Scientific paper

Incorporation of Cobalt-ferrite Nanoparticles Into a Conducting Polymer in Aqueous Micellar Medium: Strategy to Get Photocatalytic Composites

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Abstract

In this study an easy strategy for conducting polymer based nanocomposite formation is presented through the deposition of cobalt-ferrite ($CoFe_2O_4$) containing poly(3,4-ethylenedioxythiophene) (PEDOT) thin layers. The electrochemical polymerization has been performed galvanostatically in an aqueous micellar medium in the presence of the nanoparticles and the surface active Triton X-100. The nanoparticles have been characterized by Transmission electron microscopy (TEM), the thin layers has been studied by applying Scanning electron microscopy (SEM), and X-ray diffraction (XRD), and the basic electrochemical properties have been also determined. Moreover, electrocatalytic activity of the composite was demonstrated in the electrooxidation reaction of dopamine (DA). The enhanced sensitivity – related to the cobalt-ferrite content – and the experienced photocatalyitic activity are promising for future application.

Keywords: Cobalt-ferrite, PEDOT, Triton X-100, dopamine, photocatalysis

1. Introduction

Since their discovery, conducting polymers attract continuously escalating interest from both academic and industrial groups. Low cost of their synthesis, high physical and chemical stability and easily adjustable optical and electrical properties make them promising candidates for many different applications e.g. in photovoltaic devices, sensors and biosensors, corrosion protection.[1–4] Although properties of conducting polymers depend largely on the monomer, conditions of the polymerization have also crucial influence on it. Application of aqueous micellar medium, beyond its solubility increasing effect, can lead to significant improvement of the physicochemical properties of the polymer.[5,6]

Although conducting polymers show remarkable features in several fields by their own, industrial application usually makes it crucial to improve one or more of their parameters e.g. conductivity, capacitance, stability. This requirement can be most easily achieved by forming composites, by combining the polymer with some other, mostly inorganic component. The importance of such composites is well represented by the monotonous, quasi exponential growth of papers on this topic.[9]

Although it is possible to form "organic in inorganic" type composites by incorporating the conducting polymer in inorganic matrix (e.g. TiO_2 nanotube array[10]), it is more usual to embed inorganic (nano)particles in the organic matrix. This way it is easy to form composites with high

homogeneity, which ensures large contact surface between the components, and leads to the summation of individual properties, and sometimes even to synergetic effects. The variety of the incorporated component is almost infinite: metal nanoparticles, carbon nanotubes, photoactive oxides are all good examples for that.[11–13]

Ferrites containing conducting polymer composites represent a small, but well delimited, widely investigated group. Incorporation of such, redox active NP can lead to extraordinary catalytic activity, giving rise to analytical or even fuel-cell applications. Based on wide variety of their colour, crystalline size based magnetic properties and ease of their synthesis, their application is intensively studied in several fields, such as magnetic shielding or photocatalysis. Although magnetite – having a composition of Fe_3O_4 – is the most intensely investigated representative, synthesis and characterization of different metal ion (e.g. Ni^{2+}, Co^{2+}, Zn^{2+}) containing ferrites has also drawn notable attention in the last couple of years.[14,15]

Cobalt-ferrite ($CoFe_2O_4$) – similarly to magnetite – is a spinel (or inverse spinel) structured, ferromagnetic oxide. Due to its easy synthesis – performed mostly by co-precipitation method –, possible catalytic application and tuneable magnetic properties, it is getting more and more attention in scientific works.[14,16,17] Moreover, several reports have been published on the incorporation of cobalt-ferrite into conducting polymer matrix during chemical polymerization or either *via* layer by layer method.[18–21] Since these oxide nanoparticles are obtained in aqueous medium, their incorporation into a polymer is self-evident in such a phase. However, many organics can hardly be polymerized in water, because of the unwanted side reaction with this nucleophile, leading to irreversible defects. Beyond the above-mentioned advantages, the presence of micelle-forming ambipolar additives can help also to overcome this obstacle.[22,23]

In this study, we demonstrate the photo-electrocatalytic performance obtained through a one-pot electrochemical incorporation of magnetic cobalt-ferrite nanoparticles into poly(3,4-ethylenedioxythiophene) (PEDOT) matrix in aqueous micellar medium. To the best of our knowledge, no such paper has been published on this topic so far.

