Preparation of ZnO modified TiO₂ nanoporous coatings and their photocatalytic properties

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Abstract. In the present work formation of active nanoporous TiO₂ photocatalysts and their modification with ZnO were studied. TiO₂ nanoporous coatings on Ti foil with surface area 100cm² were prepared by using plasma electrolytic oxidation (PEO) method in 0.5M H₂SO₄ electrolyte and by using 160V DC voltage. For modification of TiO₂ coatings with ZnO spray pyrolysis method where used. After preparation samples were dried and calcined at 400°C for 2h in air. Photocatalytic properties of obtained samples were tested by using degradation method of methylene blue (MB) solution under UV and VIS light illumination. Degradation rate of MB were measured by using spectrophotometer. From obtained results reaction constant (k) in the pseudo first order reaction were calculated. As prepared ZnO modified TiO₂ nanoporous coating photocatalysts are with higher photocatalytic activity with respect to pure TiO₂ nanoporous coating photocatalyst.

1. Introduction

TiO₂ photocatalysis is widely used in a variety of applications and products in the environmental and energy fields. Various techniques had been widely applied to remove different types of toxic organic environmental pollutants from waste water by using methods of adsorption and degradation. One of the most promising and cost efficiently way to do it is in presence of photocatalysts and sunlight [1-2]. Due to its wide band gap (3.2eV) pure TiO₂ anatase as photocatalyst can be used only under UV irradiation. As only about 5% of sunlight that reaches the Earth contains UV irradiation modification of TiO₂ structure is required. By increasing the specific surface area and modification with various dopants efficiency of TiO₂ photocatalysts in VIS irradiation can be improved dramatically. As ZnO is well known photocatalyst with high activity in visible light as dopant it could improve light adsorption properties of TiO₂ and decrease the band gap of it. It can reduce the possibility of electron-hole recombination, causing efficient charge separation and higher photocatalytic reaction rates [3].

Plasma electrolyte oxidation is electro-chemical method that allows to obtain thin layer nanoporous oxide coatings in short time. TiO₂ coatings obtained on metal substrate have better mechanical properties and and it is easier to use in them continuously in photocatalysis because no filtration is required to remove them from the purified solution, as in the case of nanopowders [4].

Spray pyrolysis is a processing technique being considered in research to prepare thin films and ceramic coatings. It is a very simple and relatively cost-effective processing method that offers an extremely easy technique for preparing films of any composition. Typical spray pyrolysis equipment consists of an atomizer, precursor solution, substrate heater, and temperature controller [5].
The combination of both methods can allow to prepare on substrate surface fixed and visible light active photocatalysts in short time. Such materials can be used to solve environmental and energy problems.

2. Experimental

Coating of self-organized TiO$_2$ nanopore layer on Ti substrate was prepared by using plasma electrolytic oxidation of titanium foil 1 x 3cm (Sigma Aldrich, 0.25mm thick, 99.7%) in 0.5M H$_2$SO$_4$ electrolyte, using Pt foil as counter electrode. Before PEO process titanium foil was washed with acetone and etched in 1M HF for 30 sec than washed deionised water and dried in 110°C for 2 hours. Platinum foil was used as second electrode. The voltage was 160V DC and experimental process was 3 min long. During the PEO process micro sparks were noticed on the surface of titanium electrode. As obtained TiO$_2$ coating was washed with deionised water dried in 110°C for 2h and calcinated at 500°C for 2h in air.

Holmarc HO-HT-04BT spry pyrolysis system was used for modification of obtained TiO$_2$ nanoporous coatings with ZnO. 0.1M Zinc acetate solution was used as Zn source. Flow rate of solution atomization was 1ml per minute. The atomizer was programmed to move in XY coordinates in 140 x 140mm area with speed 400mm·sec$^{-1}$ in X direction and 4mm·sec$^{-1}$ in Y direction. Duration of spry pyrolysis process were in range of 0.5 to 10min. Obtained samples were calcinated at 400°C for 2 h in air.

Characterizations of physical properties as morphology, crystallization, chemical content were done by scanning electron microscopy (SEM; Tescan; Lyra), X-ray diffraction (XRD; Bruker D8 advance), X-ray fluorescence (XRF; Bruker Pioneer S4) analysis methods and instruments, respectively.

Photocatalytic activity of the prepared samples was evaluated by decomposition of MB water solution under visible light (Osram LEDVANCE floodlight, 100 W; 10000 lm). The MB solution (100 ml, 7.6·10$^{-3}$g·l$^{-1}$) was introduced in a quartz reactor equipped with obtained ZnO modified porous TiO$_2$/Ti photocatalyst. The sources of light were at distance of 110 mm from the quartz beaker. During the experiments every 30 min MB sample (2 ml) was taken out for measurement. The degradation of MB under illumination in presence of the electrode was determined by measuring light absorption by solution at light wave length of 664 nm using JENWAY-6300 spectrophotometer. As reference with 100 % transmission was used deionized water.

