UDC 544.654.2

Yu.E. Sknar, I.V. Sknar, A.A. Savchuk, A.A. Bezik, F.I. Danilov

PHOTOCATALYTIC ACTIVITY OF Ni–TiO_2 COMPOSITES ELECTRODEPOSITED ON A NICKEL MATRIX WITH DEVELOPED SURFACE

Ukrainian State University of Chemical Technology, Dnipro, Ukraine

The photocatalytic activity of Ni–TiO_2 composites obtained from a methanesulfonate electrolyte was studied. The photodegradation of methyl orange in the presence of Ni–TiO_2 composite resulted in a partial poisoning of the photocatalyst, which is manifested in a decrease of its activity over time. The photodegradation of methyl orange dye was stated to follow the pseudo-first order kinetics. The observed rate constant of the photodegradation reaction is proportional to the surface area of the photocatalyst. The dependences of the composite composition on the dispersed phase concentration in the solution and current density showed only a limited possibility of increasing the content of photocatalytically active TiO_2 particles in the coating. This paper presents a new method for increasing the photocatalytic activity of the Ni–TiO_2 composite. The authors have proposed to deposit a photocatalyst on a preformed nickel developed surface matrix. The effect of increasing the specific surface area of the matrix is achieved by nickel electrodeposition from a suspension electrolyte containing carbonyl nickel powder as a dispersed phase. The inspection of the voltammograms of hydrogen evolution reaction on smooth and developed nickel surfaces revealed that the incorporation of nickel particles into the coating leads to a significant increase in the specific surface area of the matrix. The composite Ni–TiO_2 coatings deposited on a developed surface matrix have a four times higher photocatalytic activity than those obtained on a smooth sample.

Keywords: Ni–TiO_2 composite, photocatalytic activity, developed surface, matrix, methanesulfonate electrolyte.

Introduction

Electrodeposition of composite coatings is one of the effective ways to impart special physico-chemical or mechanical properties to the surface of structural materials. Nowadays, special emphasis is laid on coatings containing titanium dioxide. These composites exhibit a photocatalytic activity due to the UV-induced formation of a hole-electron pair in TiO_2 particles. The photogenerated charge carriers can react with water and oxygen molecules adsorbed on the TiO_2 surface to form radicals that interact with various pollutants ensuring their destruction [1–4]. For many practical tasks, such as photocatalytic air purification and contaminated water treatment, titanium dioxide particles should be firmly arranged in a solid matrix.

Electrodeposition is an efficient and easily controlled method for producing composites containing TiO_2 [5–10]. The dispersed phase content of the coatings depends on the parameters of electrolysis and electrolyte composition. It was shown in study [11] that the deposition of nickel-based composites from a suspension methanesulfonate electrolyte enables obtaining deposits with an increased content of oxide particles, in particular zirconia. However, the possibility of increasing the TiO_2 content of the composites by varying the electrolysis parameters is very limited [12].

It is obvious that the degree of photocatalytic activity of the Ni–TiO_2 catalyst is determined by the content of TiO_2 particles per unit surface area. Consequently, the development of the specific surface area of the matrix is a promising way to increase the efficiency of composite catalysts. In this regard, this paper considers the electroplating method of obtaining nickel matrices with predicted specific surface areas; it also presents the results of studying the photocatalytic properties of Ni–TiO_2 composite coatings obtained on these matrices from the methanesulfonate electrolyte.

Experimental

Ni–TiO_2 composite coatings were obtained

---

from the methanesulfonate electrolyte, its composition is given in Table 1. Nickel methanesulfonate was synthesized by mixing nickel carbonate and methanesulfonic acid. The nonmetallic dispersed phase was P 25 (Degussa, Evonik) titanium dioxide nanopowder with an average particle diameter of 30 nm [13]. The nickel matrix with a developed surface was formed from an electrolyte containing PNK carbonyl nickel powder (GOST 9722-97) with a particle size of about 3 μm (Table 1). The pH values of the solutions were monitored using an EV-74 universal potentiometer with the combined ESK-10601/7 electrode. The specified pH values were adjusted using solutions of 0.1 M CH_3SO_3H or 0.1 M NaOH.

