Cellulose (2013) 20:1293–1300
DOI 10.1007/s10570-013-9906-6

ORIGINAL PAPER

Cellulose-TiO_2 nanocomposite with enhanced UV–Vis light absorption

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Received: 13 November 2012 / Accepted: 7 March 2013 / Published online: 17 March 2013
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Abstract TiO_2/N-cellulose nanocomposite was successfully prepared in the (cyclohexyl)hexyldimethylammonium acetate–dimethyl sulfoxide solution. The obtained composite was characterized with various techniques like UV–Vis/DR, FTIR/DRS, X-ray diffraction, thermogravimetric analysis, DLS method and BET SSA measurements. TiO_2/N-cellulose nanocomposite exhibited high UV–Vis light absorption with energy gap shifted to the visible region. Additive of TiO_2/N photocatalyst to cellulose-IL-DMSO solution leads to obtaining the material with higher thermostability and limited photoactivity.

Keywords TiO_2/N-cellulose nanocomposite · (cyclohexyl)hexyldimethylammonium acetate · Photostability · Visible light absorption · Ionic liquid

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Introduction

Polymer-inorganic particle composites have brought a lot of attention due to their combined properties derived from individual materials (Zhou et al. 2006). Cellulose is the structural component of primary and secondary cell walls of plants as minor and major constituents, respectively. As a chemical raw material, it is generally well known that it has been used in the form of fibers or derivatives for nearly 150 years for a wide spectrum of products and materials in daily life.

Cellulose could be used as a support for photoactive titanium dioxide (TiO_2) or as a source of different chemicals produced by cellulose decomposition in the presence of TiO_2 photocatalyst under UV–Vis radiation. Zeng et al. (2010) proposed TiO_2 immobilization in cellulose matrix for photocatalytic degradation of phenol under weak UV light irradiation. Nagaoka et al. (2002) prepared cellulose TiO_2 microsphere composite starting from viscose and titania. The microspheres were heated up and carbonized to obtain TiO_2-carbon composite as a photocatalyst.

TiO_2 photocatalyst degrades organic pollutants mainly dissolved in aqueous solution. Degradation of solid organic materials, especially polymers, was the main subject of limited number of papers. Tsumura et al. (2002) prepared acrylic resin composite with TiO_2. The authors presented almost 40 % weight loss after 1,000 h of UV–Vis exposition. Fan et al. (2011) described photodegradation of cellulose under UV light catalyzed by TiO_2. Because this biopolymer is insoluble in water the authors proposed dissolving cellulose in concentrated zinc chloride solution and then such form was put to contact with photocatalysts for organic compound degradation. The degradation mechanism of 5-hydroxymetyl furfural was proposed.

Ionic liquids (ILs) are an attractive class of solvents as they are low-melting-point salts with a unique combination of properties such as negligible volatility, high stability and easy recyclability (Stark and Seddon 2007; Chowdhury et al. 2007; Wasserscheid and Welton 2008; Petkovic and Seddon 2008; Olivier-Bourbigou et al. 2010; Tang et al. 2012). Properties and application of ILs is varied depending on their structure; it is possible to use them as feeding deterrents (Pernak et al. 2012a) or herbicides (Pernak et al. 2011a, 2012b, c). Importantly, ILs can accomplish cellulose dissolution (Wang et al. 2012). Using ionic liquids as a solvent system for cellulose enables similar to Lyocell (N-morpholine-N-oxide/water system) direct dissolution process with more advantages. The most widely used ILs for processing of cellulose are those with aromatic imidazolium or pyridinium cation. It is caused most likely because those are the first known ILs with the ability to dissolve cellulose. We have shown that another ionic liquids with 4-benzyl-4-methylmorpholinium cation demonstrate cellulose solubility (Pernak et al. 2011b). In our recent paper we presented new kind of ILs with alkyl(cyclohexyl)dimethylammonium cation as solvents of this biopolymer (Pernak et al. 2012d).

