

UDC 544.526.5+54.057

N.A. Shestopal, O.P. Linnik, N.P. Smirnova

INFLUENCE OF METAL AND NON-METAL IONS DOPING ON THE STRUCTURAL AND PHOTOCATALYTIC PROPERTIES OF TITANIA FILMS

Chuiko Institute of Surface Chemistry of National Academy of Sciences of Ukraine
17 General Naumov Str., Kyiv, 03164, Ukraine, E-mail: nat-shestopal@yandex.ua

The metal (Zn^{2+} or Zr^{4+}) and non-metal (nitrogen) doped titania films are synthesized by sol-gel method. High absorption in the visible region is observed and the band gap values are estimated for indirect electron transition. The decrease in the intensity and broadening of the anatase peaks in XRD spectra for TiO_2/N films with increasing urea contents are observed. Anatase formation in the films with double doping agents is proven by Raman measurements. XPS clarified the chemical state of the elements, their surface ratios and the incorporation of nitrogen in the matrix of the synthesized films. XPS results show that the substitutional nitrogen is only registered for $TiO_2/Zr^{4+}/N$. Photocatalytic properties are estimated in the process of tetracycline destruction reaction. The increase of the film activity by factor three is noted for TiO_2/N . Modification TiO_2/N by metal ions has no influence on the photocatalytic properties under UV and visible light.

Keywords: metal and non-metal doped titania, optical properties, XRD, Raman measurements, XPS, photocatalytic activity

INTRODUCTION

The activity of TiO_2 under solar irradiation is negligible and the modification of the semiconductors by various metal and non-metal ions is required to broaden its absorption in near ultraviolet and visible light. Non-metal doping of TiO_2 has shown the great potential in visible light active photocatalysis with nitrogen being the most promising dopant. Nitrogen can be introduced in the TiO_2 structure due to its comparable atomic size with oxygen, small ionization energy and high stability. Doping of TiO_2 by non-metals is based on: a) band gap narrowing proposed by Asashi *et al.* [1]; b) impurity energy levels formation above the valence band as a result of the substitution of oxygen atom by nitrogen in titania stated by Irie *et al.* [2]; c) formation of oxygen vacancies concluded by Ihara *et al.* [3]. It is reported that TiO_2 doped with substitutional nitrogen has shallow acceptor states above the valence state while doping with interstitial nitrogen leads to isolated impurity states in the middle of the band gap where energy levels of the impurity are mainly hybridized by $N2p$ states and $O2p$ states. [4]. The nature of the nitrogen species is under discussion in numerous scientific publications. Various

N-containing species incorporated in oxide matrix were proposed [5–8]. However, it is supposed that nitrogen causes the formation of oxygen vacancies and color centers that are responsible for the visible-light activity [9, 10]. It is reported that N-doping leads to band-gap narrowing by an anodically shifted valence band edge [11] or nitrogen-centered energy levels located just above the valence band edge [12–14]. The nature of the nitrogen species formed from mixing titania powder and urea with the following treating at 400 °C and their chemical and physical properties were investigated by group of Prof. Kisch in detail [8, 15, 16]. The obtained findings indicated that a poly(triamino-*s*-triazine) sensitizer chemically bounded to the semiconductor is formed after calcination of 1:2 (wt/wt) mixture of titania and urea at 400 °C in a rotating flask. The mechanism of this reaction is discussed: i) heating urea at 300–420 °C produces ammonia and isocyanic acid; ii) isocyanic acid in the presence of titania surface OH groups is catalytically converted into melamine in the same temperature range by cyclotrimerization of cyanamide; iii) condensation to a mixture of polytriazine amines (formation of melem and melon); iv) condensation between the *s*-triazine amino and OH groups of titania generates

Ti–N bonds. Thus, the visible light absorbing triazine derivative becomes chemically bound to the semiconductor. Accordingly, the modification is not successful when titania is dehydroxylated before use by heating it in vacuo at 400 °C. It is concluded that the visible-light photocatalytic activity of urea modified titania does not originate from the presence of nitridic, amidic, and nitrogen oxide species or color centers but does from melamine condensation products acting as visible-light sensitizers [17]. The formation of $Ti_{1-x}Zr_xO_2$ was achieved by zirconium incorporation into TiO_2 lattice by sol-gel method. It is demonstrated that the formation of Zr–O–Ti bonds has an influence on the thermal stability during sintering of the mesoporous structure of the films, surface texture and optical properties as well as in the changes of number of surface active sites for nanocomposite films [18]. In our previous paper, the co-doped with nitrogen TiO_2/ZrO_2 films were obtained by Pulsed Laser Deposition method under different synthesis conditions [19]. The films obtained in nitrogen atmosphere or its mixtures with methane are characterized by the formation of O–Ti–N bonds in the oxide matrix as shown by XPS analysis. The binary oxide materials such as TiO_2/ZnO are reported to demonstrate the improved catalytic and photocatalytic performances due to the increased adsorption and effective separation of photogenerated electron-hole pairs [20, 21].