Table 1

Electrolyte compositions for the deposition of the $Ni–TiO_2$ composites and nickel matrix

Bath component	Content (mol/l)	
	$Ni–TiO_2$ composites	Nickel matrix
$Ni(CH_3SO_3)_2$	1.0	1.0
H_3BO_3	0.7	0.7
NaCl	0.3	0.3
TiO_2	1 g/l, 2 g/l, 4 g/l, 7 g/l	–
Carbonyl nickel powder	–	0.1 g/l, 0.2 g/l, 0.5 g/l
pH	3	3

The electrodeposition of the nickel matrix and the composites was carried out at T=333 K; a magnetic stirrer was used for the electrolyte agitation. The stirring rate was 500 rpm. A copper plate was used as the cathode. The anodes were made of nickel.

The titanium content in the coatings was assessed by the X-ray fluorescence method [14] using the X-ray energy dispersion spectrometer SEF-01-M1 SPRUT. The volume of TiO_2 incorporated in the coating was determined by the formula:

$$V_{TiO_2} = \frac{(m - m_{Ni})}{\rho_{TiO_2}}, \tag{1}$$

where m is the mass of the composite coating; ρ_{TiO_2}=4.5 g/cm^3 is the density of titanium dioxide [15].

The volume of nickel in the composite coating was calculated as follows:

$$V_{Ni} = \frac{m_{Ni}}{\rho_{Ni}}, \tag{2}$$

where ρ_{Ni}=8.9 g/cm^3 is the density of nickel [15].

The volume fraction of titanium dioxide in the coating was determined by the following equation:

$$Y = \frac{V_{TiO_2}}{V_{TiO_2} + V_{Ni}}. \tag{3}$$

The photocatalytic activity of $Ni–TiO_2$ was estimated from the results of kinetic studies of UV-induced photodegradation of methyl orange dye. The composite coatings were placed in a 20 ml methyl orange solution and irradiated with an EXO TERRA Repti Glo10 lamp. The radiation range of the lamp was 280 to 315 nm. The initial concentration of methyl orange was 6 μmol/l, pH was 7. The changes in the dye concentrations were estimated by the photocolorimetric method using KFK-2–UHL–4.2 and a color filter corresponding to a wavelength of 490 nm.

The surface morphology studies were carried out using a ZEISS EVO 40XVP scanning electron microscope.

Results and discussion

A study of some factors affecting the composition of $Ni–TiO_2$ coatings showed that an increase in the TiO_2 concentration in the electrolyte leads to an increase in the dispersed phase content in the coatings electrodeposited from the methanesulfonate suspension electrolyte (Fig. 1). The dependence of the titanium dioxide amounts in the composites on the particle concentrations in the electrolyte is nonlinear. After significant increasing the TiO_2 particle content in the composite at low dispersed phase concentrations in the electrolyte, establishing the practically constant Y values is observed at higher TiO_2 concentrations in the plating bath. This form of the dependence Y vs. C can be explained by the fact that the dispersed phase occupies a fraction on the cathode surface, which is proportional to the volume fraction of particles in the coating (Y). It was shown in work [16] that the dependence of the degree of surface covering by these particles on their concentration in the electrolyte is similar to the Langmuir isotherm.

An increase in the current density of composite deposition leads to a certain decrease in the TiO_2 content in the deposits. This may be due to the redistribution of the current densities of the metal matrix electrodeposition on the electrode surfaces that are free and conventionally occupied with the particles [16]. This will obviously affect the composition of the composite.

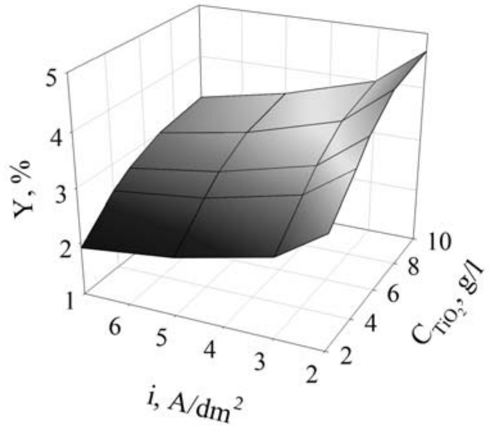


Fig. 1. TiO_2 content in the composites versus the dispersed phase concentration in the electrolyte and the current density

With a uniform distribution of the dispersed phase throughout the thickness of the composite, the surface fraction per TiO_2 particle is proportional to the TiO_2 particle volume content. Since the photocatalytic degradation is a heterogeneous reaction and its rate is proportional to the titanium dioxide surface available for the adsorption of the reagent, an increase in the TiO_2 content of the composites should result in an increase in the catalytically active surface. However, the dependence shown in Fig. 1 indicates a rather weak change in the titanium dioxide content in the composites with changing the dispersed phase concentrations in the electrolyte and the deposition current densities.