In this paper novel method of preparation of UV–Vis light absorbing TiO_2/N-cellulose composite with limited photoactivity is described. This new nanomaterial because of its properties is very perspective to produce UV protective coatings and paper with high mechanical resistivity. The crucial step of this research is an application of (cyclohexyl)hexyldimethylammonium as IL for dissolving of cellulose precursor with nano-particles TiO_2 slurry modified by nitrogen.

Experimental

Materials

Microcrystalline cellulose (CAS:9004-34-6), potassium hydroxide, acetic acid as well as all the solvents were purchased from commercial suppliers (Sigma-Aldrich, Fluka) and used without further purification. (Cyclohexyl)hexyldimethylammonium bromide was synthesized in Pernak's group at Poznan University of Technology.

Preparation of (cyclohexyl)hexyldimethylammonium acetate

(Cyclohexyl)hexyldimethylammonium bromide (0.5 mol) was dissolved in methanol and a stoichiometric amount of saturated methanolic solution of KOH was added. The solution was stirred at room temperature for 5 min, after which the partially precipitated KBr was filtrated. Then a stoichiometric amount of acetic acid was added. The solution was stirred again at room temperature for 15 min and after evaporation of the solvent, the product was dissolved in anhydrous acetone. The inorganic salt was separated and acetone was evaporated to give the product, which was finally dried under reduced pressure at 80 °C for 24 h.

Preparation of precipitated cellulose: reference material

A flask containing solution of 45.0 g of dried (cyclohexyl)hexyldimethylammonium acetate and 45.0 g of dimethyl sulfoxide (DMSO) was immersed in an oil bath at temperature 100 °C with a deviation of temperature from the set temperature of ±1 °C. Microcrystalline cellulose was added in the amount of 7.9412 g and stirred until the solution became optically clear under a microscope (Bresser Biolux LCD Microscope). Afterwards the solution was cooled down, and 150 mL of water was added. Precipitated cellulose was separated and dried under reduced pressure. Finally it was powdered in a mortar grinder Retsch RM 200.

Preparation of TiO_2/N photocatalyst

A commercial TiO_2 supplied by the Chemical Factory "POLICE" S.A. (Poland) pre-dried at 100 °C was used as a starting material in preparation process of nitrogen modified TiO_2. Nitridation of the lattice and the surface of titanium dioxide was carried out using HEL Ltd. "Autolab" E746 installation. 350 mL of ammonia water (2.5 %) and 600 g of starting nanocristalline material were placed in a chamber of pressure reactor (BHL-800, Berghof, Germany). Both, titania and NH_4OH substrates were blended using magnetic stirrer to obtain homogeneous slurry. The suspension was heated up to 100 °C for 4 h afterwards. The next step on TiO_2/N preparation process was final drying in air atmosphere at 100 °C for 4 h. The obtained material was ground with a mortar to form a fine powder (Bubacz et al. 2010). The structural and textural parameters of N-doped TiO_2 photocatalyst were listed in Table 1. The BET SSA of 235 m^2/g is formed by particles average size of 168 nm and average anatase crystallites size of 6.1 nm by TEM and 11 nm by XRD.

Preparation of TiO_2/N-cellulose nanocomposite

A flask containing solution of 45.0 g of dried (cyclohexyl)hexyldimethylammonium acetate and 45.0 g of DMSO was immersed in an oil bath at temperature 100 °C with a deviation from the set temperature of ±1 °C. Microcrystalline cellulose was added in the amount of 7.9412 g, and stirred until the solution became optically clear under a microscope. Afterwards 0.8823 g of titanium dioxide was added to the solution, stirred for 5 min and cooled down. 150 mL of water was added to the solution, and cellulose-TiO_2/N composite was precipitated. The composite was separated and dried under reduced pressure. Finally, it was powdered in a mortar grinder (Retsch RM 200). Obtained composite contained 10 wt% of N-doped titanium dioxide.