Therefore, we pointed out on the investigation of the electronic, optical and photocatalytic properties of doubly doped (metal and non-metal ions) TiO_2 films to clarify their mutual influence on the photocatalytic properties of the semiconductor.

EXPERIMENTAL PART

Mesoporous TiO_2 thin films were synthesized by the sol-gel method using titanium tetraisopropoxide as a titania source and a three-block copolymer of polyethyleneoxide and polypropyleneoxide $(PEO)_{20}(PPO)_{70}(PEO)_{20}$ (Pluronic P123) as a template in alcoholic medium. Concentrated $HClO_4$ and acetylacetone were added to the precursor as stabilizers. The molar ratio of the components in the sol for films deposition was as following: $Ti(Oi-Pr)_4$: P123 : acetylacetone : H_2O : C_2H_5OH : $HClO_4$ = 1 : 0.05 : 0.5 : 1 : 40 : 1. A solution of urea ($CO(NH_2)_2$) with 1 or 5 or 10 mol. % and zinc acetate ($Zn(OOCCH_3)_2$) or zirconium propoxide ($Zr(OCH_2CH_2CH_3)_4$) with 5 mol. % were added under vigorous stirring. The

one-layered films were deposited by dip-coating procedure at a withdrawal rate 1.5 mm/s. The films were left for 1 h for hydrolysis and heated in air at 450 °C for 1 h with the heating rate of 3 °C/min. Photocatalytic activity of the films was assessed via tetracycline hydrochloride (TC) degradation. The film was immersed in 40 ml of an aqueous solution of 2×10^{-5} mol/L TC. The reaction temperature was kept constant (20 °C) during the experimental procedure. The change of TC concentration was monitored with a Lambda 35 UV-vis spectrophotometer (PerkinElmer) every 20 min at $\lambda = 357$ nm. The film was immersed in the solution until complete adsorption in the dark occurred and then irradiated by a 1000 W middle-pressure mercury lamp for 90 min. The distance lamp-reactor was set at 90 cm. A blank experiment was carried out where a bare glass was used instead of film. No significant changes in the absorption spectra of the liquid were observed for the blank. For testing the visible light sensitivity, a filter transmitting light with $\lambda > 380$ nm was introduced into the photocatalytic setup.

RESULTS AND DISCUSSION

Absorption spectra and band gap energy values of the mesoporous films are presented in Fig. 1. Among titania film doped with different amount of urea (1, 5, and 10 mol. %), the TiO_2/N (5 %) film showed the highest absorption intensity in the visible region and significant shift of absorption edge to the longer wavelengths (Table 1).

As 1 and 10 % urea doped TiO_2 films exhibit no absorption in visible light as well as the photocatalytic activity is significantly lower than that of TiO_2/N (5 %) (see below), all further investigation have been performed with the samples doped with 5 % urea. The films of TiO_2 and TiO_2/M^{n+} doped with 5 % urea are characterized by high absorption in the range of 350–550 nm. It must be noted that the highest intensity in the visible range is observed for the $TiO_2/Zn^{2+}/N$ (Fig. 1, curve 4). It is suggested that the formation of complexes between zinc ions and urea during gel ripening occurs [22] leading to the retention of nitrogen containing species in the oxide lattice over heating. The band gap values (E_g) of the samples (Table 1) were estimated for indirect electron transition from the dependence of $(\alpha h\nu)^{1/2} \sim f(h\nu)$ and extrapolation of the linear plot of experimental curve to $(\alpha)^{1/2} = 0$. Widening of band gap for some samples in comparison with pure TiO_2 can be caused by the decrease in the

crystalline particle size, i.e. the quantum-size effect [23]. The band gap of urea doped films (except $\text{TiO}_2/\text{Zr}^{4+}/\text{N}$) is narrowed suggesting the formation of sublevels above the valence band as a result of oxygen substitution by nitrogen.

