

SYNTHESIS OF COBALT FERRITE MODIFIERS OF CARBON PASTE ELECTRODE

D. Jovanović¹, R. Karkalić², D. Cucić³, M. Lakić⁴, V. Maslak⁵, S. Pavić-Vidić⁵, D. Stanković⁵,
A.S. Nikolić⁵

¹Technical Testing Centre, Belgrade, Serbia

²Military Academy, University of Defense, Belgrade, Serbia

³RCT "Mihajlo Pupin", Pančevo, Serbia

⁴INS "Vinča", Belgrade, Serbia

⁵Faculty of Chemistry, University of Belgrade, Belgrade, Serbia

Abstract

The paper presents a new type of modified glassy carbon paste electrode with different Co- ferrites. First part of this work was the preparation of ferrites by five different methods such as hydrothermal, ultrasound and microwave-assisted hydrothermal, mechanochemical and sol-gel synthesis. Ferrite nanoparticles were characterized using scanning electron microscopy (SEM) and X-ray diffraction (XRD). They were used for preparation new modified glassy carbon paste electrode (CoFeMGCPE). The electrode was used for determination of nanomolar level of copper ions in waste waters using electrochemical methods such as differential pulse anodic stripping voltammetry, DPASV. A significant increase in current was achieved at the modified electrode in comparison with the bare glassy carbon paste electrode. Detection limit for the proposed electrode was 30nM Cu when percentage of modifier was 3%, pH 4.5, deposition potential -0.3 V and deposition time 4min. This electrode was successfully applied for determination of copper ions in waste water without any pre-treatment.

Key words: cobalt ferrite, copper, modified electrode, glassy carbon paste, electrochemistry

1. INTRODUCTION

The development of new functional nano-sized ferrites is relentlessly growing, not only due to their special magnetic properties, but due to their unique properties and various ideas about their potential uses in the modern scientific fields. Polycrystalline spinel ferrites show many interesting physical and chemical phenomena, such as high electrical resistivity, high Curie temperature, large magnetocrystalline anisotropy, high coercitivity, mechanical hardness, chemical stability, and temperature specific saturation magnetization, and so forth (Lu et al. 2007). Therefore, nano-sized ferrites can be used as magnetic devices and catalysts. They also play an important role in ferrofluid technology and biomedical fields. In the last years, their usability in electrochemical purposes has been widely investigated (McCurrie et al. 1994, Konishi et al. 2004). Cobalt ferrites present a promising candidates for electrode material due to their similar electronic properties, mechanical strength and electrochemical performances, providing significant improvements of electrodes for determination of metal ions in waste water, and some organic and biological active substances (Janegitz et al. 2009 and Kalcher et al. 2006). Nowadays, great effort has been devoted to the electrochemical determination of toxic metals at new different electrodes (Kalcher et al. 1985). Carbon paste electrodes (CPE) have been widely used in electrochemistry since they are chemically inert, suitable for different types of analysis and can be simply modified (Kalcher et al. 1990).

It is well-known fact that characteristics of ferrites strongly depends on the synthesis methods. There are many well-known and easily modified methods for their preparation, such as co-precipitation, ball-milling, sol-gel, pyrolysis etc. Among them, co-precipitation is used widely because of its low cost and moderate operation conditions. Some new improved co-precipitation methods have been developed, such as sonochemical and microwave-assisted co-precipitation.

In order to find the most efficient modifier of the CPE, synthesis of mixed Co/Ferrites was performed by five different methods: hydrothermal (Byrappa et al. 2001), ultrasound (Suslick et al. 1989), microwave-assisted hydrothermal (Bilecka et al. 2010), mechanochemical (Manova et al. 2009) and sol-gel (Song et al. 2010). Moreover, obtained materials were characterized by XRD and SEM analysis. The usability of Co-Ferrites as modifiers of CPE for the determination of Cu in waste water was studied and the electrochemical properties were investigated by fabricating a simple and sensitive electrochemical sensor based on Co-Ferrites/CPE.

