

*Full Paper*

## **Facile Approach for Synthesis of Cobalt Aluminate Nanoparticles and Study of its Behavior in Electrochemical Sensing of Acyclovir**

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**Abstract-** Spherical-like cobalt aluminate nanoparticles were successfully synthesized by sol-gel method by new capping agent. The X-ray diffraction spectrum confirms the pure phase cobalt aluminate nanoparticles. The presence of stretching and bending vibrations of Co-O and Al-O confirmed by FT-IR analysis in the cobalt aluminate nanoparticles. The mean size of cobalt aluminate nanoparticles were examined by TEM techniques between 20 to 40 nm. The synthesized nanoparticle was used for determination of acyclovir. In the electrochemical section, the effects of pH, scan rate and Acyclovir concentration were studied. The peak current was linear with the acyclovir concentration in the range of 1  $\mu$ M to 30  $\mu$ M and the detection limit was found to be 0.4  $\mu$ M.

**Keywords -** Cobalt aluminate, Sol-gel method, Acyclovir, Nanoparticles

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## 1. INTRODUCTION

The field of nanotechnology is one of the highly active analytic areas to develop modern material [1-4]. Nanoparticles show new or interesting behaviors supported with specific characteristics including shape, distribution, and size [5-9]. Nowadays no one can deny developed the field of nanotechnology is. Such developments have led to preparation of nanoparticles with particular size and shape [10-14]. Modern application of nanosized materials is on the rise. Through such new approach, we are able to comprehend some fields such as biology much to a great extent. Therefore, this success has come with making use of nanoparticles in our daily life [15-18].

Pigments, spinel-type structures with general formula of  $A^{2+}B^{3+}O_4$ , have been used to furnish porcelains and other paints, ceramics, glazes, plastics, rubbers, glass, and cement [19]. Such structures are highly stable when they are subjected to heat, are in low temperature to a small extent, and are mechanically resistant to a large extent [20]. Cobalt aluminates as a blue pigment with spinel-type structure has interesting behaviors; it is resistant to acids and considerably stable to heat, color, and chemical compound, as well as it has great refractive index [21]. These distinctive characteristics have tailored cobalt aluminate to be used in paint, glass, plastics, ceramics, rubber, and color tubes [22]. Thanks to these extensive range of applications, a number of procedures have been developed to fabricate cobalt aluminates, including, sonochemical, glycine chelated, EDTA chelating precursor, sol-gel, co-precipitation, polymerized complex, molten salt, and combustion [23-28]. Due to some properties of pigment such as size of particle and color which can be assigned to the pigment fabrication methods, developing a new procedure could be challenging.

In the current work, we successfully fabricated spherical-like cobalt aluminate nanoparticles by sol-gel method with using polysorbate 20 (Tween 20) as capping agent and verified its magnetic, structural, and morphological properties making use of X-ray diffraction (XRD), vibrating sample magnetometers (VSM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR). After synthesizing and optimizing the conditions, these nanoparticles were used for studying its electrochemical characteristics and electrochemical measurement of acetaminophen as an anti-nociceptive and anti-nocentric drug have been performed using a modified carbon paste electrode.

## 2. EXPERIMENTAL PART

### 2.1. Materials and physical measurements

$Co(NO_3)_2 \cdot 6H_2O$  and  $Al(NO_3)_3 \cdot 5H_2O$  as chemical reagents in this research were employed in analytical grade. The XRD results were obtained using a Philips-X'pertpro instrument with a Ni-filtered Cu K $\alpha$  radiation. The FT-IR spectra were acquired using a Nicolet Magna- 550 spectrometer and KBr pellets. Transmission electron microscopy (TEM) images were

obtained using a Philips EM208 TEM at an accelerating voltage of 200 kV. The magnetic measurement of sample was carried out in a vibrating sample magnetometer (VSM) (Meghnatis Daghigh Kavir Co.; Kashan Kavir; Iran) at room temperature. The Voltammetric experiments were performed with Autolab PGSTAT-302 (Eco Chemie B. V.) potentiostat/galvanostat instrument controlled by a computer using GPES software. A conventional three-electrode system was used with a bare or modified carbon paste electrode as the working electrodes, an Ag/AgCl (3 M KCl) and a Pt wire as the reference and counter electrodes, respectively.

## 2.2. Synthesis of cobalt aluminate nanoparticles

Current study includes a new green and simple approach which was used in synthesis of cobalt aluminate nanoparticles [23, 24]. At first, a mixed solution comprising  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (1 mmol) and  $\text{Al}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (1 mmol) was prepared in deionized water. Afterwards, appropriate amount of Tween 20 was added within the above container and was stirred for 0.33 h at 45 °C. Intended for the dehydration and greatly viscous gel formation, the obtained solution was evaporated. Eventually, the highly viscous gel was calcined at 900 °C for 120 min.