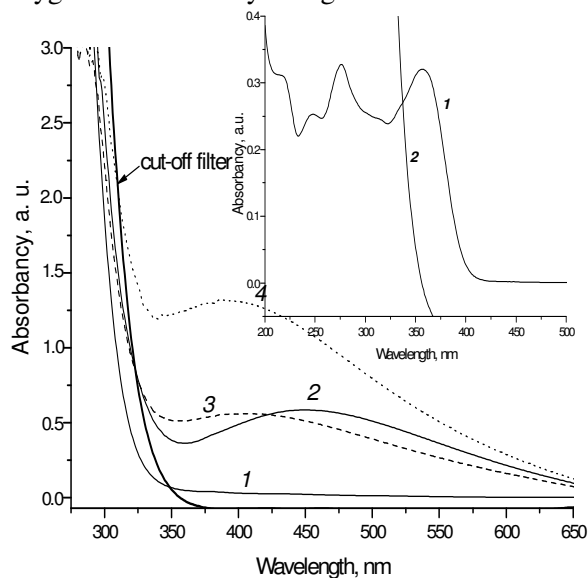


Fig. 1. Absorption spectra of TiO_2 (1), TiO_2/N (2), $\text{TiO}_2/\text{Zr}^{4+}/\text{N}$ (3), $\text{TiO}_2/\text{Zn}^{2+}/\text{N}$ (4) and the cut-off filter with $\lambda \geq 340$ nm (bold line). Insert: absorption spectra of TC (1) and the cut-off filter with $\lambda \geq 340$ nm (2)

Table 1. The band gap energy values of TiO_2 doped films for indirect transition

Film	E_g , eV
TiO_2	3.6
$\text{TiO}_2/\text{N}(1\%)$	3.8
$\text{TiO}_2/\text{N}(5\%)$	3.3
$\text{TiO}_2/\text{N}(10\%)$	3.9
$\text{TiO}_2/\text{Zr}^{4+}$	3.7
$\text{TiO}_2/\text{Zr}^{4+}/\text{N}(5\%)$	3.7
$\text{TiO}_2/\text{Zn}^{2+}$	3.8
$\text{TiO}_2/\text{Zn}^{2+}/\text{N}(5\%)$	3.5

XRD measurements (not shown here) revealed that anatase in TiO_2/N films (1, 5 and 10 %) was formed. However, the intensity of the XRD peaks and their broadening with increasing urea content is observed due to the deceleration of TiO_2 crystallization. As a result, the formation of numerous titania crystallization centers onto TiO_2/N occurs where the aggregation and growth of nanoparticles don't take place. It is known that the presence of nitrogen-containing species (up to

10 %) in TiO_2 structure lowers the crystallization to anatase [24, 25]

As a proof of anatase formation in nitrogen-containing films, the Raman spectra of TiO_2/N and $\text{TiO}_2/\text{Zn}^{2+}/\text{N}$ are presented in Fig. 2. The high intensive Raman peaks at 145, 398, 518 and 640 cm^{-1} (Fig. 2 curve a) are observed for TiO_2/N films. These peaks are related to the formation of photocatalytically active anatase phase. The intensity of these lines is drastically decreased for the sample contained zinc ions (Fig. 2 curve b). It could be caused by the formation of much lower particle size of titania in $\text{TiO}_2/\text{Zn}^{2+}/\text{N}$ in comparison with TiO_2/N . Since no lines belonged to zinc oxide is registered, it is concluded about effective incorporation of Zn^{2+} ions into semiconductive matrix.

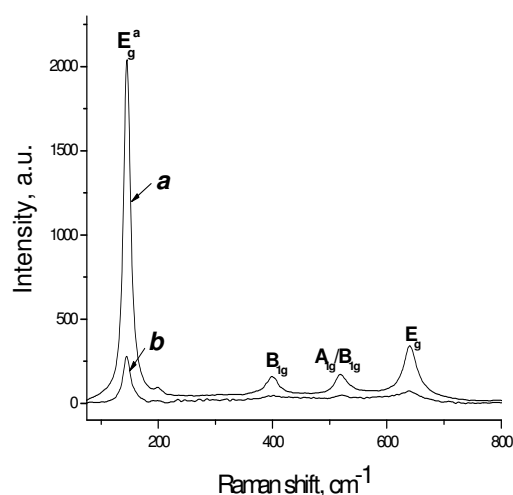


Fig. 2. Raman spectra of TiO_2/N (a) and $\text{TiO}_2/\text{Zn}^{2+}/\text{N}$ (b) treated at $450\text{ }^\circ\text{C}$

XPS is used to clarify the chemical state of elements, their surface ratio and the key point is whether the nitrogen is incorporated into the oxide matrix and its state. The XPS analysis of Ti, N, O and C atomic levels and their intensity are presented in the Table 2.