2. MATERIALS AND METHODS

2.1. Apparatus

The voltammetric changes of the CME were measured with the *Metrohm 797 VA Computance instrument (Herisau, Switzerland)*. The triple-electrode system consisted of a working electrode, our modified GC paste electrode, a reference Ag/AgCl, KCl (3 M) (*Model 6.0728.010*) and an auxiliary separate platinum rod electrode (*Model 6.0340.000*). All measurements were taken at ambient temperature. During the measurements the sample was stirred.

The morphology of the ferrite powders was examined by SEM *Joel JSM-6610LV*. The X-ray powder diffraction (XRPD) analysis was conducted using *Philips PW-1710* automatized diffractometer with graphite monochromator and a Xe-filled proportional counter, using a Cu-tube operated at 40 kV and 30 mA. Data were collected in the 2θ range $15-60^\circ$ with a counting time of 2.5 s/step and a step size of 0.05° . A fixed 2° divergences and 0.2 mm receiving slits were used.

2.2. Reagents

All reagents used, were p.a. quality, obtained from *Sigma-Aldrich* and *Alfa Aesar* suppliers.

Cu(II) stock solution (1×10^{-3} mol/L) were prepared from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and standardized complexometrically. Working solution for ASV investigations were prepared by diluting the appropriate amount of the stock solutions in electrolytes. Acetate buffer solutions 0.1 mol/L (different pH) were used to control the pH. All other reagents were of analytical grade. Ultrapure water (*Milli-Q plus 185 system, Millipore*) was used in all experiments.

3. EXPERIMENTAL

3.1 Synthesis of electrode materials

3.1.1 Hydrothermal synthesis of Co-ferrites

Synthesis was slightly modified procedure described by Almeida et al. (2012). $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were mixed in stoichiometric (2:1 molar) ratio in distilled water. With the vigorous stirring, aqueous solution of salt were heated, and the pH was adjusted to 9.5 with NaOH 10% solution. The synthesis temperature being maintained at $90-95^\circ\text{C}$ for 1 hour under vigorous magnetic agitation. Ferrite solution was cooled to room temperature and filtered on a Buchner funnel, washed with distilled water (3x10 ml, until chloride was out) and with 0.1M solution of HNO_3 (3x10ml). Precipitate was dried at 105°C .

3.1.2. Microwave-assisted hydrothermal synthesis of Co-ferrites

Co ferrites were prepared under microwave-hydrothermal condition (D'Arrigo et al. 1998) Co(II) and Fe(III) nitrates were dissolved in ethylene glycol in stoichiometric ratio, neutralized with ammonia, and microwave treated at 2.45 GHz in Teflon reaction flask (*Ethos Milestone*). Powder was filtered on a Buchner funnel, washed with ethanol (3x10ml), and dried at 105°C .

3.1.3. Ultrasound synthesis of Co- ferrites

Synthesis was slightly modified procedure described by Goswami et al. (2013). Co(II) and Fe(III) chlorides were dissolved in pure water in stoichiometric ratio, and mixed, stirred and heated to 80°C

for one hour in ultrasonic bath *Sonorex RK255H*, operated at 35 kHz. Dark precipitate formed. It was filtered on a Buchner funnel and washed with pure water several times (until chloride was out) and with 0.1M solution of HNO_3 (3x10ml). Powder was dried at 105°C.

3.1.4. Mechanochemical synthesis of Co-ferrites

The synthesis (Manova et al. 2005) was performed by two steps: co-precipitation and mechanical milling of the co-precipitated precursors. The starting materials used were $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and Na_2CO_3 . In the co-precipitation phase, a 0.5M solution of metal salts containing Co and Fe were taken in a stoichiometric molar ratio (1:2). Mixtures of cobalt and iron hydroxide carbonates precursors were formed when a 1M sodium carbonate solution was added at pH 9. The precipitates were washed and dried at 105°C for 3 h. The as-obtained precursors were milled using a *PM 100, RETSCH* planetary mill in a hardened steel vial of 200 cm³ volume, filled with 10 hardened steel balls with a diameter of 8mm. The mass of powder mixtures was 5 g and the balls to powder mass ratio was 20:1. The milling was carried out in air atmosphere without any additives. Milling time was 10h, at 500 rpm (Manova et al. 2009).