## 2.3. Preparation of modified electrode

The amount of 0.3 g of graphite with 0.015 g of the modifier and 0.09 g of the nujol oil was poured into the sample container and mixed by stirring. To ensure uniformity and homogenization of the sample, some ethanol was added to the sample and then sample was completely mixed. After that, the sample was placed inside the oven to remove existing ethanol and obtain the desired carbon paste. The resulted modified carbon pastes were used as dough for the preparation of modified electrodes. The paste was compressed manually into a cavity (2 mm in diameter) located at the end of a 2 mL plastic syringe. At each time of using the pastes, after pouring the chosen paste on the oiled paper, the electrode surface was pulled to the dough to a sufficiently smooth surface. The electrical connection of carbon paste with the device was made through a copper wire connected to the dough located in the inner cavity of the plastic syringe. The dough was stored at room temperature and in dark and dry conditions.

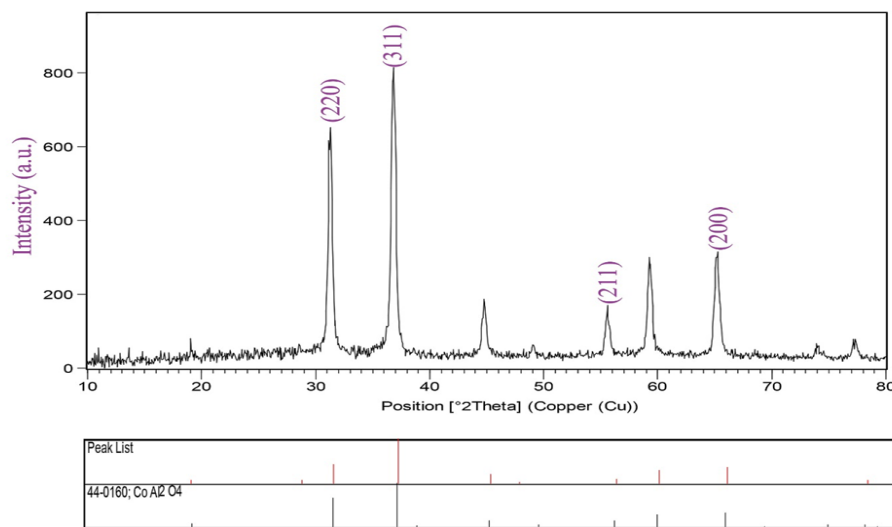
## 3. RESULTS AND DISCUSSION

For investigation of the crystalline nature and the purity level of the nanostructures, XRD characterization technique has been used [29-38]. XRD diffractogram corresponding to cobalt aluminate nanoparticles produced with Tween 20 suggested that the obtained cobalt aluminate is pure (see Fig. 1). The appeared peaks can be related to position of 31.08°

line(220), 36.4° line(311), 55.46° line(211) and 49.92° line (200) respectively which is in good compatible with JCPDS 01-072-0860 and cubic phase and space group of I41/amd). Corresponding to XRD information and with aid of Scherrer formula the average crystallite diameter of Cobalt aluminate found to be 10 nm [39-42].

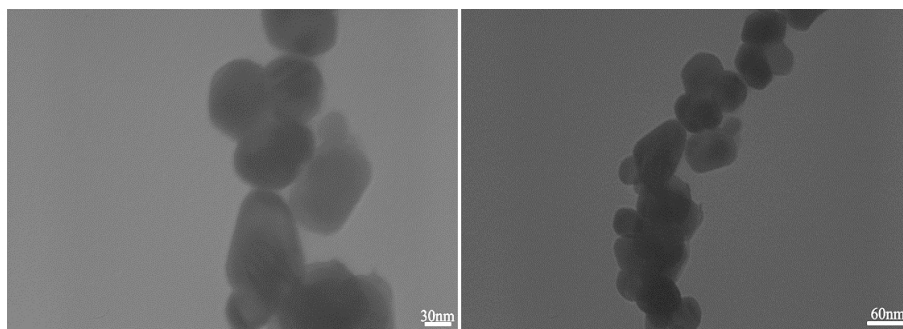
$$D_c = K\lambda/\beta\cos\theta; \quad (1)$$

Where  $\beta$  suggests the breadth of a diffraction line at its half intensity maxima, K is a shape factor (which nearly is 0.9), and  $\lambda$  is the X-ray wavelength used for obtaining average crystallite diameter of cobalt aluminate nanoparticles. For this compound the domain sizes of assessed crystalline have been computed to be 11 nm.