To increase an active surface of the photocatalyst at constant dimensions of the sample, it is possible to deposit a composite coating on a preformed metal substrate with a developed surface. One of the possible options for developing the surface of a matrix is the formation of coatings in the presence of a metal dispersed phase in plating bath. Electrodeposition of composites with a metal dispersed phase in order to increase their functional characteristics was proposed in studies [17,18]. The authors [17] investigated the effect of electrolysis parameters on the content of aluminum and titanium particles in nickel–based composites. In work [18], an increase in the corrosion resistance and microhardness of copper composites with incorporated niobium particles was reported. In present study, nickel carbonyl powder was used as a dispersed phase as the granulometric characteristics of nickel carbonyl powder allow creating irregularities on the matrix being formed.

The nickel matrix was electrodeposited under the galvanostatic conditions from an electrolyte containing carbonyl nickel powder (Table 1). The thickness of nickel electrodeposited at a current density of 2 A/dm^2 was about 15 mm. Before the introduction of the nickel powder into the matrix deposition electrolyte, the powder was activated in a solution of 1 M HCl and rinsed five times with distilled water.

It should be noted that the ferromagnetic properties of nickel can contribute to an increase in the amount of incorporated nickel powder particles in a nickel matrix during the matrix electrodeposition in a magnetic field. This can be employed if a magnetic stirrer is used to agitate the suspension electrolyte.

During the electrodeposition of the matrix from nickel plating electrolyte containing nickel metal powder, an electrodeposit is formed with the inclusion of electrically conductive nickel particles in it; nickel ions are also discharged on their surfaces (Fig. 2). This promotes the development of the metal matrix surface and stronger bonds of the incorporated nickel particles to the electrodeposit. The nickel matrix has a high adhesion to the substrate; it is a coating with firmly embedded particles of carbonyl nickel powder and it obviously has a developed surface.

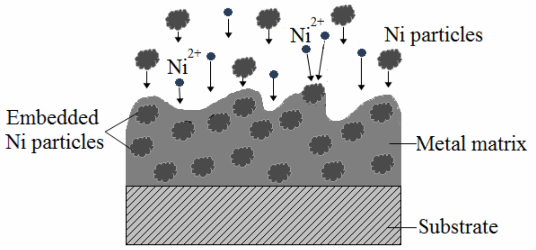
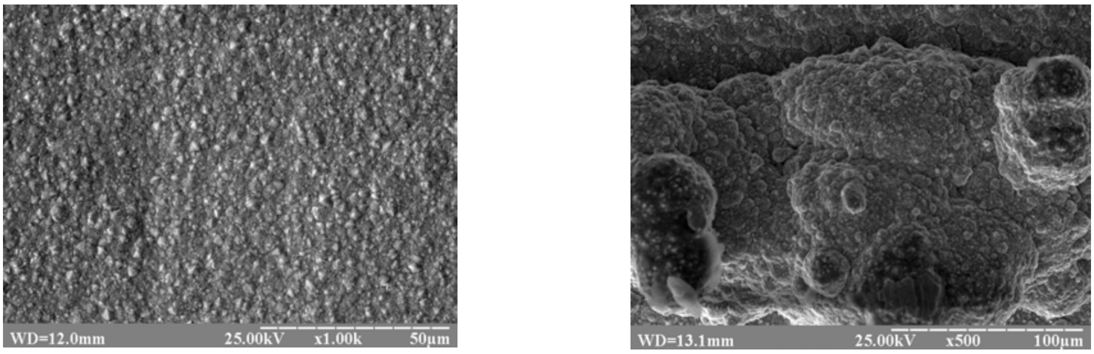


Fig. 2. Scheme of formation of a developed surface matrix

Indeed, it is evident from Fig. 3 that the surface morphology of the composite coating deposited on the preformed nickel matrix differs significantly from the that of the composite obtained on a «smooth» electrode.