3.1.5. Solid state synthesis of Co-ferrites

To obtain Co-ferrite by sol-gel method (Shinde et al. 2016) the following chemicals were used: $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, KCl and PEG 1500. Mixtures of salts, made in stoichiometric ratio were made in a minimum amount of distilled water and heated and mixed in an ultrasonic bath (*Eurosonic 4D*, 35 kHz), at 80°C. The solution thus obtained was stirred for 10 minutes and then citric acid followed by ethylene glycol was added. The solution was again stirred till gel formation. The mixture was heated on the hot plate till it ignites and continues heating 4 h on 300 °C. Obtained ferrite nanopowders were washed with pure water several times (until chloride was out) and with 0.1M solution of HNO_3 (3x10ml). Powder was dried at 105°C.

3.2. The fabrication of the modified carbon paste electrodes (CoFeGCPE)

Bare carbon paste electrode was prepared by carefully hand mixing 380 µL of paraffin oil with 1 g of graphite powder in an agate mortar. After standing overnight a portion of the resulting paste was packed into the end of a Teflon tube (an inner diameter 5 mm, outer diameter 10mm) and the surface was polished using a PTFE plate. The carbon paste was modified by adding 3 % (m/m) of Co-ferrite. The amount of modifier was selected according to our experience and previously described articles (Schachl et al., 1997). Whenever regeneration was required, a layer of the surface was removed and replaced by fresh paste. Electrical contact was made with a copper wire the center of the tube (Mou et al., 2013)

3.3. Analytical procedure

Co-ferrites, synthesized by described ways were used as a modifiers of carbon paste electrodes in order to improve the sensitivity of the electrodes, and the current signal. The electrode was used for the determination of nanomolar amounts of copper 2+ ions in waste water by differential stripping voltammetry (Carnival, DPASV). Ferrite nanoparticles were characterized using scanning electron microscopy (SEM) and X-ray powder diffraction (XRPD) and were determined by electrochemical parameters. Thus prepared electrodes show the detection of copper 2+ ions and successfully applied for the determination of copper ions in water samples.

All measurements were carried out in acetate buffers different pH value. The potential range was set from -0.4 V to 0.2 vs. Ag/AgCl electrode with scan in anodic direction. The electrochemical parameters were optimized by differential pulse anodic stripping voltammetry. A series of standard solutions of Cu(II) for calibration curves and the recovery studies was measured by DPASV under the optimized working parameters describe above. The influence of some interference was included. The same procedure, with best modifier and best parameters, was applied to natural water sample and the results were compared with other reference method.

3.4. Optimization of analytical conditions

In order to obtain the optimum experimental conditions, some variables affecting the peak current i.e. pH, the amount of modifier, accumulation time, accumulation potential for a 1.0×10^{-6} mol/L Cu(II) solution were studied.

pH	6.0	5.5	4.5	4.0	3.5
I(nA)	260	1360	2010	1520	865

Table 1

The best conditions for determination of copper at the bare glassy carbon electrode using DPASV were determined [Table 1 and Fig. 1]. The highest value for peak current for cobalt at bare glassy carbon electrode was at pH 4.5 (acetic buffer), deposition potential -0.4 V and deposition time 3min for 10^{-5} M concentration of copper. After that the best percentage of the CoFe_2O_4 modifier were investigated. At the same condition as the bare glassy carbon electrode the percentage of 3% CoFe_2O_4 has the highest current for determination of copper. According to this, all electrodes were prepared with 77% of glassy carbon powder, 3% of modifier, and 20% of paraffin oil.