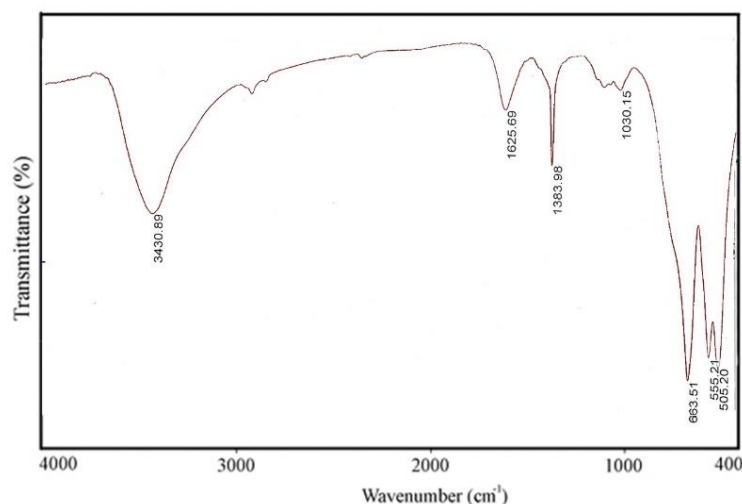
**Fig. 1.** XRD pattern of Cobalt aluminate nanoparticles obtained in the presence of Tween 20

TEM photographs of cobalt aluminate nanoparticles prepared in Tween 20, captured at several magnifications, showed the grain size and morphology of the green-based method for preparation of nanostructures. The production of cobalt aluminate nanoparticles with a grain size covering between 20 to 40 nm was corroborated from TEM images as showed in Fig. 2.



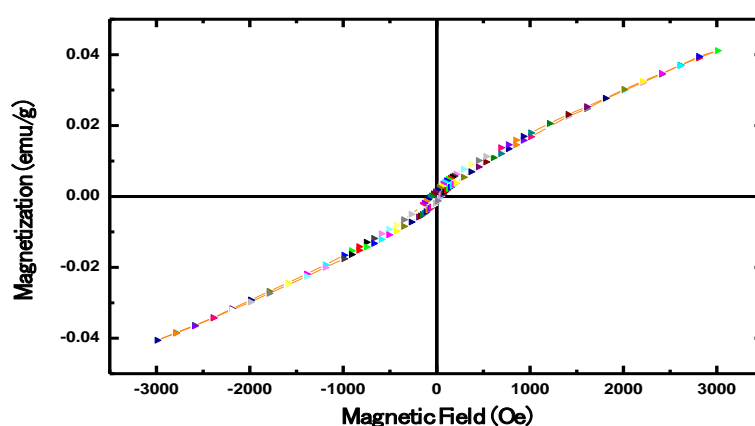
**Fig. 2.** TEM image of cobalt aluminate nanoparticles obtained in the presence of Tween 20

The production of cobalt aluminate nanoparticles is also evident by FTIR data (Fig. 3). FTIR spectrum of the cobalt aluminate illustrates the appearance of three peaks at 505.20, 555.21 and 663.51  $\text{cm}^{-1}$  that can be allocated to cobalt aluminate nanoparticles. The peaks around 3430.89 and 1625.69  $\text{cm}^{-1}$  can arise owing to the vibrations of water molecules. And two peaks in 1030.15 and 1383.96 related to the bending vibrations of Tween 20 molecules [43-48].



**Fig. 3.** FT-IR spectra of Cobalt aluminate nanoparticles obtained in the presence of Tween 20

We computed the magnetic property of cobalt aluminate nanoparticles through VSM at 300 K and the results have been displayed in Fig. 4. It suggests that sample has paramagnetic behavior and magnetization value of 0.04 emu/g.