Nanocomposite characterization

The photocatalysts and cellulose were characterized by UV–Vis/DR using V-630 spectrophotometer (Jasco, Japan) equipped with an integrating sphere accessory for diffuse reflectance spectra ($BaSO_4$ was used as a reference material). FTIR/DRS spectra of tested photocatalyst was recorded using FT/IR 4200 spectrometer (Jasco, Japan) equipped with DR accessory of Harrick Company (USA). N_2 adsorption measurements at 77 K for calculation of N_2-BET SSA were performed using Quadrasorb SI (Quantachrome, the USA) instrument. The total organic carbon (TOC) measurements were conducted using Multi N/C 2000 analyzer (Analytik Jena, Germany). Thermogravimetric analysis on STA-449C (Netzsch Company, Germany) was managed to check the character of cellulose precipitated from (cyclohexyl)hexyldimethylammonium acetate IL-DMSO solution and composite of cellulose and 10 wt% of TiO_2/N catalyst. The sample was heated from 25 to 950 °C (10°/min) under nitrogen atmosphere (gas flow 30 mL/min). X-ray diffraction patterns were obtained by using X'Pert PRO diffractometer with Cu Kα radiation ($\lambda = 1.54056\text{Å}$). Dynamic light scattering DLS was used to measure the particles size distribution of prepared TiO_2/N photocatalyst (Zetasizer Nano series ZS, Malvern Instruments, Great Britain). Emission spectrum of UV–Vis irradiation source (6 lamps × 20 W each, Philips), presented in Fig. 1, was measured using USB4000 equipment (Ocean Optics, Netherlands). The radiation intensity was measured using radiation intensity meter LB 901 (Lab-El, Poland) equipped with CM3 and PD204AB *Cos* sensors.

Purity and photostability measurements

0.1 g of cellulose-TiO_2 nanocomposite with 10 wt% of TiO_2/N catalyst was stirred (500 rpm) in the dark and under UV light radiation in 500 mL of demineralized water to check the purity of cellulosic material (measurements of total organic carbon TOC). It was noted that demi water contained 0.26 mg/L of organic carbon and 0.09 mg/L of inorganic carbon. Aqueous solution of model organic compound—mono azo dye Reactive Red 198 (RR 198) with the concentration of 20 mg/L was also stirred in the dark to check the adsorption abilities of tested material. Secondly, UV–Vis lamp radiated high UV intensity was switched on to check the photocatalytic activity of above-mentioned materials.

Table 1 The structural and textural parameters of N-doped TiO_2 photocatalyst

Crystalline size according to TEM (nm)	Crystalline size according to XRD (nm)	Average particle size according to DLS (nm)	SSA_{BET} (m^2/g)
6.1	11	168	235

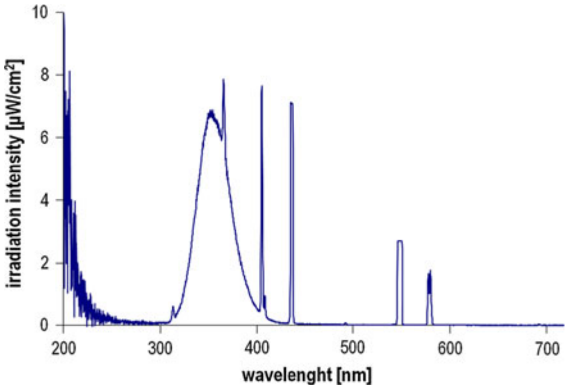

Fig. 1 Emission spectrum of UV–Vis lamp with high UV irradiation (6 lamps × 20 W each Philips), 183 W/m^2 UV and 167 W/m^2 Vis

Results and discussion

General

Synthesis route, full characteristic of (cyclohexyl)hexyldimethylammonium acetate and dissolution of cellulose was described earlier (Pernak et al. 2012d).