2. Experimental

2. 1. Materials

2. 1. 1. Synthesis of $CoFe_2O_4$ Nanoparticles

NPs were synthesized by co-precipitation method. 1:2 ratio $FeCl_3$ and $CoCl_2$ containing water based solution (having concentrations of 0.1 and 0.05 M, respectively) was added drop wise to rigorously stirred, 80 °C hot 0.8 M NaOH solution. The reaction mixture was kept at for 3 hours, meanwhile the formation of black powder was observed.

The black precipitate was separated magnetically, and washed repeatedly with deionized water to remove traces of the precursors and to reach neutral pH. The product was freeze dried to get NPs in powder form, and placed in oven at 600 °C for 4 hours.

All polymerization solutions contained 0.03 M of the EDOT monomer, 0.5 M sodium p-toluenesulfonate (NaTos) and 0.1 M Triton X-100 in deionized water. The amount of cobalt ferrite NPs was 1 g dm^{-3}. Poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(3,4-ethylenedioxythiophene)–cobalt-ferrite (PEDOT/$CoFe_2O_4$) composite films were deposited galvanostatically (j = 0.4 mA cm^{-2}) with a charge density of 300 mC cm^{-2}. For further voltammetric studies the solution was changed after the polymerization to phosphate buffer solution (pH = 7, c = 100 mM).

Analytical grade 3,4-ethylene-dioxythiophene (EDOT) was the kind donation of Bayer AG, while $FeCl_3 \cdot 6H_2O$ was purchased from Sigma-Aldrich, $CoCl_2 \cdot 6H_2O$ from Molar Chemicals, NaTos from Chemische Fabrik, Triton X-100 from Amresco and NaOH, $NaH_2PO_4 \cdot H_2O$ and $Na_2HPO_4 \cdot 2H_2O$ from Reanal. Dopamine hydrochloride – used for analytical measurements – was purchased from Sigma-Aldrich.

2. 2. Methods

All electrochemical measurements were performed on a PGSTAT 10 (Autolab) instrument, in a classical three-electrode electrochemical cell, kept in a dark box. Glassy carbon disk (A = 0.07069 cm^{-2}) and Pt ring were used as working and counter-electrodes, respectively. The reference electrode was an Ag/AgCl/3 M NaCl electrode, having a potential of 0.200 V vs. SHE.

Transmission electron microscopic (TEM) investigation of the NPs was performed using a FEI Tecnai G^2 20 X-Twin type instrument, operating at an acceleration voltage of 200 kV.

XRD experiments were performed by a MiniFlex II instrument, by applying $Cu_{K,\alpha}$ (λ = 0,154 nm) as source. Diffractograms were recorded between 10–80 2Θ degrees, by applying 2 degrees/minute scan speed.

Before SEM analysis, the samples were coated by gold in a Balzers Union SCD 40 sputter-coater. SEM pictures were taken by a Cambridge Stereoscan 120 instrument at an accelerating voltage of 2.5 kV.

3. Results and Discussion

3. 1. Synthesis and Characterization of $CoFe_2O_4$ Nanoparticles

Although the nanoparticles were synthesized by a method, resulting cobalt-ferrite, XRD measurements have been carried out to get direct evidence on the presence of
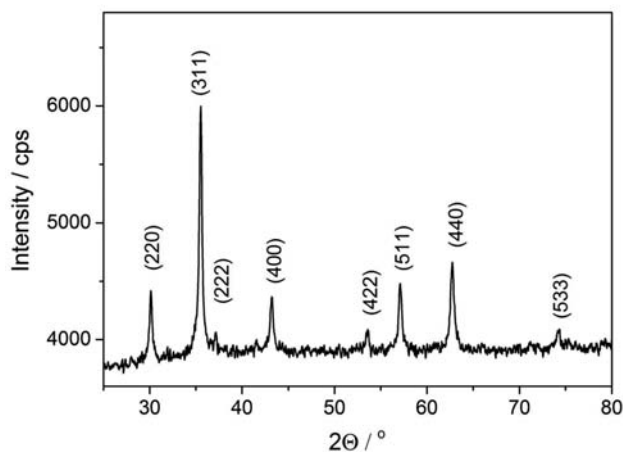
Fig. 1. XRD spectra recorded for the $CoFe_2O_4$ nanoparticles

cobalt-ferrite particles. Five most intensive diffractions of the obtained material were compared with the literature values of $CoFe_2O_4$.