The true specific surface area of a nickel matrix thus formed was determined by a comparison of the overpotentials of hydrogen evolution reaction in 1 M NaOH solution at i=const on the nickel matrix with developed surface and on a smooth sample of equal geometric dimensions, respectively.

If we assume that the area of a smooth electrode is, in the first approximation, equal to the visible one, then, using the slow-discharge equation for galvanostatic conditions, we can obtain the following



a **b**

Fig. 3. Surface morphology of Ni–TiO_2 composites obtained on a smooth electrode (a) and on a developed surface matrix (b)

expression for the specific surface of the matrix:

$$S = \exp\left(-\frac{\alpha F(\eta_1 - \eta_2)}{RT}\right), \qquad (5)$$

where α is the transfer coefficient; R is the universal gas constant; T is the thermodynamic temperature; η_1 and η_2 are overpotentials of hydrogen evolution reaction on the electrode with a smooth and developed surface, respectively.

Chronopotentiograms of hydrogen evolution reaction recorded at a current density of 3.5 A/dm^2 on electrodes with different values of the true surface area are shown in Fig. 4. The results of the calculations according to the equation (5) showed that the specific area of the matrix obtained in the presence of nickel powder in the plating electrolyte is an order of magnitude larger than that of a smooth sample (Table 2).

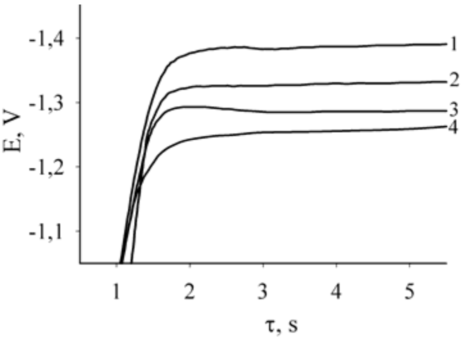


Fig. 4. Chronopotentiograms of hydrogen evolution reaction on a nickel matrix obtained in the presence of nickel powder, g/l: 1 – 0; 2 – 0.1; 3 – 0.2; 4 – 0.5

The composites deposited on these matrices expectedly exhibit enhanced photocatalytic activity (Fig. 5). The rate of the dye photodegradation varies simbatically with the concentration of the nickel powder in the matrix deposition electrolyte, i.e. with an increase in the specific surface area of the catalyst.

Table 2

Geometric and photocatalytic characteristics of coatings obtained at different concentrations of nickel powder

Concentration of nickel powder in the matrix deposition electrolyte, g/l	Specific surface of the matrix S, cm^2	Observed constant of photodegradation rate K, min^{-1}
–	1	0.6×10^{-3}
0.1	9	2.1×10^{-3}
0.2	20	3.1×10^{-3}
0.5	50	5.9×10^{-3}

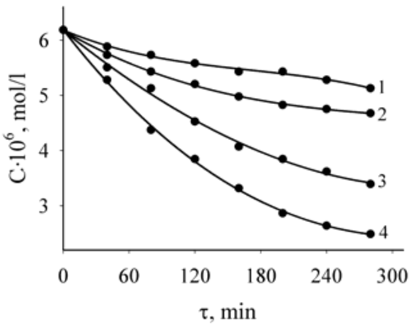


Fig. 5. Kinetic curves of the dye photodegradation occuring on Ni–TiO_2 photocatalysts deposited at different nickel powder concentrations in the electrolyte, g/l: 1 – 0; 2 – 0.1; 3 – 0.2; 4 – 0.5

It should be noted that when the Ni–TiO_2 composites are deposited onto a developed surface matrix, the true current density proves to be substantially lower than on a smooth sample. However, the influence of the current density on the dispersed phase content in the composite is insignificant (Fig. 1) and this circumstance cannot play a decisive role in the effect of increasing the photocatalytic activity of the composites which is observed in Fig. 5.

For a quantitative description of the photocatalytic activity of the composites, it is necessary to take into account the effect of a number of side processes accompanying the UV-induced heterogeneous reaction of methyl orange degradation on the Ni–TiO_2 surface.