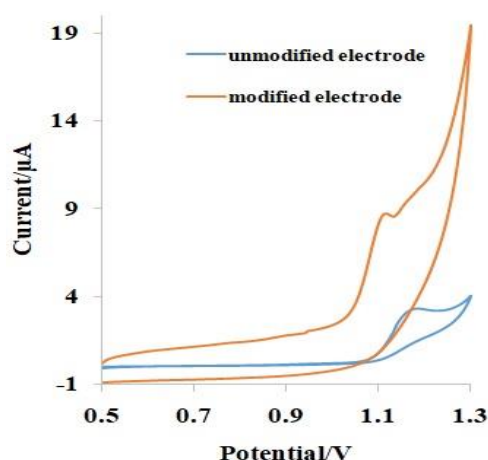


**Fig. 4.** VSM curve of cobalt aluminate nanoparticles obtained in the presence of Tween 20

### 3.1. The behavior of Acyclovir at the surface of a modified electrode

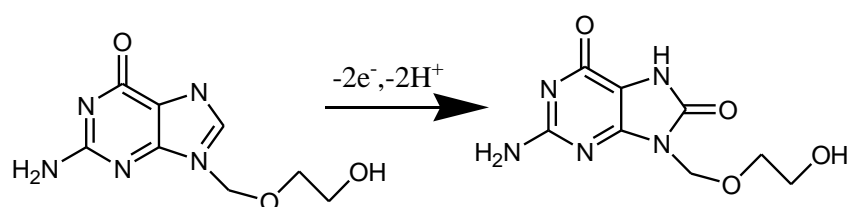
Nowadays, considering the excellent performance of different nanomaterials in electrochemistry, many electrochemical scientists have focused on this field [49-56]. The

electrochemical behavior of acyclovir on the surface of the modified electrode was carried out with the cyclic voltammetry (CV). Fig. 5 shows cyclic voltammogram of 10  $\mu\text{M}$  of acyclovir on the surface of the modified and unmodified electrode in the phosphate buffer solution with pH = 3. The oxidation peak of the drug at the surface of the unmodified electrode was observed at 1.17 V, however, the oxidation peak at the surface of the modified electrode with little variation was detected at a potential of 1.13 V. Also, the current at the surface of the modified electrode is almost 2 times the current at the surface of the unmodified electrode, so the modified electrode has a good performance for measuring this drug.

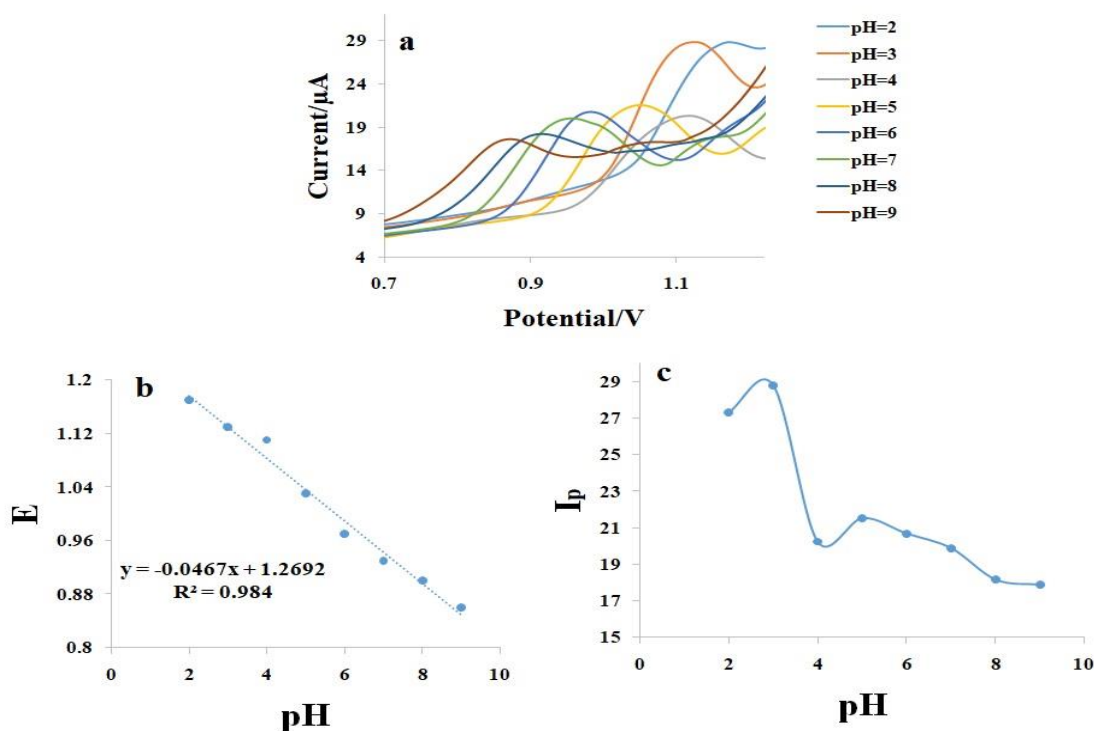


**Fig. 5.** Cyclic voltammograms of the unmodified electrode and modified electrode in phosphate buffer with pH=3 at scan rate of 50 mV/s for 10 $\mu\text{M}$  of Acyclovir