There is no definite opinion about the XPS measurements of N1s binding energy where the values of 396–397 eV assigned to the N–Ti–N [26, 27] or O–Ti–N bonds [7] are reported. The formation of N–N or N–C or N–O groups or chemisorbed dinitrogen is suggested at higher energies of 400–403 eV [7, 8, 28–30]. Nitrogen 1s binding energies of 399.2 and 400.5 eV are measured for a mixture of solid urea and TiO_2 powder calcined at $400\text{ }^\circ\text{C}$ corresponded to carbon nitrides (399–400 eV, C=N–C) and similar

graphite-like phases (400.6 eV, N–C_{sp2}), and of polycyanogen (399.0, 400.5 eV (–C=N–)_x) [15]. The authors reported the production of poly(triamino-*s*-triazine) derivatives covalently attached to the semiconductor after thermal treatment.

Since urea is used as the doping agent and the calcination temperature is the same for our films and the samples reported herein [31], the N1s peak of TiO₂/N films at 400.6 eV could be related to the N–C species in TiO₂ matrix. However, the additional investigation of urea conversion in the

metal alkoxide sol used for the film preparation is required. It must be noted that the values of the binding energy of N1s peak are lowered for TiO₂/M^{nt}/N films. The appearance of N1s peak with E_B = 400.0 eV for TiO₂/Zn²⁺/N is also attributed to the formation of N–C species in TiO₂ matrix. An increase in the relative intensities of N1s peak for TiO₂/Zn²⁺/N in 2.5 times in comparison with TiO₂/N shows the effect of zinc ions on the building up of such species on the oxide surface.

Table 2. Binding energy values and their relative intensities of Ti, N, O and C elements

Element	TiO ₂ /N		TiO ₂ /Zn ²⁺ /N		TiO ₂ /Zr ⁴⁺ /N	
	E _B , eV	I, %	E _B , eV	I, %	E _B , eV	I, %
Ti2p _{3/2}	459.4	4.7	459.0	4.4	459.2	3.5
N1s	400.6	0.6	400.0	1.6	396.0	0.4
O1s	530.9	20.5	530.5	23.3	530.7	23.8
C1s	283.9	73.1	283.2	70.1	283.7	71.8
Zn2p _{3/2}	–	–	1024.2	0.6	–	–
Zr3d _{5/2}	–	–	–	–	182.7	0.5

XPS results of TiO₂/Zn²⁺ films revealed the presence of separated ZnO phase with E_B = 1021.7 eV corresponding O–Zn–O bonds (not shown here). The shift of Zn2p_{3/2} line maximum to 1024.2 eV in TiO₂/Zn²⁺/N is caused by the formation of Ti–O–Zn bonds [31]. The similar observation was reported for TiO₂/Zn²⁺ and gold-containing TiO₂/Zn²⁺ films suggesting the complexes formation between tetrachloroauric ions and zinc ions during sol ripening [32]. We predict that urea could also form the complexes with zinc(II) acetate in the sol leading to Ti–O–Zn bonds formation. The relative intensities of N1s peak for TiO₂/Zn²⁺/N is higher in 2.5 times in comparison with TiO₂/N and suggest keeping of not only zinc ions but also N-species onto oxide surface. For TiO₂/Zr⁴⁺/N film the nitrogen in the form of substitutional atom (O–Ti–N) is incorporated in to TiO₂ matrix as the binding energy of N1s electrons is situated at 396.0 eV [33, 34]. Hence, the oxygen substitution by nitrogen is more efficient in zirconium containing films.

Line of Ti2p_{3/2} of all samples contains a single peak in the range of 459.2–459.4 eV and confirms the presence of TiO₂ [35, 36]. The XPS peak in the range of 530–531 eV for all samples corresponds to O²⁻ ions of crystalline oxide matrix. The

presence of C–C (elemental carbon) bonds is confirmed by E_B = 283.9 eV [37].