The XRD pattern measured for the synthesised NPs is in perfect agreement with the literature values, proving the formation of cobalt-ferrite. Moreover, the nanoparticles showed ferromagnetic behaviour, which is also a good, qualitative indication for the successful synthesis.

To investigate the size and shape of the formed NPs, TEM pictures were taken (see Fig. 2.). Upon these images, the NPs show poly-disperse size distribution in the range of 20–100 nm, with an average value of 50 nm (see inset on Fig. 2.).
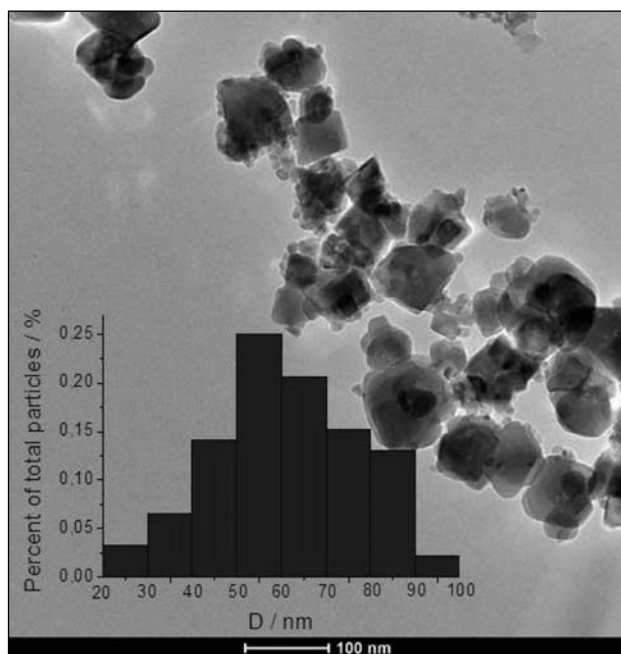

Fig. 2. TEM image of $CoFe_2O_4$ nanoparticles, taken at 88000 x magnification. Inset shows the size distribution of the nanoparticles

3. 2. Electrodeposition of PEDOT and PEDOT/CoFe$_2$O$_4$ Thin Layers

Electrodeposition of the polymer and the composite thin films were performed galvanostatically, under identical circumstances (except the presence of the nanoparticles). As it is clearly seen on Fig. 3, the chrono-potential curves, registered for the two different systems, are very close to each other, which indicates similar processes during polymerization. Notice however, that the potential is slightly lower in the case of NPs containing polymerization solutions, which effect was reported earlier in the literature for magnetite containing composite synthesis, and hence it can be an indication on nanoparticle incorporation inside the polymer film.[24]
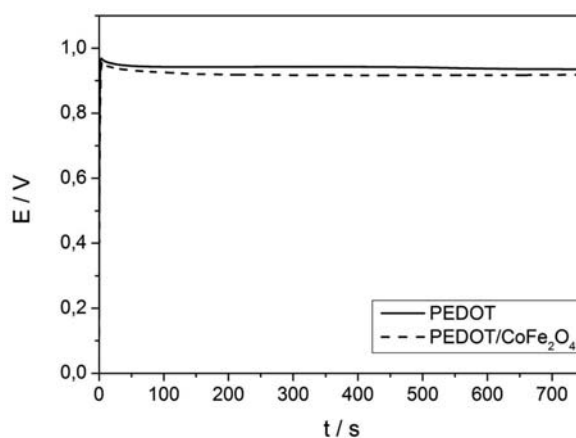

Fig. 3. Polymerization curves registered for PEDOT and PEDOT/CoFe$_2$O$_4$ during electrodeposition

3. 3. Morphological and Compositional Characterization PEDOT/CoFe$_2$O$_4$ Composite

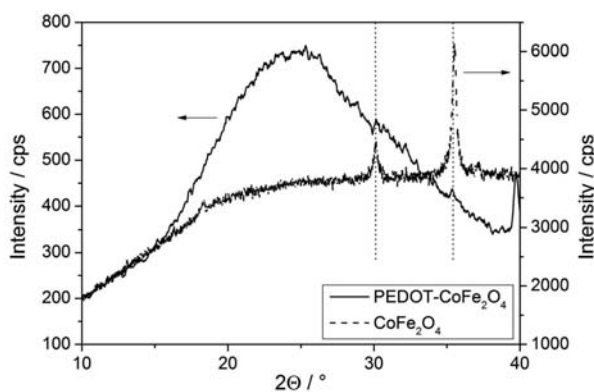Presence of the cobalt-ferrite in the composite was proved by XRD measurements. As it is seen on Figure 4.,