The effect of pH variation on the determination of acyclovir at the surface of the modified electrode was investigated on the pH range of 2-9. These results are shown in Fig. 6. As can be seen by changing the pH from 2 to 9 the flow was change and the maximum flow is obtained at pH = 3, so this pH is selected as optimal pH value. The diagram of oxidation peak potential versus pH shows the slope equivalent to  $Y = 0.043(X) + 1.26$ , which itself indicates that the number of electrons and protons involved in the reaction is equal. Therefore, the oxidative mechanism of acyclovir is expressed as follows:

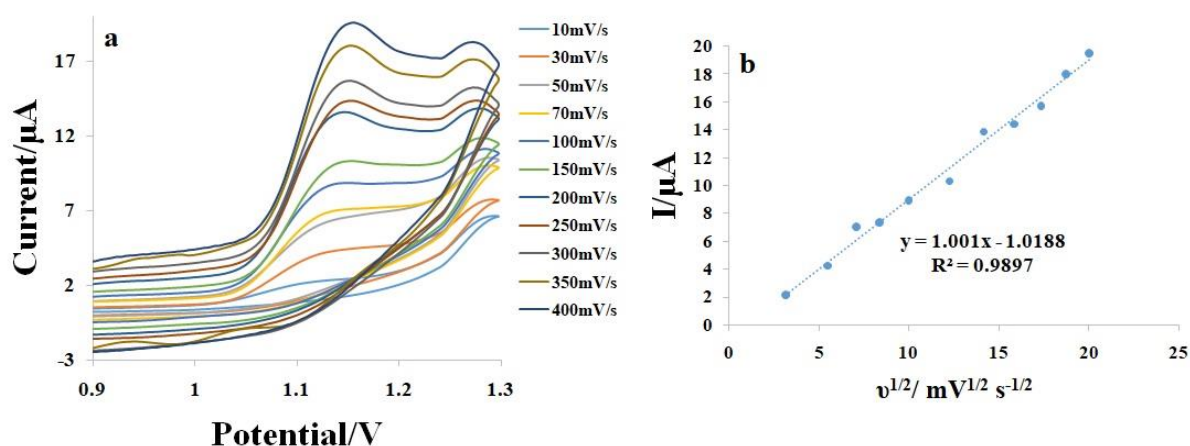


**Scheme 1.** Mechanism of Acyclovir electrooxidation



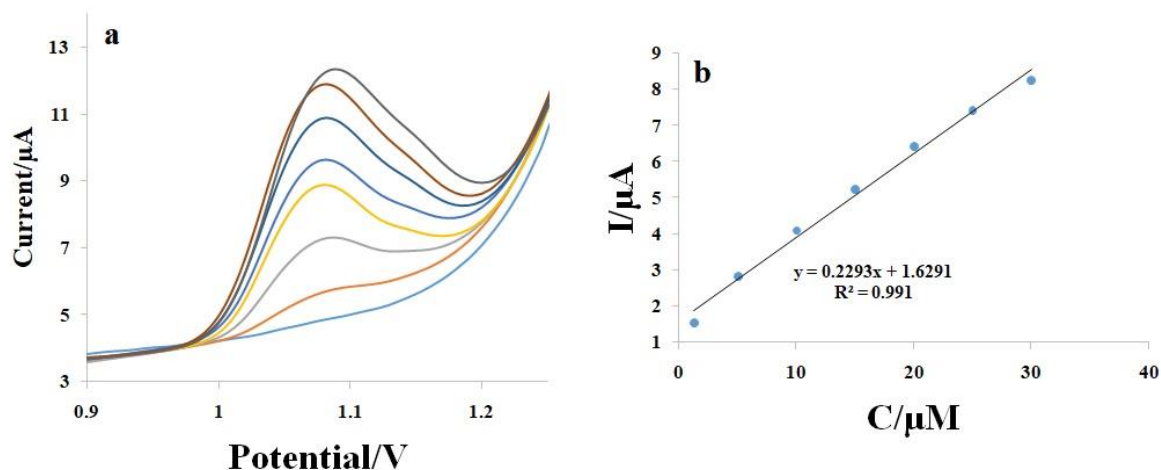
**Fig. 6.** (a) Differential-pulse voltammetry of 50  $\mu\text{M}$  Acyclovir in phosphate buffer at various pH values, (b)  $E_p$  vs. pH and (c)  $I_p$  vs. pH

Another parameter that was evaluated in the electrochemical measurement of acyclovir was the effect of the scan rate on the oxidation peak of this drug. Cycle voltammogram of the various scan rate is shown in Fig. 7. As the scan rate increased, however, the oxidation peaks current of acyclovir increased too. The current versus the square root of scan rate is also a linear graph (Fig. 7b). According to the results shows good linearity which indicates that the electrochemical reaction of acyclovir is diffusion-controlled process.