Fig. 6 shows that the investigated dye is UV-degraded regardless of the presence of a photocatalyst. Consequently, the observed photocatalytic degradation upon the introduction of Ni–TiO_2 is a combined effect and includes the above component. In addition, it is necessary to pay a regard to the partial poisoning of the photocatalyst by the photodegradation products adsorbed on its surface. This can be assessed if a fresh-prepared sample of Ni–TiO_2 is used in each experiment in the photocatalytic degradation study. The data obtained in this way (Fig. 5, curve 3) indicate that the photocatalytic effect decreases with the time of use of the catalyst.

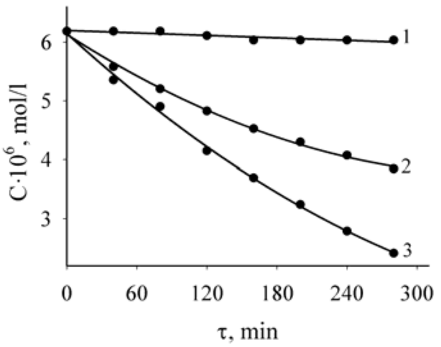


Fig. 6. Kinetic curves of photodegradation of methyl orange in the absence of the composite (1), with the same sample of Ni–TiO_2 throughout the experiment (2), with Ni–TiO_2 samples replaced every 40 minutes during the experiment (3)

The kinetic curves corrected considering the side processes are linearized in semi-logarithmic coordinates (Fig. 7) which is indicative of a pseudo-first order reaction of the methyl orange photodegradation on the Ni–TiO_2 composite surface. This is in good agreement with the data obtained in study [19] for Fe–TiO_2 composites.

The observed experimental rate constants of the photodegradation reaction (K), which correspond to the lines 1–4 (Fig. 7), are given in Table 2. The values of K obviously depend on the specific surface of the sample:

$$K=K_1S, \qquad (6)$$

where K_1 is the photodegradation in terms of surface area-normalized rate constant; and S is the specific surface area of the sample.

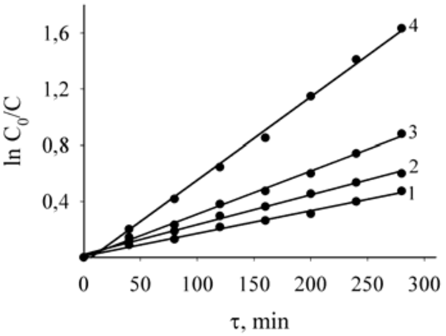


Fig. 7. Semi-logarithmic dependences of the relative changes in the methyl orange concentration versus time under the action of UV-irradiation on Ni–TiO_2 composites. Concentrations of nickel powder in the matrix deposition electrolyte, g/l: 1 – 0; 2 – 0.1; 3 – 0.2; 4 – 0.5

If we assume that the mechanism and kinetics of the photodegradation do not change with the development of the catalyst true surface, then the observed change in the values of the constant K should be related to the increase in the specific surface. In this case, the K–S dependences would be as shown in Fig. 8 (solid line). However, if we assume that the surface on which the photocatalytic reaction occurs is really the same as that indicated in Table 2 and estimated by the equation (5) for the hydrogen evolution reaction, then the K–S dependence will look like a straight line shown in Fig. 8 by a dashed line. Thus, in order to maintain the assumption that K is proportional to the sample area, it should be assumed that the true surface of the catalyst is proportional, though to a lesser degree, to the surface of the matrix. That is why we should write the product bS with $b<1$ in equation (6) instead of S. A comparison of the curve slopes shown in Fig. 8 allows calculating the value of b, which is equal to 6.

The effect of reducing the true surface of the composite in comparison with the matrix can be caused by equalizing the matrix microroughness (Fig. 9) when Ni–TiO_2 coatings of significant thickness (about 15 мм) are deposited, and by the mismatch of the electrode surface available to the hydrogen evolution and incorporation of TiO_2 particles.