To test the photocatalytic activity of TiO₂/N and TiO₂/Me^{nt}/N, tetracycline hydrochloride (TC) is chosen as the antibiotic recognized as a new type of pollutants. The uncontrolled use of antibiotics in farm industry and medicine leads to their building up in the water sources and soil. Its accumulation results in the bacteria resistance and consecutive mutagenation in the living organisms [38].

Table 3. The percentage of adsorbed and destructed TC (λ = 357 nm) over the TiO₂/N, TiO₂/M^{nt} and TiO₂/Me^{nt}/N films after 90 min UV or visible irradiation

Film	UV, %	Vis., %	Ads., %
Blank (glass)	6	2	0.6
TiO ₂	11	5	2.0
TiO ₂ /N (1 %)	26	9	4.0
TiO ₂ /N(5 %)	30	16	2.4
TiO ₂ /N(10 %)	16	9	5.1
TiO ₂ /Zr ⁴⁺	29	11	8.4
TiO ₂ /Zr ⁴⁺ /N	26	10	1.6
TiO ₂ /Zn ²⁺	25	11	6.2
TiO ₂ /Zn ²⁺ /N	25	13	2.8

The photocatalytic activity of TiO₂/N films is increased in comparison with pure TiO₂ film under both UV and visible light (Table 3). The highest activity is observed for the film with 5 % of urea

(in three times higher than TiO_2). The increase in photocatalytic activity under UV light for $\text{TiO}_2/\text{Zn}^{2+}$ and $\text{TiO}_2/\text{Zr}^{4+}$ films is explained by higher surface acidity comparing with TiO_2 film and the appropriate positions of the conduction and valence bands (CB and VB) of the semiconductor [23, 39].

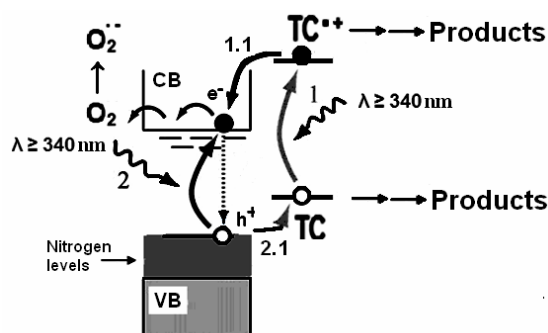


Fig. 3. Possible routes of photocatalytic processes of TC destruction over TiO_2/N and $\text{TiO}_2/\text{Me}^{n+}/\text{N}$ films under visible light irradiation

Photocatalytic activity of the films under visible light is studied using a cut-off filter with $\lambda \geq 340$ nm (Fig. 1). It is obvious that the absorption edge of semiconductor is cut and the photocatalytic process can only occur through the excitation of an electron from the additional N-sublevels formed in the valence band of TiO_2 . However, the cut-off filter does not prevent the excitation of TC molecule (Fig. 1, insert) that is why the TC degradation can follow via the two different ways such as i) the photoexcitation of TC molecule, i.e. indirect photocatalysis (Fig. 3, route 1) and ii) the excitation of the electron from the N-sublevels in VB to CB (Fig. 3, route 2). It is clear that the pure TiO_2 film is inactive under visible light showing the low probability for both photocatalytic pathways. Since the nitrogen doping does not

change the CB and VB positions of semiconductor, the formation of additional energetic N-sublevels could be proposed [40]. Therefore, the route 2 is more feasible for TiO_2/N films: the electron is transferred to the CB and the photoformed hole reacts with the TC molecule (steps 2.1). In the case of $\text{TiO}_2/\text{M}^{n+}$ films the higher activity (2 times in comparing with TiO_2) under visible light can be caused by the change of the CB and the VB due to the metal ions doping [23, 39] leading to the better adsorption of TC molecules onto the surface and more easier electron transfer from the excited TC molecule (route 1.1). No difference in the photocatalytic activity is noted for $\text{TiO}_2/\text{M}^{n+}/\text{N}$ under visible light comparing with $\text{TiO}_2/\text{M}^{n+}$ films. It is supposed that the route 1 is only possible for doubly doped samples due to the low probability of the electron excitation from the N-sublevels. It is possible due to the formation of the structure defects by double doping that makes easier the recombination process.