UV–Vis/DR measurements

In Fig. 2 the UV–vis/DR spectra of microcrystalline cellulose, precipitated cellulose (reference material), TiO_2/N photocatalyst and TiO_2/N-cellulose composite are presented. Crystalline cellulose absorbs radiation in both, UV range with the efficiency of ca. 50 % and visible range with efficiency of ca. 15 %. In the case of reference material the increase of light absorption (ca. 35 % for UV range and ca. 30 % for visible range) was caused by yellowish color of prepared sample. Addition of even 10 wt% of TiO_2/N leads to change of absorption range. As it can be seen cellulose mixed with 10 wt% of TiO_2/N catalyst absorbs light stronger than crystalline cellulose, increases absorption under UV to complete 100 % as well as under visible range (400–800 nm) up to 50 %. This could be assigned to the presence of nitrogen in the lattice of TiO_2 (Wawrzyniak and Morawski 2006; Janus et al. 2009) and also because of the yellow colour of new composite. The colour of obtained nanocomposite was noted to be more intensive than precipitated cellulose. The UV–vis/DR spectra was plotted in Kubelka–Munk function, that allows to calculate the reflectance from the materials which both scatter and absorb light. Equation 1 represents the modified form of Kubelka–Munk function

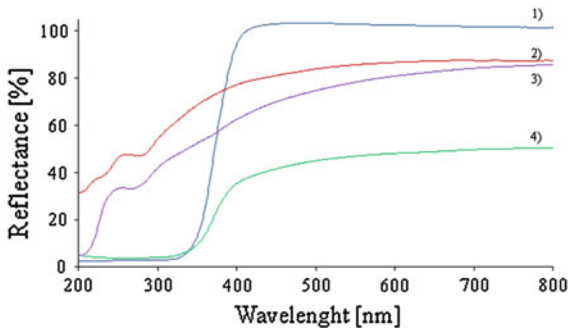

Fig. 2 UV–vis/DR spectra of: *1*) TiO_2/N photocatalyst, *2*) crystalline cellulose, *3*) precipitated cellulose—reference material, *4*) cellulose-TiO_2/N nanocomposite

$$kh\upsilon = A\left(h\upsilon - E_g\right)^2 \tag{1}$$

where k—excitation coefficient, h—Planck's constant [Js], υ—light frequency [s^{-1}], A—absorption constant, E_g—band gap energy [eV].

Thus the E_g can be calculated by extrapolating to zero a linear fit to a plot of $(khv)^{1/2}$ against hv. The E_g value estimated for initial TiO_2/N and cellulose mixed with 10 wt% of TiO_2/N material was 3.31 and 3.09 eV, respectively. This means that the presence of nitrogen in a titania structural lattice results with decreasing of band gap energy and extends the light absorption to the visible region what was also confirmed e.g. by Wawrzyniak and Morawski (2006). Another factor that might contribute to the decrease in band-gap value is the smaller crystalline size of tested photocatalyst due to a quantum size effect.

FTIR/DRS measurements

In Fig. 3 FTIR/DRS spectra of used TiO_2/N photocatalytic nanomaterial, crystalline cellulose, precipitated cellulose and composite of cellulose with 10 wt% of TiO_2/N catalyst are presented. Strong hydrogen-bonded OH stretching at around 3,800–2,995 cm^{-1} is commonly observed in all cellulosic materials' spectra. For material prepared by mixing of cellulose and TiO_2/N, the maximum absorbance of hydrogen-bonded OH stretching is shifted to higher wavenumber (from 3,455 to 3,470 cm^{-1}). Nevertheless, this change was insignificant and it was caused by the presence of ionic liquid in tested samples. The intensity of

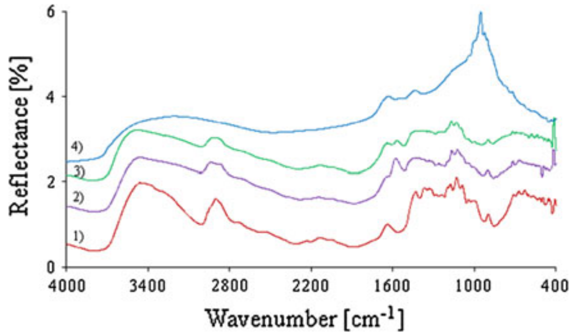

Fig. 3 FTIR/DRS spectra of: *1*) crystalline cellulose, *2*) precipitated cellulose *3*) cellulose mixed with 10 wt% of TiO_2/N catalyst, *4*) TiO_2/N photocatalyst