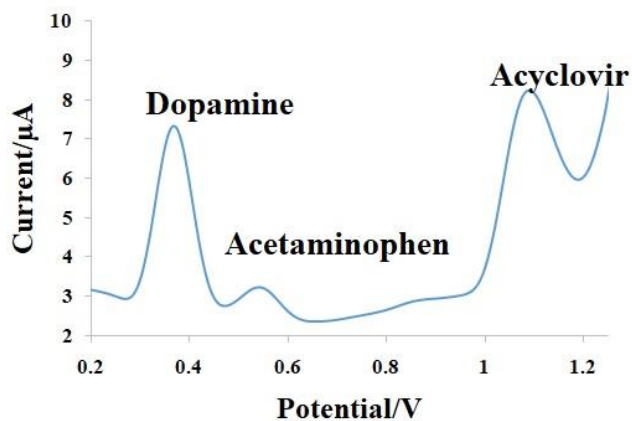
**Fig. 7.** (a) Cyclic voltammograms of 10  $\mu\text{M}$  Acyclovir phosphate buffer solution at different scan rates, (b)  $I_p$  vs.  $v^{1/2}$

The analytical application of the modified electrode for determination of acyclovir at various concentrations of this drug was performed using DPV method, the resulting voltammograms are given in Fig. 8 and the calibration graph is shown in Fig. 8b with a linear range of 1 to 30  $\mu\text{M}$  and a limit of 0.4  $\mu\text{M}$  for determination of acyclovir.



**Fig. 8.** a) Differential pulse voltammograms of 0-30  $\mu\text{M}$  Acyclovir phosphate buffer solution with pH =3 at the surface of modified electrode. b) Linear relationship between peak current and Acyclovir concentration.

Acyclovir measurements were investigated in the presence of acetaminophen and 50  $\mu\text{M}$  dopamine drugs (Fig. 9). The results showed no significant changes in the current responses of modified electrode for acetaminophen in the presence of these species. The results showed that the presence of these two drugs did not interfere with the measurement of acyclovir at the surface of the modified electrode. Therefore, this electrode can be used to determination of acetaminophen in the presence of several other compounds that may be present in real samples.



**Fig. 9.** Differential pulse voltammograms acetaminophen, dopamine and Acyclovir



#### 4. CONCLUSION

Cobalt aluminate nanoparticles with a mean size of 40–60 nm were prepared through sol-gel method. The shape and crystal structure of the as-prepared cobalt aluminate were characterized by transmission electron microscopy and X-ray diffraction. Magnetic properties of the as-synthesized cobalt aluminate nanoparticles showed to behave as a paramagnetic compound. The carbon paste electrode was modified with a synthesized nanoparticle and was used to measure the acyclovir drug. At this work, the optimum pH of maximum sensitivity which was obtained for acyclovir drug as pH 3 and the detection limit of the method was also 0.4  $\mu\text{M}$ .

