; thus the uniform nanofibers in powder form are synthesized. At higher pulse frequencies (more than 8 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 thiosulfate ion). For the pulse frequency of 8 Hz, the "on" and "off" durations were 31 ms and 93 ms, respectively.
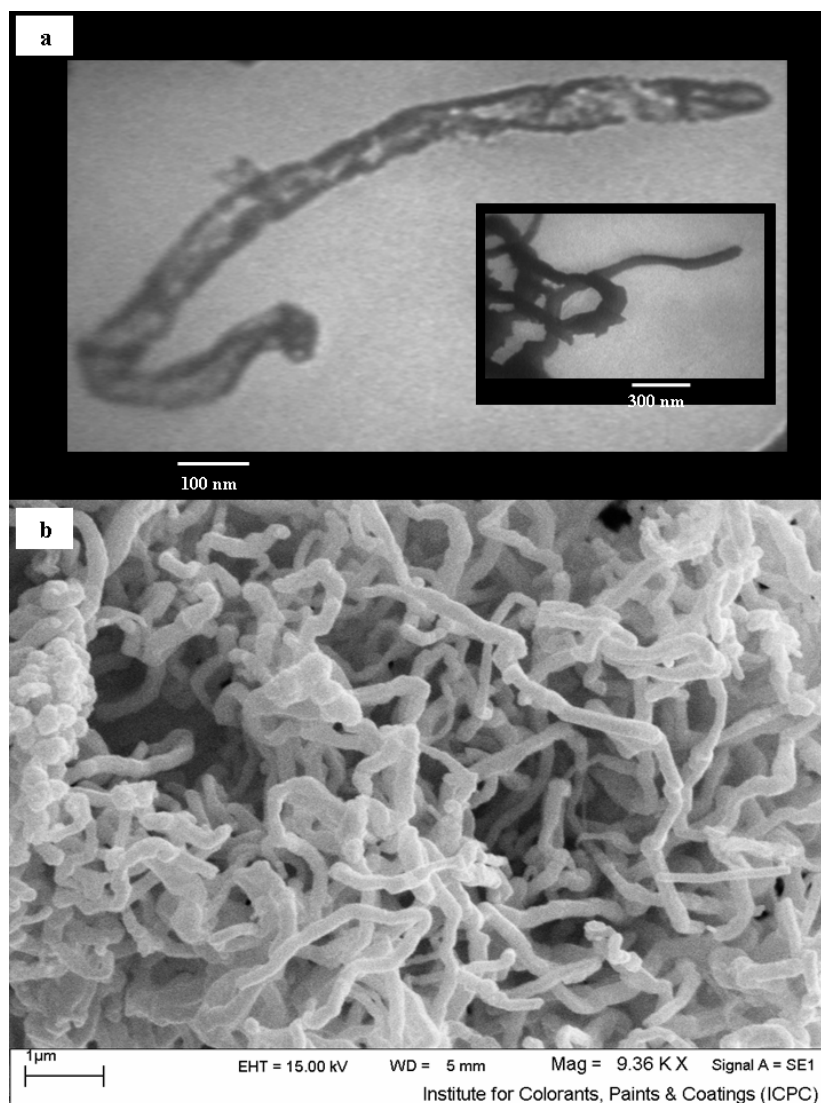