Hence, the chemical state of nitrogen in $\text{TiO}_2/\text{M}^{n+}/\text{N}$ films is strongly dependent on the type of the metal ions as shown by XPS measurements. In addition, this study showed that doping of TiO_2/N by zinc ions brings to the keeping of nitrogen ions onto the film surface due to the complex formation on the stage of the gel formation. The crystallization rate of titania is lowered by doping higher content of urea as well as by metal ions signed by XRD and Raman investigations. Nitrogen-containing TiO_2 exhibits the activity enhance in photocatalytic destruction of TC under both UV and visible light. Doping TiO_2/N by metals changes the route of photocatalytic process.

Вплив допування йонами металу та неметалу на структурні і фотокаталітичні властивості плівок діоксиду титану

Н.О. Шестопаль, О.П. Ліннік, Н.П. Смірнова

Институт хімії поверхні ім. О.О. Чуйка Національної академії наук України
вул. Генерала Наумова, 17, Київ, 03164, Україна, nat-shestopal@yandex.ua

Золь-гель методом синтезовані плівки діоксиду титану, допованого йонами металу (Zn^{2+} або Zr^{4+}) та неметалу (азот). Спостерігається значне поглинання плівки в видимій області та оцінено значення ширини забороненої зони для непрямих електронних переходів. Результати рентгенофазового аналізу свідчать про утворення кристалічної фази анатазу, однак спостерігається зниження інтенсивності та уширення його піку зі збільшенням вмісту сечовини. Методом комбінаційного розсіювання також показано, що відбувається формування анатазу в плівках з подвійним допантом. Хімічний стан елементів, їх співвідношення на поверхні та впровадження азоту в кристалічну матрицю досліджено за допомогою рентгенофотоелектронної спектроскопії. Отримані результати показали, що азот заміщує атоми кисню тільки в структурі $TiO_2/Zr^{4+}/N$. Досліджено фотокаталітичні властивості в процесі розкладання тетрацикліну гідрохлориду. Збільшення активності в три рази спостерігалось для плівки TiO_2/N . Модифікація йонами металів не вплинула на фотокаталітичні властивості під ультрафіолетовим та видимим світлом.

Ключові слова: допований йонами металу та неметалу діоксид титану, оптичні властивості, РФА, метод комбінаційного розсіювання, РФЕС, фотокаталітична активність

Влияние допирования ионами металла и неметалла на структурные и фотокаталитические свойства пленок диоксида титана

Н.А. Шестопаль, О.П. Линник, Н.П. Смирнова

Институт химии поверхности им. А.А. Чуйко Национальной академии наук Украины
ул. Генерала Наумова, 17, Киев, 03164, Украина, nat-shestopal@yandex.ua

Золь-гель методом синтезированы пленки диоксида титана, допированного ионами металла (Zn^{2+} или Zr^{4+}) и неметалла (азот). Наблюдается значительное поглощение пленки в видимой области и оценено значение ширины запрещенной зоны для непрямых электронных переходов. Результаты рентгенофазового анализа свидетельствуют об образовании кристаллической фазы анатаза, однако наблюдается понижение интенсивности и уширение его пика с увеличением содержания мочевины. Методом комбинационного рассеяния показано также, что происходит формирование анатаза в пленках с двойным допантом. Химическое состояние элементов, их соотношение на поверхности и внедрение азота в кристаллическую матрицу исследовано с помощью рентгенофотоелектронной спектроскопии. Полученные результаты показали, что азот замещает атомы кислорода только в структуре $TiO_2/Zr^{4+}/N$. Исследованы фотокаталитические свойства в процессе разложения тетрациклина гидрохлорида. Увеличение активности в три раза наблюдалось для пленки TiO_2/N . Модификация ионами металлов не влияла на фотокаталитические свойства под ультрафиолетовым и видимым светом.

Ключевые слова: допированный ионами металла и неметалла диоксид титана, оптические свойства, РФА, метод комбинационного рассеяния, РФЭС, фотокаталитическая активность