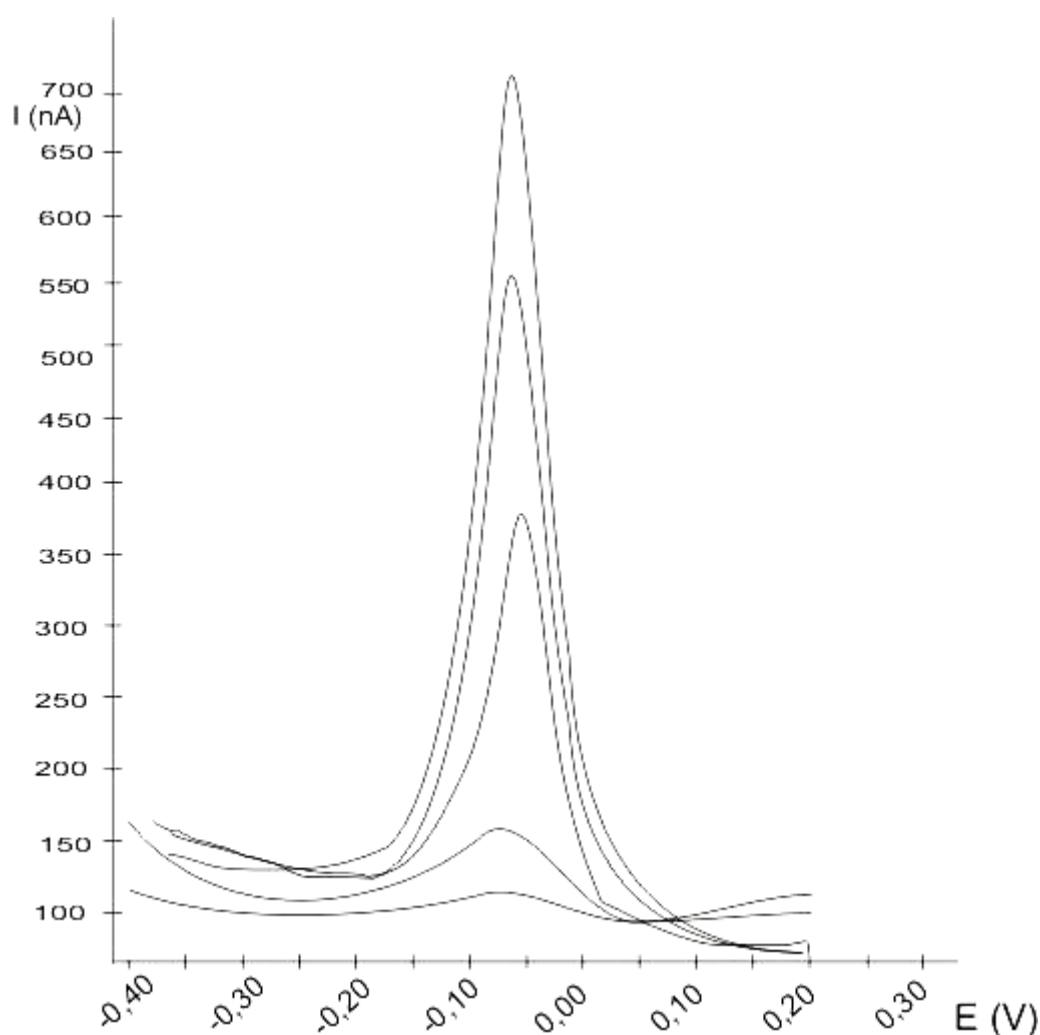


Figure 1

3.5. Preparation of water samples

The water samples were obtained from three rivers (*Table 2*, Kolubara W1, Gradac W2 and Djetinja W3 from Western Serbia) without any pre-treatment. Each sample was filtered to obtain a clear filtrate, transferred to volumetric flask, and stored in a fridge (4°C). The determination of copper was performed by mixing 2 mL of river water with addition of calculated amount of Cu standard, with 8 mL of supporting electrolyte solution.

Sample	Cu ²⁺ before adding of standard	Added Cu ²⁺ μM	Found (avv.)	Recovery
W1	n.d.	1	1.03	103
W2	n.d.	1	1.01	101
W3	n.d.	1	1.04	104

Table 2

4. RESULTS AND DISCUSSION

4.1. Characterization of Co-ferrites

Result of XRD analysis [*Fig. 2*] shows that all ferrite materials shows high ferritization ratio, and the line widths confirms ultra-fine structure of them.