#### REFERENCES

- [1] M. Aghazadeh, *Materials Letters* 211 (2018) 225.
- [2] S. M. Hosseinpour-Mashkani, and A. Sobhani-Nasab, *J. Mater. Sci. Mater. Electron.* 27 (2016) 3240.
- [3] S. M. Pourmortazavi, Z. Marashianpour, M. Sadeghpour Karimi, M. Mohammad-Zadeh, *J. Mol. Struct.* 1099 (2015) 232.
- [4] F. Ahmadi, M. Rahimi-Nasrabadi, A. Fosooni, and M. Daneshmand. *J. Mater. Sci. Mater. Electron.* 27 (2016) 9514.
- [5] A. Sobhani-Nasab, M. Behpour, M. Rahimi-Nasrabadi, F. Ahmadi, S. Pourmasoud, *J. Mater. Sci. Mater. Electron.* 30 (2019) 5854,
- [6] Sobhani Nasab, S. Pourmasoud, F. Ahmadi, M. Wysokowski, T. Jesionowski, H. Ehrlich, and M. Rahimi-Nasrabadi, *Mater. Lett.* 238 (2019) 159.
- [7] Sobhani-Nasab, M. Rangraz-Jeddy, A. Avanes, and M. Salavati-Niasari, *J. Mater. Sci. Mater. Electron.* 26 (2015) 9552.
- [8] S.M. Pourmortazavi, M. Taghdiri, N. Samimi, M. Rahimi-Nasrabadi, *Mater. Lett.* 121 (2014) 5.
- [9] A. Sobhani-Nasab, M. Behpour, *J. Mater. Sci. Mater. Electron.* 27 (2016) 1191.
- [10] M. Rahimi-Nasrabadi, M. Behpour, A. Sobhani-Nasab, and M. Rangraz Jeddy, *J. Mater. Sci. Mater. Electron.* 27 (2016) 11691.
- [11] M. Rahimi-Nasrabadi, M. Behpour, A. Sobhani-Nasab, and S. M. Hosseinpour-Mashkani, *J. Mater. Sci. Mater. Electron.* 26 (2015) 9776.
- [12] M. Rahimi-Nasrabadi, S.M. Pourmortazavi, M. Aghazadeh, M.R. Ganjali, M. Sadeghpour Karimi, P. Novrouzi, *J. Mater. Sci. Mater. Electron.* 28 (2017) 3780.
- [13] S. M. Hosseinpour-Mashkani, A. Sobhani-Nasab, and M. Mehrzad, *J. Mater. Sci. Mater. Electron.* 27 (6) (2016) 5758.
- [14] A. Sobhani-Nasab, M. Behpour, M. Rahimi-Nasrabadi, F. Ahmadi, S. Pourmasoud, *J. Mater. Sci. Mater. Electron.* 30 (2019) 5854.

- [15] S. M. Hosseinpour-Mashkani, and A. Sobhani-Nasab, *J. Mater. Sci. Mater. Electron.* 27 (7) (2016) 7548 .
- [16] M. Rahimi-Nasrabadi, F. Ahmadi, and M. Eghbali-Arani, *J. Mater. Sci. Mater. Electron.* 27 (2016) 11873.
- [17] F. Ahmadi, M. Rahimi-Nasrabadi, M. Behpour, *J. Mater. Sci. Mater. Electron.* 28 (2017) 1531.
- [18] M. Rahimi-Nasrabadi, F. Ahmadi, and A. Fosooni, *J. Mater. Sci. Mater. Electron.* 28 (2017) 537.
- [19] D.V. Sanghani, G.R. Abrams, P.J. Smith, *Trans.J. Br. Ceram. Soc.* 80 (1981) 210.
- [20] W. Li, J. Guo, J. Li, *J. Eur. Ceram. Soc.* 23 (2003) 2289.
- [21] S. Akdemir, E. Ozel, E. Suvaci, *Ceram. Int.* 37 (2011) 863.
- [22] M. Salavati-Niasari, M. Farhadi-Khouzani, F. Davar, *J. Sol-Gel Sci. Technol.* 52 (2009) 321.
- [23] M. Zayat, D. Levy, *Chem. Mater.* 12 (2000) 2763.
- [24] W. Lv, Q. Qiu, F. Wang, S. Wei, B. Liu, Z. Luo, *Ultrason. Sonochem.* 17 (2010) 793.
- [25] W.S. Cho, M. Kakihana, *J. Alloy. Compd.* 287 (1999) 87.
- [26] F. Meyer, R. Hempelmann, S. Mathur, and M. Veith, *J. Mater. Chem.* 9 (1999) 1755.
- [27] C.O. Are´an, M.P. Mentrut, E.E. Platero, F.X. Llabr´es i Xamena, J.B. Parra, *Mater. Lett.* 39 (1999) 22.
- [28] E.E. Platero, C.O. Arean, J.B. Parra, *Res. Chem. Intermed.* 25 (1999) 187.
- [29] M. Ramezani, S. M. Hosseinpour-Mashkani, A. Sobhani-Nasab, and H. Ghasemi Estarki, *J. Mater. Sci. Mater. Electron.* 26 (2015) 7588.
- [30] M. Ramezani, A. Sobhani-Nasab, and S. M. Hosseinpour-Mashkani, *J. Mater. Sci. Mater. Electron.* 26 (2015) 4848.
- [31] M. Eghbali-Arani, A. Sobhani-Nasab, M. Rahimi-Nasrabadi, and S. Pourmasoud, *Journal of Electronic Materials.* 47 (2018) 3757.
- [32] S. S. Hosseinpour-Mashkani, and A. Sobhani-Nasab, *J. Mater. Sci. Mater. Electron.* 28 (2017) 16459.
- [33] M. Rahimi-Nasrabadi, M. Rostami, F. Ahmadi, A.F. Shojaie, M.D. Rafiee, *J. Mater. Sci. Mater. Electron.* 27 (2016) 11940
- [34] S. Mostafa Hosseinpour-Mashkani, and A. Sobhani-Nasab, *J. Mater. Sci. Mater. Electron.* 28 (2017) 4345.
- [35] A. Sobhani-Nasab, and M. Behpour *J. Mater. Sci. Mater. Electron.* 27 (2016) 11946.
- [36] S. M. Hosseinpour-Mashkani, M. Maddahfar, and A. Sobhani-Nasab, *J. Electron. Mater.* 45 (2016) 3612.
- [37] S. M. Asgarian, S. Pourmasoud, Z. Kargar, A. Sobhani-Nasab, and M. Eghbali-Arani, *Mater. Res. Express* 6 (2019) 15023.