Fig. 4. XRD pattern registered for the PEDOT/CoFe$_2$O$_4$ thin layer. Diffractogram of the $CoFe_2O_4$ is also presented for comparison.
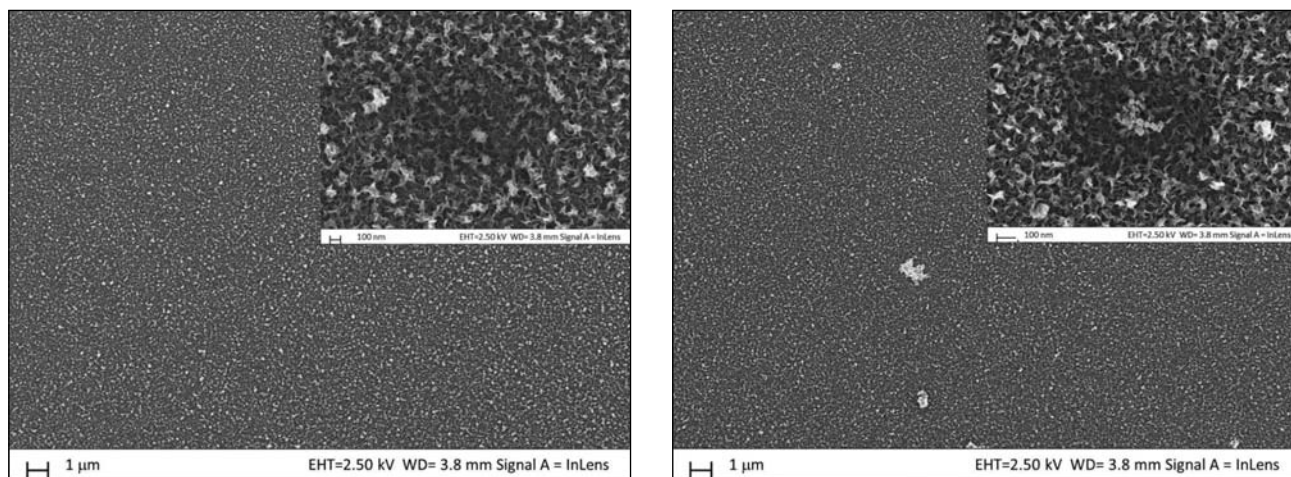
Fig. 5. A&B Morphology of PEDOT (A) and PEDOT/CoFe$_2$O$_4$ (B) thin layers in 1K and 10K (inset) times magnification

the composite shows broad reflection between 10–40 2Θ degrees, which is typical behaviour for amorphous polymeric systems.[25] Although this broad, "hill like" reflection is dominant, the two most intense reflection of the NPs at 30.1 and 35.4 2Θ degrees appear beyond doubt, super positioned on the hill. This result is clear and obvious indication of the presence of cobalt-ferrite in the composite.

Morphological characteristics of both PEDOT and PEDOT/CoFe$_2$O$_4$ thin layers were determined by SEM. As it is seen on Figure 5. A&B, in contrast with the usual cauliflower like structure,[26] both layers have very smooth surface. Since similar behaviour was reported earlier for a conducting polymer – polybithiophene –, synthesised in micellar medium, we believe that the formation of such structure is due to the presence of Triton X-100 during the synthesis.[27]

Although the two different thin layers have very similar surface morphology, larger magnification can reveal some small but characteristic differences between them (see inset on Fig. 5. A&B). In case of the composite film, we can find well dispersed, crystalline aggregates on the surface, which can be attributed to the incorporated NPs.