Figure 7. SEM image (a) and TEM image (b) of the cadmium sulfide nanofibers synthesized in the optimum conditions
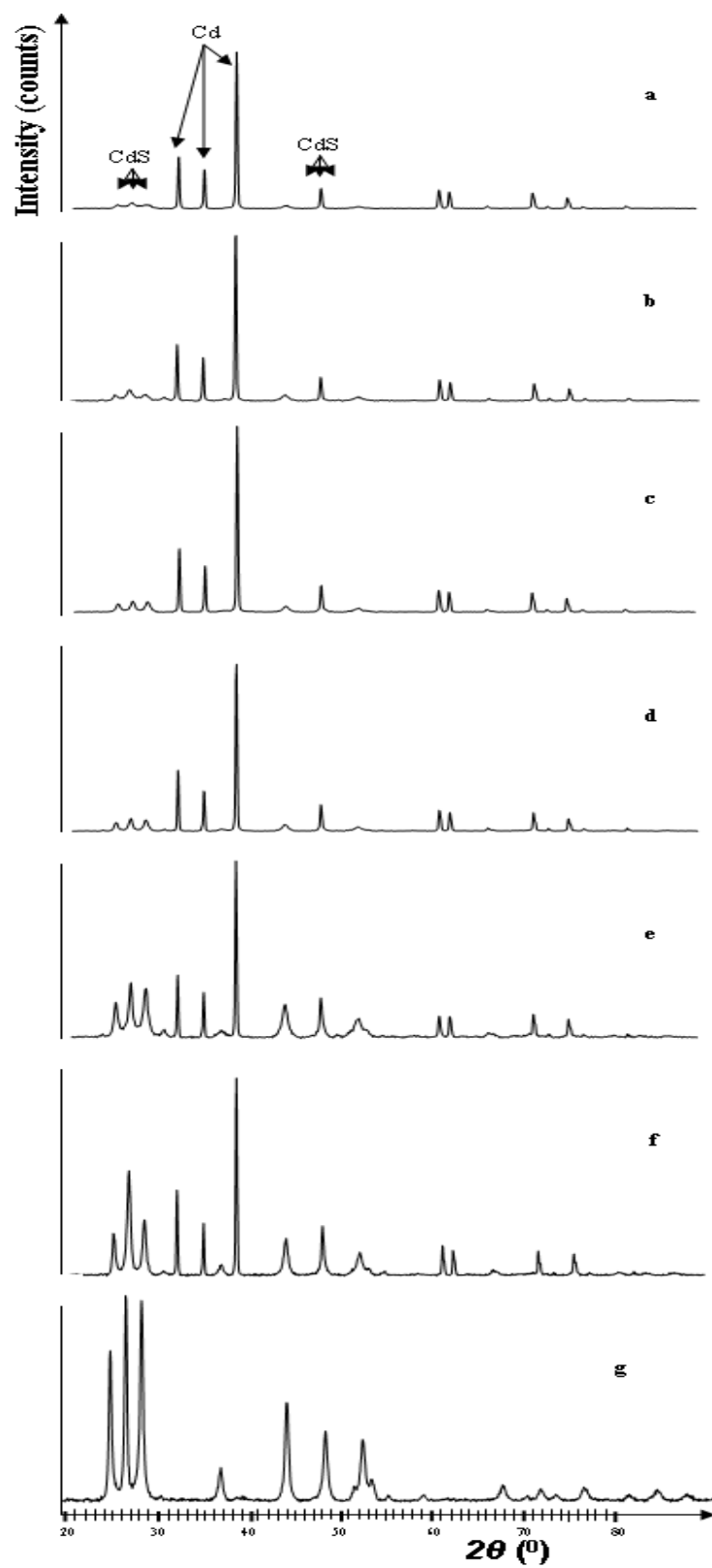
Figure 8. XRD patterns for the samples which synthesized at different solution temperatures: (a) 0°C, (b) 25°C, (c) 50°C, (d) 75°C, (e) 95°C, (f) 125°C and (g) 150°C.

3.6. Optimized sample

After investigating of all effective parameters of synthesis of cadmium sulfide/cadmium nanocomposite, a sample was synthesized at optimum conditions. Figure 7 shows the SEM image and TEM image of the optimum sample. Based on Fig. 7, at optimum conditions, cadmium sulfide/cadmium nanocomposite can be synthesized in excellent uniform nanofibers with 80 to 100 nm in diameter (average amount of 90 nm) and 5 to 7 μm in length (average amount of 6 μm).