- [38] H. Kooshki, AliSobhani-Nasab, M. Eghbali-Arani, F. Ahmadi, V. Ameri, M. Rahimi-Nasrabadi, *Sep. Purif. Technol.* 18 (2019) 873
- [39] M. Salavati-Niasari, F. Soofivand, A. Sobhani-Nasab, M. Shakouri-Arani, and S. Bagheri, *Adv. Powder Technol.* 27 (2016) 2066.
- [40] F. Ahmadi, M. Rahimi-Nasrabadi, A. Fosooni, M. Daneshmand, *J. Mater. Sci. Mater. Electron.* 27 (2016) 9514.
- [41] S. Zarrin F. Heshmatpour, *J. Hazard. Mater.* 351, (2018) 147.
- [42] F. Sedighi, M. Esmaeili-Zare, A. Sobhani-Nasab, and M. Behpour, *J. Mater. Sci. Mater. Electron.* 29 (2018) 13737.
- [43] M. Maddahfar, M. Ramezani, M. Sadeghi, and A. Sobhani-Nasab, *J. Mater. Sci. Mater. Electron.* 26 (2015) 7745.
- [44] M. Rahimi-Nasrabadi, S.M. Pourmortazavi, M.R. Ganjali, P. Norouzi, F. Faridbod, M. Sadeghpour Karimi, *J. Mater. Sci. Mater. Electron.* 27 (2016) 12860.
- [45] M. Rahimi-Nasrabadi, S. M. Pourmortazavi, M. Aghazadeh, M. R. Ganjali, M. Sadeghpour Karimi, and P. Norouzi, *J. Mater. Sci. Mater. Electron.* 28 (2017) 9478.
- [46] M. Rahimi-Nasrabadi, V. Pourmohamadian, M. Sadeghpour Karimi, H. R. Naderi, M. A. Karimi, K. Didehban, and M. R. Ganjali, *J. Mater. Sci. Mater. Electron.* 28 (2017) 12391.
- [47] M. Rahimi-Nasrabadi, S. M. Pourmortazavi, Z. Rezvani, K. Adib, and M. R. Ganjali, *Mater. Manuf. Processes* 30 (2015) 34.
- [48] M. Rahimi-Nasrabadi, *J. Mater. Sci. Mater. Electron.* 28 (2017) 2200.
- [49] A. Khoshroo, L. Hosseinzadeh, A. Sobhani-Nasab, M. Rahimi-Nasrabadi, H. Ehrlich, *J. Electroanal. Chem.* 823 (2018) 61.
- [50] Sobhani-Nasab, H.R. Naderi, M. Rahimi-Nasrabadi, M. R. Ganjali, *J. Mater. Sci. Mater. Electron.* 28 (2017) 8588.
- [51] M. Rahimi-Nasrabadi, H. R. Naderi, M. Sadeghpour Karimi, F. Ahmadi, and S. M. Pourmortazavi, *J. Mater. Sci. Mater. Electron.* 28 (2017) 1877.
- [52] J. Amani, M. Malekia, A. Khoshroo, A. Sobhani-Nasab, M. Rahimi-Nasrabadi. *Anal. Biochem.* 548 (2018) 53
- [53] M. Aghazadeh, I. Karimzadeh, M.R. Ganjali, *J. Mater. Sci. Mater. Electron.* 28 (2017) 13532
- [54] M. Aghazadeh, M.R. Ganjali, *Ceram. Int.* 44 (2018) 520.
- [55] M. Aghazadeh, M.R. Ganjali, *J. Mater. Sci.* 53 (2018) 295.
- [56] M. Aghazadeh, A.A.M. Barmi, H.M. Shiri, S. Sedaghat, *Ceram. Int.* 39 (2014) 1045.