Although the relatively small difference between the morphologies, and the XRD measurements indicates low NP content of the composite, even a small amount of incorporated cobalt-ferrite is expected to cause large differences in the catalytic activity.[18]

3. 4. Electrochemical Behaviour of the PEDOT/CoFe$_2$O$_4$ Composite Thin Layer

Electrochemical behaviour of the composite was investigated by cyclic voltammetry. As it is seen on Figure 6, the composite shows mostly capacitive behaviour, which is typical for PEDOT based composites.[28]
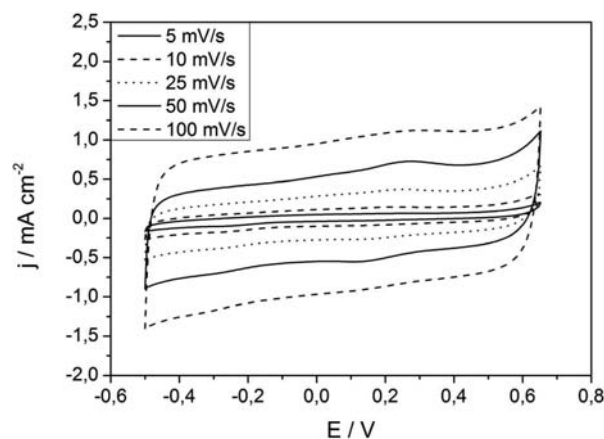

Fig. 6. Sweep rate dependence of cyclic voltammetric behaviour of PEDOT/CoFe$_2$O$_4$ in phosphate buffer solution (c = 100 mM, pH = 7)

3. 5. Electrocatalytic Activity of the PEDOT/CoFe$_2$O$_4$ Composite Thin Layer

Since electrocatalytic activity of ferrite containing composites in anodic processes was reported in the literature earlier, electrooxidation of dopamine (DA) was chosen as test reaction to make studies in this respect.[29,30]

To separate DA oxidation from the background current – arising from the redox transformation of the polymer –, cyclic voltammetric measurements were performed. In order to identify a proper potential for further quantitative experiments, the composite thin layer electrode has been studied both in the pure, and in a 200 μM DA containing phosphate buffer solution.

As it can be seen from Figure 7, in the presence of dopamine there is a current increase from 0.1 V in the anodic region, which reaches a maximum at about 0.2 V. On the reverse cycle, cathodic current surplus can be observed, starting from 0.2 V and reaching its maximum at
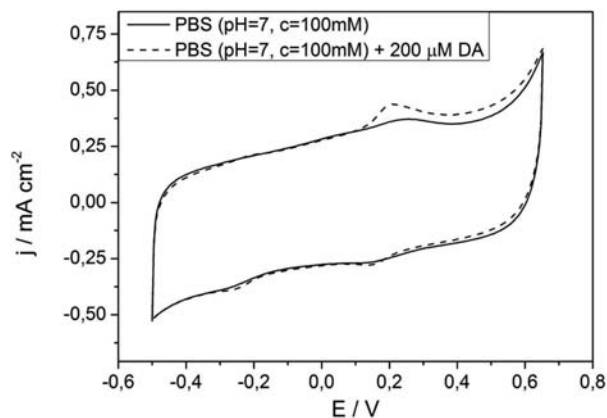
Fig. 7. Cyclic voltammetric curves registered for PEDOT/CoFe$_2$O$_4$ in phosphate buffer solution (c = 100 mM, pH = 7) in the absence (black) and in the presence (red) of 200 μM dopamine at a sweep rate of 50 mV/s

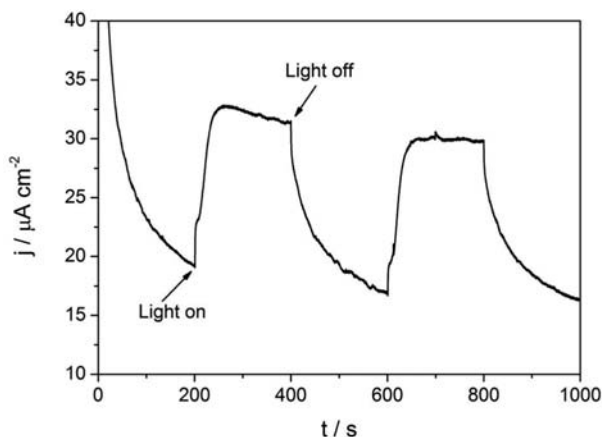**Fig. 9.** Effect of illumination on the electrooxidation of dopamine on PEDOT/CoFe$_2$O$_4$ electrode at +0.2 V in 200 μM dopamine containing phosphate buffer solution (c = 100 mM, pH = 7)
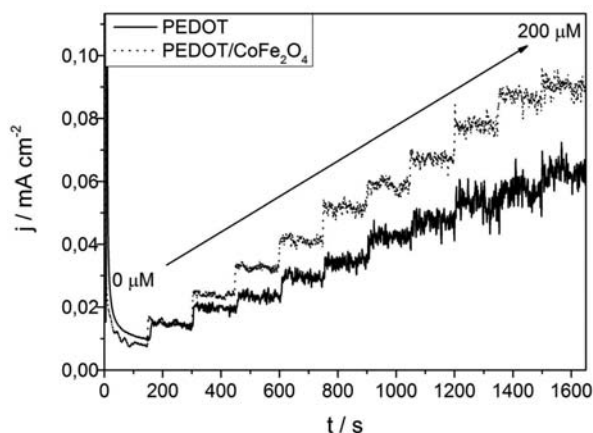