REFERENCES

1. *Asahi R., Morikawa T., Ohwaki T. et al.* Visible-light photocatalysis in nitrogen-doped titanium dioxide, *Science*, 293 (2001) 269.
2. *Irie H., Watanabe Y., Hashimoto K.* Nitrogen-concentration dependence on photocatalytic activity of $\text{TiO}_{2-x}\text{N}_x$ powders, *J. Phys. Chem. B*, (2003) 5483.
3. *Ihara T., Miyoshi M., Triyama Y. et al.* Visible-light-active titanium oxide photocatalyst realized by an oxygen-deficient structure and by nitrogen doping, *Appl. Catal.*, 42 (2003) 403.
4. *Zhao Z., Liu Q.* Mechanism of higher photocatalytic activity of anatase TiO_2 doped with nitrogen under visible-light irradiation from density functional theory calculation. *J. Phys. D. Appl. Phys.*, 41 (2008) 1.
5. *Sato S.* Photocatalytic activity of NO_x -doped TiO_2 in the visible light, *Chem. Phys. Lett.*, 123 (1986) 126.
6. *Beranek R., Neumann B., Sakthivel S. et al.* Exploring the electronic structure of nitrogen-modified TiO_2 photocatalysts through photocurrent and surface photovoltage studies, *Chem. Phys.*, 339 (2007) 11.
7. *Cong Y., Zhang J., Chen F., Anpo M.* Synthesis and characterization of nitrogen-doped TiO_2 nanophotocatalyst with high visible light activity. *J. Phys. Chem. C*, 111 (2007) 6976.
8. *Kisch H., Sakthivel S., Janczarek M., Mitoraj D.* A low-band gap, nitrogen-modified titania visible-light photocatalyst, *J. Phys. Chem. C*, 111 (2007) 11445.
9. *Emeline A.V., Sheremetyeva N.V., Khomchenko N.V. et al.* Photoinduced formation of defects and nitrogen-stabilization of color centers in N-doped titanium dioxide, *J. Phys. Chem. C*, 111 (2007) 11456.
10. *Kuznetsov V.N., Serpone N.* Photo-induced coloration and photobleaching of titanium dioxide in TiO_2 /polymer compositions on UV- and visible-light excitation into the color centers' absorption bands. Direct experimental evidence negating band gap narrowing in anion-/cation-doped TiO_2 , *J. Phys. Chem. C*, 111 (2007) 15277.
11. *Nakano Y., Morikawa T., Ohwaki T., Taga Y.* Band-gap narrowing of TiO_2 films induced by N-doping, *Phys.*, 376 (2006) 823.
12. *Di Valentin C., Pacchioni G., Selloni A. et al.* Characterization of paramagnetic species in N-doped TiO_2 powders by EPR spectroscopy and DFT calculations, *J. Phys. Chem. B*, 109 (2005) 11414.
13. *Livraghi S., Paganini M.C., Giamello E.G. et al.* Origin of photoactivity of nitrogen-doped titanium dioxide under visible light., *J. Am. Chem. Soc.*, 128 (2006) 15666.
14. *Batzill M., Morales E.H., Diebold U.* Influence of nitrogen doping on the defect formation and surface properties of TiO_2 rutile and anatase, *Phys. Rev. Lett.*, 96 (2006) 026103.
15. *Mitoraj D., Kisch H.* On the mechanism of urea-induced titania modification, *Chem. Eur. J.*, 16 (2010) 261.
16. *Mitoraj D., Kisch H.* The nature of nitrogen-modified titanium dioxide photocatalysts active in visible light., *Angew. Chem. Int. Ed.*, 47 (2008) 9975.
17. *Kisch H.* Semiconductor photocatalysis—mechanistic and synthetic aspects., *Angew. Chem. Int. Ed.*, 52 (2013) 812.
18. *Gnatuk Yu., Smirnova N., Korduban O., Eremenko A.* Effect of zirconium incorporation on the stabilization of TiO_2 mesoporous structure, *Surface and Interface Analysis*, 42 (2010) 1276.
19. *Linnik O., Petrik I., Smirnova N. et al.* $\text{TiO}_2/\text{ZrO}_2$ thin films synthesized by PLD in low pressure N-, C- and/or O-containing gases: structural, optical and photocatalytic properties, *Digest Journal of Nanomaterials and Biostructures*, 7 (2012) 1343.
20. *Ptashko T., Smirnova N., Eremenko A. et al.* Synthesis and photocatalytic properties of mesoporous TiO_2/ZnO films with improved hydrophilicity, *Adsorpt. Sci. Technol.*, 25 (2007) 35.
21. *Zhang P., Shao C., Li X. et al.* *In situ* assembly of well-dispersed Au nanoparticles on TiO_2/ZnO nanofibers: A three-way synergistic heterostructure with enhanced photocatalytic activity, *J. Hazard. Mater.*, 237 (2012) 331.
22. *Gyoryova K., Balek V.* Thermal stability of new Zn acetate-based complex compounds. *J. Therm. Anal.*, 40 (1993) 519.
23. *Smirnova N., Gnatyuk Yu., Eremenko A. et al.* Photoelectrochemical characterization and photocatalytic properties of mesoporous $\text{TiO}_2/\text{ZrO}_2$ films, *International Journal of Photoenergy*, Article ID 85469 (2006) 1.