Thus, it has been shown that there is a possibility of a substantial increase in the photocatalytic activity of Ni–TiO_2 composites by the development of the active surface of the electrode. The authors are the first who propose a method of applying composites with a preformed developed surface matrix which was a nickel electrodeposit with carbonyl nickel powder particles incorporated into it. The photocatalytic activity of Ni–TiO_2 composites obtained from a methanesulfonate electrolyte on a matrix with developed surface is four times higher than the photocatalytic activity of a composite electro-deposited on a smooth electrode. The enhanced photocatalytic properties and resistance to mechanical wear instill well-founded optimism regarding the prospects for using these composites as photocatalysts in wastewater treatment and in solar power industry.

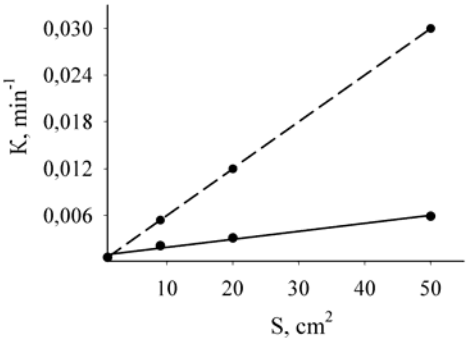


Fig. 8. Dependence of the observed rate constant of the methyl orange photodegradation reaction versus the area of the Ni–TiO_2 composite matrix

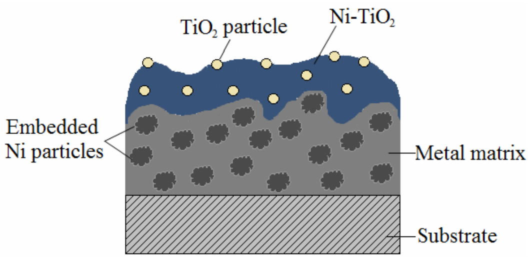


Fig. 9. Schematic representation of Ni–TiO_2 composite formation on a nickel developed surface matrix

REFERENCES

1. *Fujishima A., Zhang X., Tryk D.A.* TiO_2 photocatalysis and related surface phenomena // Surface Science Reports – 2008. – Vol.63. – P.515-582.

2. *Chen X., Mao S.S.* Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications // Chemical Reviews – 2007. – Vol.107. – P.2891-2959.

3. *Shan A.Y., Mohd Ghazi T.I., Rashid S.A.* Immobilisation of titanium dioxide onto supporting materials in heterogeneous photocatalysis: a review // Applied Catalysis A: General – 2010. – Vol.389. – P.1-8.

4. *Henderson M.A.* A surface science perspective on TiO_2 photocatalysis // Surface Science Reports – 2011. – Vol.66. – P.185-297.

5. *Thiemig D., Bund A.* Characterization of electrodeposited Ni–TiO_2 nanocomposite coatings // Surface and Coatings Technology – 2008. – Vol.202. – P.2976-2984.

6. *Spanou S., Pavlatou E.A., Spyrellis N.* Ni/nano-TiO_2 composite electrodeposits: textural and structural modifications // Electrochimica Acta – 2009. – Vol.54. – P.2547-2555.

7. *Huang S., Hu Y., Pan W.* Relationship between the structure and hydrophobic performance of Ni–TiO_2 nanocomposite coatings by electrodeposition // Surface and Coatings Technology – 2011. – Vol.205. – P.3872-3876.

8. *Rajeshwar K., de Tacconi N.R., Chenthamarakshan C.R.* Semiconductor-based composite materials: preparation, properties, and performance // Chemistry of Materials – 2001. – Vol.13 –P.2765-2782.

9. *Tungsten* trioxide-titanium dioxide composite films prepared by occlusion electrosynthesis in a nickel matrix / C.R. Chenthamarakshan, N.R. De Tacconi, R. Shiratsuchi, K. Rajeshwar // Journal of Electroanalytical Chemistry – 2003. – Vol.553. – P.77-85.

10. *Development* of Ag–TiO_2 (anatase) particle composite coating film for photocatalyst and effect of the matrix metal / K. Ui, T. Fujita, N. Koura, F. Yamaguchi // Journal of the Electrochemical Society – 2006. – Vol.153. – P.C449-C454.

11. *Electrodeposition* of Ni–ZrO_2 nanocomposites from methanesulfonate electrolytes / Yu.E. Sknar, N.V. Amirulloeva, I.V. Sknar, F.I. Danylov // Materials Science. – 2016. – Vol.51. – P.877-884.