Fig. 8. Chronoamperometric response of PEDOT and PEDOT/CoFe$_2$O$_4$ layers at +0.2 V in dopamine containing phosphate buffer solution (c = 100 mM, pH = 7). Concentration of dopamine is gradually increased by 20 μM in each step (150 s).

In order to see the photocatalytic behaviour of the polymer hybrid, the effect of the illumination on the electrocatalytic process was also investigated. As it is seen on Figure 9., upon illumination of the electrode in the visible wavelength range by white light, there is a rapid increase in the amperometric current density, indicating the photocatalytic activity of the composite. After turning the lamp off, cease of the photocurrent reflects a much slower process. This effect can be interpreted by assuming a mechanism, in which light-induced current growth is attributed to the photogeneration and accumulation of a reactive intermediate. After having the lamp turned off, this intermediate is still present in the vicinity of the electrode, hence the current doesn't fall back to its dark value instantly, but the photocurrent diminishes slowly. Similar mechanism was demonstrated earlier for magnetite containing conducting polymer composites.

4. Conclusions

PEDOT/CoFe$_2$O$_4$ composite thin layers were successfully prepared by galvanostatic one-pot electrodeposition in aqueous micellar medium, in the presence of Triton X-100. Morphological and compositional analysis revealed slight differences between the pristine PEDOT and the composite layer, assumingly due to the modest NP content. Even so, the composite showed enhanced sensitivity in the electrooxidation reaction of dopamine (DA) during chronoamperometric experiments compared to its nanoparticles free counterpart. Moreover, photocatalytic effect was demonstrated for the PEDOT/CoFe$_2$O$_4$ thin layer, which is promising for future application. The applied method is expected to serve as a general strategy for obtaining ferrite nanoparticle containing polythiophenes with good catalytic or photocatalytic activity.

0.15 V. Since this redox couple wasn't observed in the same solution in the absence of dopamine, it is obviously related to the redox transformation of the analyte. Based on the results of these voltammetric experiments, E = 0.2 V was chosen for further amperometric studies.

Chronoamperometric experiments were carried out for both PEDOT and PEDOT/CoFe$_2$O$_4$ thin layers. The electrodes were polarized at +0.2 V, and the concentration of dopamine was gradually increased in the continuously stirred phosphate buffer solution. As it is seen in Figure 8., both thin layers show catalytic activity on the electrooxidation of dopamine. Moreover, both layers give linear response to the increasing concentration of the analyte. Note however, that the sensitivity of the cobalt-ferrite containing electrode is much higher than that of the neat PEDOT, which can be attributed to the contribution of the incorporated nanoparticles.

5. Acknowledgements

6. References

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Povzetek

Predstavili smo enostavno strategijo priprave nanokompozitov na osnovi prevodnih polimerov in sicer skozi depozicijo kobaltovega ferita ($CoFe_2O_4$), ki vsebuje tanko plast poli(3,4-etilenedioksitiofena). Elektrokemijska polimerizacija je potekala galvanostatski v vodni micelarni raztopini ob prisotnosti nanodelcev in površinsko aktivne snovi Triton X-100. Nanodelce smo analizirali s transmisijsko elektronsko mikroskopijo, tanke plasti pa z vrstično elektronsko mikroskopijo in rentgensko difrakcijo. Določili smo tudi osnovne elektrokemijske parametre. Elektrokatalitično aktivnost kompozita smo pokazali skozi reakcijo elektrooksidacije dopamina. Povečana občutljivost, ki je povezana s prisotnostjo kobaltovega ferita, in fotokatalitična aktivnost sta pomembni za bodoče aplikacije pripravljenih nanokompozitov.