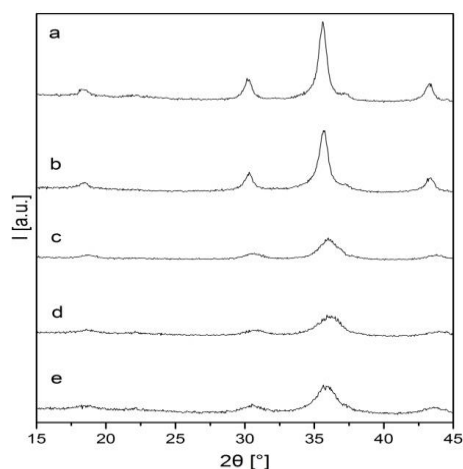


Figure 2

From the pictures obtained by SEM [*Fig. 3*], it is clear that a sample of Co ferrite [d], obtained by microwave-assisted hydrothermal method have better defined ultra-grained surface than others, obtained by other ways (hydrothermal [a], ultrasound assisted [c], mechanochemical [b] and sol-gel[e]). That may be a reason for its highest reactivity.

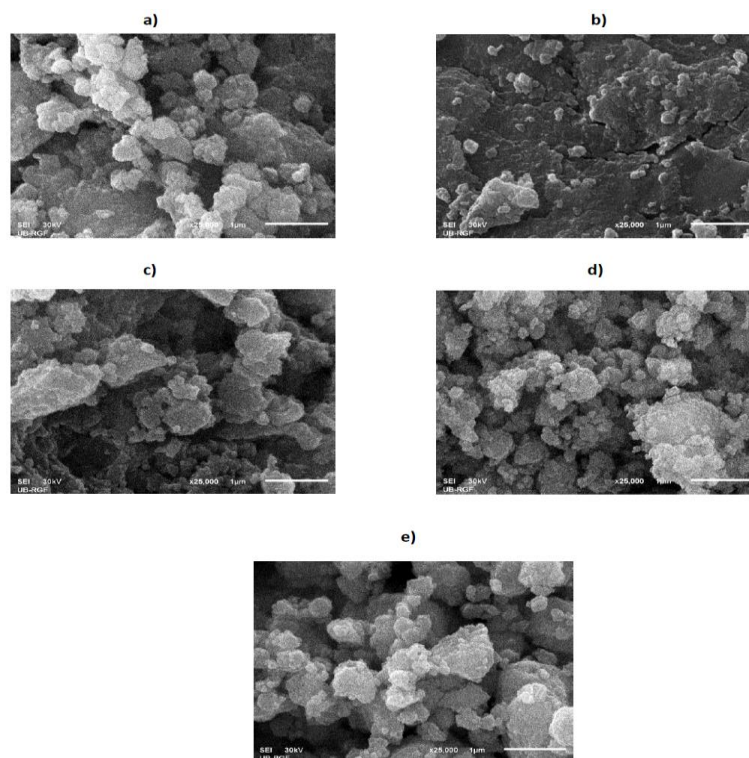


Figure 3

5. CONCLUSION

The preparation of Co-ferrite modifiers of glassy carbon paste electrode and its analytical application for determination of copper in natural waters samples was investigated. The cobalt ferrites were synthesized by five different ways and characterized. The modified electrode with low detection limit were successfully applied for determination of copper ions in natural waters.