3. Results and discussion

XRD patterns of obtained samples are shown in Figure 1. All samples showed strong maxima of titanium, anatase and rutile. Rutile phase was formed due to the high temperature on the surface during PEO process. Only sample that was modified with ZnO in 10min long spry pyrolysis process showed also maxima of zincite. No other phases were obtained. Thermal treatment at 500°C allowed to divest from sulphur particles that precipitates in small amount during the PEO process.
Figure 1. XRD pattern of ZnO modified porous TiO$_2$ coatings depending on spray pyrolysis process duration: 1) 0.5 min; 2) 1 min; 3) 3 min; 4) 4 min; 5) 5 min; 6) 10 min; 7) pure TiO$_2$ porous coating.

SEM micrographs (Figure 2.) confirmed that during the PEO process porous TiO$_2$ coatings were obtained on the surface of the titanium foil. It was noticed that micropores and also nanopores are processed in the TiO$_2$ layer. Some individual ZnO nanocrystals were observed on the surface of porous TiO$_2$ coating.

Figure 2. SEM micrographs at different magnifications of 0.14% ZnO modified TiO$_2$ porous coatings on titanium.

The results of photocatalytic degradation of MB are shown in Figure 3. The highest result 82.1% of degraded MB solution in 4 hours was shown by sample prepared in 0.5 min long spray pyrolysis process. The lowest photocatalytic activity shows sample prepared in 4 min long experiment and it reaches only 63.2% MB degradation rate in 4 hours. Comparing photocatalysis results with the results of XRF (Table 1.) analysis it can be notice that there is no linear connection between the amount of ZnO and the result of MB degradation. This means that the most active ZnO concentration should be investigated in experimental way. The results of XRF analysis shows that by increasing the duration of spray pyrolysis process the amount of ZnO in photocatalysts increases.
To estimate the kinetic rate of the MB degradation reaction, an equation form of power law is used [6]:

$$-r_{\text{dye}} = kC_{\text{cat}}mC^n$$  \hspace{1cm} (1)

Where $k$ is removal rate constant, $C_{\text{dye}}$ is dye concentration, $n$ is reaction order respect to the dye concentration, $C_{\text{cat}}$ is photocatalyst concentration and $m$ is reaction order respect to the photocatalyst concentration.

As the catalyst concentration is constant, the rate equation can be stated with observed rate constant ($k_{\text{obs}}$) as follows:

$$-r_{\text{dye}} = -\frac{dC_{\text{dye}}}{dt} = k_{\text{obs}}C_{\text{dye}}n$$  \hspace{1cm} (2)

$$k_{\text{obs}} = k . C_{\text{cat}}m$$  \hspace{1cm} (3)

The pseudo-first order kinetic model ($n=1$) provide equation 3 to following form:

$$- \ln \frac{C_{\text{dye}}}{C_{\text{dye}0}} = k_{\text{obs}}t$$  \hspace{1cm} (4)

$$k_{\text{obs}} = \left( - \ln \frac{C_{\text{dye}}}{C_{\text{dye}0}} \right)/t$$  \hspace{1cm} (5)

Results of calculated average pseudo first-rate reaction kinetic constant are shown in Table 1 and are in range of $0.581 \text{ s}^{-1} \cdot 10^{-4}$ to $0.871 \text{ s}^{-1} \cdot 10^{-4}$. Calculated average pseudo first-rate reaction kinetic constant values increase in the same order as photocatalytic activity results.

![Figure 3. Photocatalytic activity of ZnO modified TiO$_2$ porous coatings under visible irradiation.](image)

| Duration of spry pyrolysis process, min | ZnO content, Wt% | Average pseudo first-rate reaction kinetic constant $k_t$, s$^{-1} \cdot 10^{-4}$ |
|----------------------------------------|------------------|----------------------------------|
| 0.5                                    | 0.14             | 0.871                            |
| 1                                      | 0.18             | 0.635                            |
| 3                                      | 0.25             | 0.674                            |
| 4                                      | 0.36             | 0.581                            |
| 5                                      | 0.56             | 0.609                            |
| 10                                     | 1.26             | 0.677                            |
4. Conclusions

Porous TiO$_2$ coatings were successfully fabricated through a simple and fast plasma electrolytic oxidation process. Obtained porous TiO$_2$ nano and micro porous coatings were modified with ZnO nanoparticles by using spray pyrolysis method. All samples showed strong maxima of titanium, anatase and rutile. Rutile phase was formed due to the high temperature on the surface during PEO process. Only sample that was modified with ZnO in 10min long spry pyrolysis process showed also maxima of zincite. No other phases were obtained. Modification with ZnO allows to increase photocatalytic activity of TiO$_2$ coatings up to 62-82% under visible light irradiation. The highest photocatalytic activity was shown by sample containing 0.14wt% ZnO that was prepared in 0.5 minutes long spray pyrolysis process. Calculated pseudo-first order kinetic constants are in range of $0.581 \cdot 10^{-4}$ s$^{-1}$ to $0.871 \cdot 10^{-4}$ s$^{-1}$. Prepared photocatalysts are perspective for hydrogen generation in water photocatalytic electrolysis process under visible light irradiation and also for degradation of harmful organic compounds in waste water.

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