24. Haiying W., Yanchun H. The photocatalytic property of nitrogen-doped TiO₂ nanoball film, *International Journal of Photoenergy*, Article ID 179427 (2013) 6.
25. Peng W.Q., Yanagida M., Han L.Y. Rutile-anatase TiO₂ photoanodes for dye-sensitized solar cells, *Journal of Nonlinear Optical Physics and Materials*, 19 (2010) 673.
26. Nosaka Y., Matsushita M., Nishino J., Nosaka A.Y. Nitrogen-doped titanium dioxide photocatalysts for visible response prepared by using organic compounds, *Sci. Technol. Adv. Mater.*, 6 (2005) 143.
27. Kobayakawa K., Murakami Y., Sato Y. Visible-light active N-doped TiO₂ prepared by heating of titanium hydroxide and urea, *J. Photochem. Photobiol. A.*, (2005) 170, 177.
28. Beranek R., Kisch H. Tuning the optical and photoelectrochemical properties of surface-modified TiO₂, *Photochem. Photobiol. Sci.*, 7 (2008) 40.
29. Yuan J., Chen M., Shi J., Shangguan W. Preparation and photocatalytic hydrogen evolution of N-doped TiO₂ from urea and titanium tetrachloride, *Int. J. Hydrogen Energy*, 31 (2006) 1326.
30. Yin S., Ihara K., Aita Y. *et al.* Visible-light induced photocatalytic activity of TiO_{2-x}A_y (A = N, S) prepared by precipitation route, *J. Photochem. Photobiol. A.*, 179 (2006) 105.
31. Wang C.T., Wang, Lin J.C. Surface nature of nanoparticle zinc-titanium oxide aerogel catalysts, *Appl. Surf. Sci.*, 254 (2008) 4500.
32. Linnik O., Smirnova N., Korduban O., Eremenko A. Gold nanoparticles in Ti_{1-x}Zn_xO₂ films: synthesis, structure and application, *Materials Chemistry and Physics*, 142 (2013) 318.
33. Matsubara K., Danno M., Inoue M. *et al.* Characterization of nitrogen-doped TiO₂ powder prepared by newly developed plasma-treatment system, *Chemical Engineering Journal*, 181 (2012) 754.
34. Zuoli H., Wenxiu Q., Yucheng H. *et al.* Electrochemical behavior and photocatalytic performance of nitrogen-doped TiO₂ nanotubes arrays powders prepared by combining anodization with solvothermal process, *Ceramics International*, 39 (2013) 5545.
35. Alam M.J., Cameron D.C. Preparation and characterisation of TiO₂ thin films by sol-gel method, *J. Sol-Gel Sci. Technol.*, 25 (2002) 137.
36. Shu T., Xiang P., Zhou Z. *et al.* Mesoscopic nitrogen-doped TiO₂ spheres for quantum dot-sensitized solar cells, *Electrochimica Acta.*, 68 (2012) 166.
37. Mai L., Huang C., Wanga D. *et al.* Effect of C doping on the structural and optical properties of sol-gel TiO₂ thin films, *Appl. Surf. Sci.*, 255 (2009) 9285.
38. Trautweina C., Kummererc K. Degradation of the tricyclic antipsychotic drug Chlorpromazine under environmental conditions, identification of its main aquatic biotic and abiotic transformation products by LC-MS(n) and their effects against environmental bacteria, *J Chromatogr. B: Analyt. Technol. Biomed. Life Sci.*, 889-890 (2012) 24.
39. Smirnova N., Vorobets V., Linnik O. *et al.* Photoelectrochemical and photocatalytic properties of mesoporous TiO₂ films modified with silver and gold nanoparticles, *Sur. Interface Anal.*, 42 (2010) 1205.
40. Serpone N. Is the band gap of pristine TiO₂ narrowed by anion- and cation-doping of titanium dioxide in second-generation photocatalysts, *J. Phys. Chem. B*, 110 (2006) 24287.

Received 25.07.2014, accepted 23.04.2015