REFERENCES

- Ait Sidi Mou, A., Datche, T., Ouarzane, A., El Rhazi, M. 2013, Study of Carbon Paste Electrode modified with Takawt plant for determination of Cu (II) by differential pulse voltammetry, *Journal of Materials and Environmental Sciences* vol. 4 (4), pp. 460-465.
- Almeida, T.P., Fay, M.W., Zhu, Y., and Brown, P.D. 2012, Hydrothermal synthesis of mixed cobalt – nickel ferrite nanoparticles, *Journal of Physics: Conference Series* 371 012074
- Bilecka, I., and Niederberger, M. 2010, Microwave chemistry for inorganic nanomaterials synthesis, *Nanoscale*, vol. 2 (8), pp. 1358–1374.
- Byrappa, K., Yoshimura M. 2001, *Handbook of Hydrothermal Technology*, Noyes Publications, New Jersey, USA pp. 780.
- D'Arrigo, M.C., Leonelli, C., and Pellacani, G.C. 1998, Microwave –Hydrothermal Synthesis of nanophase ferrites, *Journal of American Ceramical Society*, vol. 81 (11), pp. 3041-43.
- Goswami, P.P., Choudhury, H.A., Chakma, S., and Moholkar, V.S., 2013, Sonochemical Synthesis of Cobalt Ferrite Nanoparticles, *International Journal of Chemical Engineering*, 934234, 6 p.
- Janegitz, B.C., Marcolino-Juniorb, L.H., Campana-Filhoc, S.P., Faria, R.C., Fatibello-Filho, O. 2009, Anodic Stripping Voltammetric Determination of Cobalt (II) using a functionalized carbon nanotubes paste electrode modified with cross-linked Chitosan, *Sensors and Actuators*, vol. 142, pp. 260-266.

- Kalcher, K. 1985, Voltammetric determination of trace amounts of gold with a chemically modified carbon paste electrode, *Analytica Chimica Acta*, vol. 177, pp. 175-182.
- Kalcher, K. 1990, Chemically Modified Carbon Paste Electrodes in Voltammetric Analysis, *Electroanalysis*, vol. 2, pp. 419-433.
- Kalcher, K., Švancara, I., Metelka, R., Vytrás, K., Walcarius, A. 2006, "Heterogeneous Carbon Electrochemical Sensors", in: *Encyclopedia of Sensors* (C. A. Grimes, E. C. Dickey, M. V. Pishko, eds.), American Scientific Publishers, Stevenson Ranch, USA, vol. 4, pp. 283-429.
- Konishi, Y., Nomura, T., Mizoe, K., and Nakata, K. 2004, Preparation of Cobalt Ferrite Nanoparticles by Hydrolysis of Cobalt-Iron (III) Carboxylate Dissolved in Organic Solvent, *Materials Transactions*, vol. 45, pp. 81-85.
- Lu, A.H., Salabas, E.L. and Schuth, F. 2007, Magnetic Nanoparticle: Synthesis, Protection, Functionalization and Application, *Angewandte Chemistry International Edition*, vol. 46, pp. 1222-1244.
- Manova, E., Estournès, C., Paneva, D., Rehspringer, J.-L., Tsoncheva, T., Kunev, B., Mitov, I. 2005, Mössbauer study of nanodimensional nickel ferrite – mechanochemical synthesis and catalytic properties, *Hyperfine Interactions*, vol. 165, pp. 215-220.
- Manova, E., Paneva, D., Kunev, B., Estournès, C., Rivière, E., Tenchev, K., Léaustic, A., Mitov, I. 2009, Mechanochemical synthesis and characterization of nanodimensional iron-cobalt spinel oxides, *Journal of Alloys and Compounds*, vol. 485 (1-2), pp. 356-361.
- McCurrie, R.A. 1994, *Ferromagnetic materials: structure and properties*, Academic Press, London, San Diego
- Schachl, K., Alemu, H., Kalcher, K., Jezkova, J., Svancara, I., Vytras, K. 1997, Amperometric Determination of Hydrogen Peroxide With a Manganese Dioxide-modified Carbon Paste Electrode Using Flow Injection Analysis, *Analyst*, vol. 122, pp. 985–989.
- Shinde, A.B. 2016, Dielectric Behavior of the Cobalt ferrite Nanoparticles Synthesized by the sol-gel Auto-Combustion Method, *International Journal of Research in Engineering and Applied Sciences*, vol. 6 (3), pp. 71-74
- Song, J., Ma, Z.Y., Li, C., Wu, R.J. 2010, Synthesis of Ferric Oxide Nanoparticles with Controllable Crystal Phases by Salt-assisted Combustion Method, *Journal of Inorganic Materials*, vol. 25 (7), pp. 780-784
- Suslick, K.S., Casadonte, D.J., Doktycz, S.J. 1989, The effect of ultrasound on nickel and copper powders, *Solid State Ionics*, vol. 32-33, pp. 414-416