abovementioned OH stretching and CH stretching bonds at 2,901 cm^{-1} decreased after mixing with ionic liquid and TiO_2/N and the CH bond was shifted to 2,924 cm^{-1}. This TiO_2/N modification leads to intensity decrease of OH bending of adsorbed water at 1,640 cm^{-1}, the HCH and OCH on-plane bending vibrations at 1,371–1,378 cm^{-1}, the COC, CCO and CCH deformation modes and stretching vibrations at 897 cm^{-1} and also the C–OH out-of-plane bending mode at 673–675 cm^{-1}. All of these changes could prove that interaction between cellulose and TiO_2/N photocatalyst lead to immobilization of modified titania nanoparticles in the cellulose matrix. On the TiO_2/N spectrum it was possible to observe bonds associated with OH vibrations (3,300–3,500 cm^{-1}) assigned to the dissociated and molecularly adsorbed water and OH groups at 1,630–1,640 cm^{-1} assigned for molecular water. The narrow bond at 1,428 cm^{-1} in the synthesized catalysts was attributed to the ammonium groups (NH_4^+) (Randorn et al. 2004), which may suggest that nitrogen was not only successfully incorporated into the structural lattice but also bounded with the surface of TiO_2. A weak bond at 1,536 cm^{-1} in TiO_2/N sample (named as 4) could be assigned to either NH_2 or NO_2 and NO groups as it was described by Janus et al. (2009). As it can be seen after mixing of cellulose with TiO_2/N material the bond assigned to Ti^{4+} at 955 cm^{-1} disappeared. This means that during preparation of composite there was a reaction between cellulose and TiO_2/N nanocatalyst. In general, on the surface of TiO_2/N-cellulose composite the bonds of cellulose dominates whereas bonds of TiO_2 is practically disappeared, in spite of presence 10 wt%.

X-ray diffraction and BET SSA measurements

Figure 4 shows the X-ray diffraction patterns of tested materials. In starting cellulose only crystalline phase of this cellulose was found (JCPDS card no 00-056-1718) with BET SSA of 4.06 m^2/g. Peaks at $2\theta = 14.5°$, 16.6°, 22.7° and 34.4° are corresponding to $(1\bar{1}0)$, (110), (200) and (004) planes of crystalline cellulose which peaks have been separated by Wada et al. (1993). It is generally accepted that peak broadening is due to the amorphous cellulose. In the case of nitrogen modified TiO_2 photocatalyst several characteristic peaks attributed to anatase at 25.4°, 38.0°, 48.3°, 53.8° and 62.8° are observed. A weak diffraction line of rutile at 27.5° could be also possible to observe what was associated with the addition of rutile nuclei during the production process (sulfate technology). It was noted that additive of TiO_2/N material to crystalline cellulose leads to disappearance of peaks corresponding to cellulose. The XRD pattern indicates that anatase TiO_2 phase dominates.

In spite of high BET SSA of TiO_2/N (235 m^2/g), the total BET SSA of cellulose-TiO_2/N nanocomposite was small and practically the same as microcrystalline cellulose, e.g. 4.64 m^2/g. The BET SSA measured for reference material-precipitated cellulose was 3.7 m^2/g.

Photostability measurements

In Fig. 5a the results of studies on water resistivity carried out without light radiation (in dark) for both the precipitated cellulose and cellulose-TiO_2/N composite

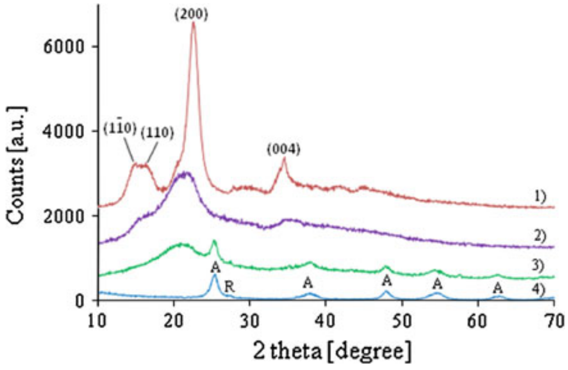

Fig. 4 XRD patterns of: *1*) crystalline cellulose, *2*) precipitated cellulose *3*) composite of cellulose and TiO_2/N, 4) TiO_2/N photocatalyst measured with Cu Kα (A—anatase, R—rutile)