12. *Properties* of Ni-TiO_2 composites electrodeposited from methanesulfonate electrolyte / Yu.E. Sknar, O.O. Savchuk, I.V. Sknar, F.I. Danilov // Functional Materials – 2017. – Vol.24. – P.469-475.

13. *What* is Degussa (Evonik) P25? Crystalline composition analysis, reconstruction from isolated pure particles and photocatalytic activity test / B. Ohtani, O.O. Prieto-Mahaney, D. Li, R. Abe // Journal of Photochemistry and Photobiology A: Chemistry – 2010. – Vol.216. – P.179-182.

14. *Perspectives* of development of X-ray analysis for material composition / I.F. Mikhailov, A.A. Baturin, A.I. Mikhailov, L.P. Fomina // Functional Materials. – 2016. – Vol.23. – P.5-14.

15. *Rabinovich* V. A., Khavin Z.Ya. Brief chemical reference – Leningrad: Khimiya, 1978. – 432 p.

16. *Kinetics* of electrodeposition of Ni–ZrO_2 nanocomposite coatings from methanesulfonate electrolytes / F.I. Danilov, Yu.E. Sknar, N.V. Amirulloeva, I.V. Sknar // Russian Journal of Electrochemistry – 2016. – Vol.52. – P.494-499.

17. *Electrodeposition* of composite Ni-based coatings with the addition of Ti or/and Al particles / I. Napyoszek-Bilnik,

A. Budniok, B. Losiewicz, L. Pajak, E. Lagiewka // Thin Solid Films – 2005. – Vol.474. – P.146-153.

18. *Robin A., Rosa J.L., Silva M.B.* Electrodeposition and characterization of Cu–Nb composite coatings // Surface and Coatings Technology – 2010. – Vol.205. – P.2152-2159.

19. *Electrodeposition* of composite Fe–TiO_2 coatings from methanesulfonate electrolyte / E.A. Vasil'eva, A.V. Tsurkan, V.S. Protsenko, F.I. Danilov // Protection of Metals and Physical Chemistry of Surfaces. – 2016. – Vol.52. – P.532-537.

Received 01.11.2017

PHOTOCATALYTIC ACTIVITY OF Ni–TiO_2 COMPOSITES ELECTRODEPOSITED ON A NICKEL MATRIX WITH DEVELOPED SURFACE

Yu.E. Sknar, I.V. Sknar, A.A. Savchuk, A.A. Bezik, F.I. Danilov
Ukrainian State University of Chemical Technology, Dnipro, Ukraine

The photocatalytic activity of Ni–TiO_2 composites obtained from a methanesulfonate electrolyte was studied. The photodegradation of methyl orange in the presence of Ni–TiO_2 composite resulted in a partial poisoning of the photocatalyst, which is manifested in a decrease of its activity over time. The photodegradation of methyl orange dye was stated to follow the pseudo-first order kinetics. The observed rate constant of the photodegradation reaction is proportional to the surface area of the photocatalyst. The dependences of the composite composition on the dispersed phase concentration in the solution and current density showed only a limited possibility of increasing the content of photocatalytically active TiO_2 particles in the coating. This paper presents a new method for increasing the photocatalytic activity of the Ni–TiO_2 composite. The authors have proposed to deposit a photocatalyst on a preformed nickel developed surface matrix. The effect of increasing the specific surface area of the matrix is achieved by nickel electrodeposition from a suspension electrolyte containing carbonyl nickel powder as a dispersed phase. The inspection of the voltammograms of hydrogen evolution reaction on smooth and developed nickel surfaces revealed that the incorporation of nickel particles into the coating leads to a significant increase in the specific surface area of the matrix. The composite Ni–TiO_2 coatings deposited on a developed surface matrix have a four times higher photocatalytic activity than those obtained on a smooth sample.

Keywords: Ni–TiO_2 composite; photocatalytic activity; developed surface; matrix; methanesulfonate electrolyte.

REFERENCES

1. Fujishima A., Zhang X., Tryk D.A. TiO_2 photocatalysis and related surface phenomena. *Surface Science Reports*, 2008, vol. 63, pp. 515-582.

2. Chen X., Mao S.S. Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications. *Chemical Reviews*, 2007, vol. 107, pp. 2891-2959.