3.7. Temperature studies

For investigation of the synthesis temperature effect on the structure, morphology and particle size of samples, seven synthesizes were carried out at temperatures of 0, 25, 50, 75, 95, 125 and 150ºC. Figure 8 shows the XRD patterns of the samples synthesized at different temperatures. Based on XRD patterns, Cd content of the samples is decreased when synthesis temperature is increased.

Based on XRD patterns showed in Fig. 8, Cd amount in the different samples synthesized at different temperatures was extracted and shown in Fig. 9. As it can be seen from Fig. 9, Cd content of samples decreases from 75%wt to 0%wt when the synthesis temperature decreases from 0 to 150°C. The obtained results shows that the kinetics of $Cd^{2+} + 2e \rightarrow Cd$ and $S_2O_3^{2-} + 6H^+ + 8e \rightarrow 2S^{2-} + 3H_2O$ depend on the synthesis temperature with different coefficients. Not only reduction rate of $S_2O_3^{2-}$ increases but also, reduction rate of Cd^{2+} decreases when the synthesis temperature is increased.
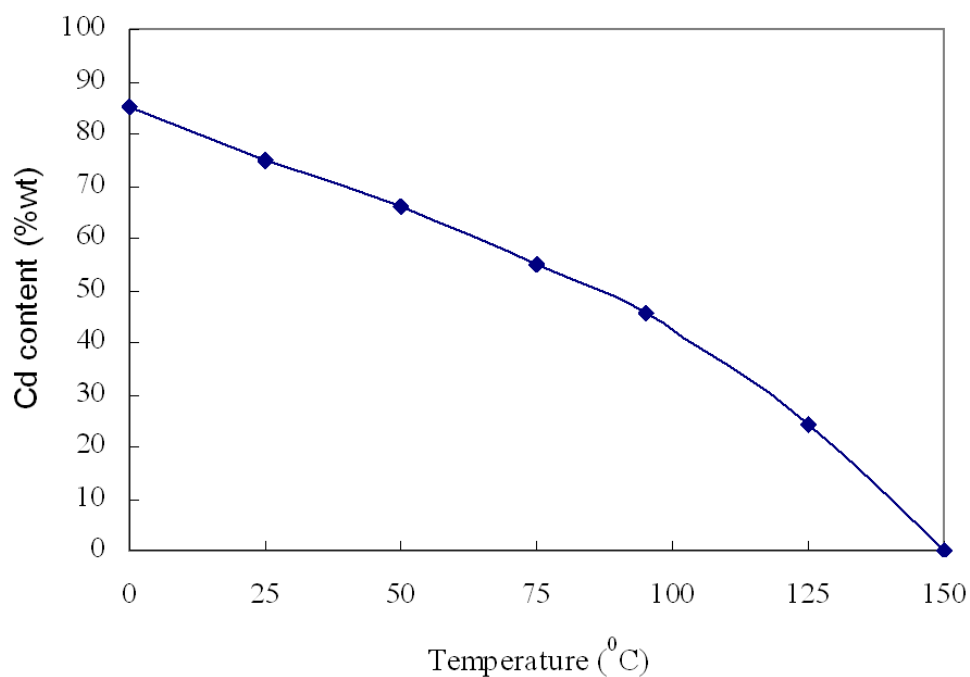

Figure 9. Effect of synthesis temperature on the Cd contents of cadmium sulfide samples.

4. CONCLUSIONS

The obtained results in this work indicate which the pulsed current electrochemical method can be used as a confident and controllable method for the electrosynthesis of cadmium sulfide/cadmium nanocomposite and cadmium sulfide in nanofibers forms. When a synthesis is carried out under a pulse frequency of 8 Hz, a pulse height (current amplitude) of 100 mA cm^{-2}, a synthesis solution temperature of 50ºC, an initial cadmium chloride concentration of 0.2 M, sodium thiosulfate concentration of 0.02 M in hydrochloric acid solution with pH of 2, nanocomposite of cadmium sulfide/cadmium in nanofiber form can be obtained. At high pressure and high temperature, cadmium sulfide nanostructures can be synthesized without any impurity of cadmium.

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