3. Shan A.Y., Mohd Ghazi T.I., Rashid S.A. Immobilisation of titanium dioxide onto supporting materials in heterogeneous photocatalysis: a review. *Applied Catalysis A: General*, 2010, vol. 389, pp. 1-8.

4. Henderson M.A. A surface science perspective on TiO_2 photocatalysis. *Surface Science Reports*, 2011, vol. 66, pp. 185-297.

5. Thiemig D., Bund A. Characterization of electrodeposited Ni–TiO_2 nanocomposite coatings. *Surface and Coatings Technology*, 2008, vol. 202, pp. 2976-2984.

6. Spanou S., Pavlatou E.A., Spyrellis N. Ni/nano-TiO_2 composite electrodeposits: textural and structural modifications. *Electrochimica Acta*, 2009, vol. 54, pp. 2547-2555.

7. Huang S., Hu Y., Pan W. Relationship between the structure and hydrophobic performance of Ni–TiO_2 nanocomposite coatings by electrodeposition. *Surface and Coatings Technology*, 2011, vol. 205, pp. 3872-3876.

8. Rajeshwar K., de Tacconi N.R., Chenthamarakshan C.R. Semiconductor-based composite materials: preparation, properties, and performance. *Chemistry of Materials*, 2001, vol. 13, pp. 2765-2782.

9. Chenthamarakshan C.R., de Tacconi N.R., Shiratsuchi R., Rajeshwar K. Tungsten trioxide–titanium dioxide composite films prepared by occlusion electrosynthesis in a nickel matrix. *Journal of Electroanalytical Chemistry*, 2003, vol. 553, pp. 77-85.

10. Ui K., Fujita T., Koura N., Yamaguchi F. Development of Ag-TiO_2 (anatase) particle composite coating film for photocatalyst and effect of the matrix metal. *Journal of the Electrochemical Society*, 2006, vol. 153, pp. C449-C454.

11. Sknar Yu.E., Amirulloeva N.V.,_Sknar I.V., Danylov F.I. Electrodeposition of Ni–ZrO_2 nanocomposites from methanesulfonate electrolytes. *Materials Science*, 2016, vol. 51, pp. 877-884.

12. Sknar Yu.E., Savchuk O.O., Sknar I.V., Danilov F.I. Properties of Ni–TiO_2 composites electrodeposited from methanesulfonate electrolyte. *Functional Materials*, 2017, vol. 24, pp. 469-475.

13. Ohtani B., Prieto-Mahaney O.O., Li D., Abe R. What is Degussa (Evonik) P25? Crystalline composition analysis, reconstruction from isolated pure particles and photocatalytic activity test. *Journal of Photochemistry and Photobiology A: Chemistry,* 2010, vol. 216, pp. 179-182.

14. Mikhailov I.F., Baturin A.A., Mikhailov A.I., Fomina L.P. Perspectives of development of X-ray analysis for material composition. *Functional Materials*, 2016, vol. 23, pp. 5-14.

15. Rabinovich V.A., Khavin Z.Ya., *Kratkii khimicheskii spravochnik* [Brief chemical reference]. Khimiya, Leningrad, 1978. (*in Russian*).

16. Danilov F.I., Sknar Yu.E., Amirulloeva N.V., Sknar I.V. Kinetics of electrodeposition of Ni–ZrO_2 nanocomposite coatings from methanesulfonate electrolytes. *Russian Journal of Electrochemistry*, 2016, vol. 52, pp. 494-499.

17. Napyoszek-Bilnik I., Budniok A., Losiewicz B., Pajak L., Lagiewka E. Electrodeposition of composite Ni-based coatings with the addition of Ti or/and Al particles. *Thin Solid Films*, 2005, vol. 474, pp. 146-153.

18. Robin A., Rosa J.L., Silva M.B. Electrodeposition and characterization of Cu–Nb composite coatings. *Surface and Coatings Technology*, 2010, vol. 205, pp. 2152-2159.

19. Vasil'eva E.A., Tsurkan A.V., Protsenko V.S., Danilov F.I. Electrodeposition of composite Fe–TiO_2 coatings from methanesulfonate electrolyte. *Protection of Metals and Physical Chemistry of Surfaces*, 2016, vol. 52, pp. 532-537.