dissolved in water are presented. It was found that for precipitated cellulose the TOC values of filtered water are very high (up to 38 mg/L of TOC) in comparison to cellulose-TiO_2/N composite. This means that on the surface of prepared cellulosic material some impurities are adsorbed (residues of components used in preparation process). The TOC concentration calculated for tested nanocomposite with titania rises insignificantly with stirring time from 3.09 to 3.82 mg/L (after 24 h of stirring). It was proved that immobilization of nitrogen modified titania in cellulose matrix stabilizes the surface of new complex and suppresses the releasing of organic residues to aqueous solution.

The experiments described above for both samples were repeated in aqueous solution under UV light irradiation. Results of these tests are presented in Fig. 5b. After 24 h of radiation the concentration of organic carbon in water was higher than after stirring in the dark (44 vs. 37.7 mg/L of TOC). This was related to the loss of solution volume because dissolved TOC did not evaporated with a steam as well as photodecomposition the precipitated cellulose because for composite cellulose with titania the reached TOC level was almost the same as without UV radiation.

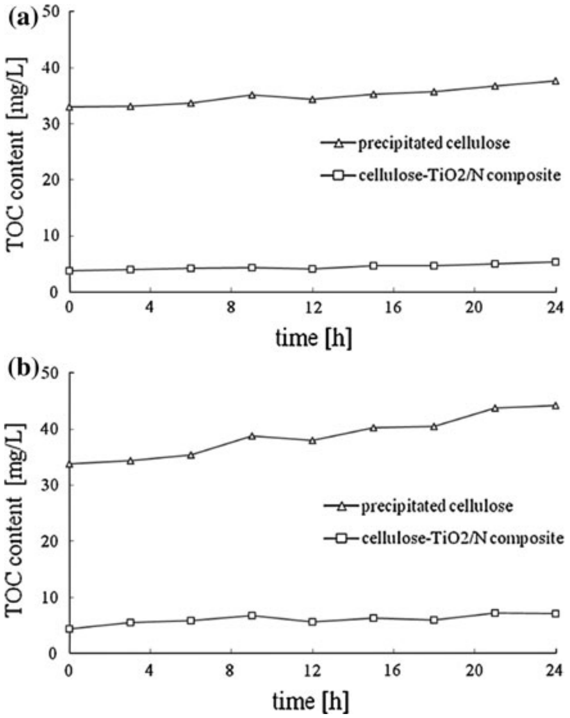

Fig. 5 Purity test of precipitated cellulose and cellulose-TiO_2/N (10 wt%) composite during: **a** stirring in the dark, **b** UV-vis light with strong UV radiation

Photostability measurements were also carried out in azo dye solution under UV lamp (Fig. 6). Adsorption of RR 198 was conducted in the dark during 24 h of stirring. It was noted that adsorption abilities of crystalline cellulose and precipitated cellulose were insignificant what is related with small specific surface area of tested materials. Addition of TiO_2/N catalyst cellulose matrix leads to stabilization of the surface of composite. It could be deduced that particles of TiO_2/N photocatalyst are loaded on the surface of precipitated cellulose and these nitrogen modified titania particles effectively block the releasing of ionic liquid residues to aqueous solution. It is worth mentioning that minor photoactivity of tested composite was observed. No photodegradation of used azo dye was possible to observe. This was also confirmed by UV–Vis spectroscopy measurements and no changes in RR 198 concentration was observed.

In Fig. 7 thermal stability of crystalline cellulose, ionic liquid ((cyclohexyl)hexyldimethylammonium acetate), precipitated cellulose and TiO_2/N immobilized in cellulose matrix are shown. A small mass loss observed at 70–130 °C is related to the release of moisture from the samples. In TiO_2/N-cellulose nanocomposite sample mass loss in a range of 150–280 °C is possible to observe. This could be assigned to the presence of ionic liquid residues. The thermal decomposition of pure (cyclohexyl)hexyldimethylammonium acetate could be observe in a temperature range from 150 to 250 °C with the maximum rate at 163 °C.

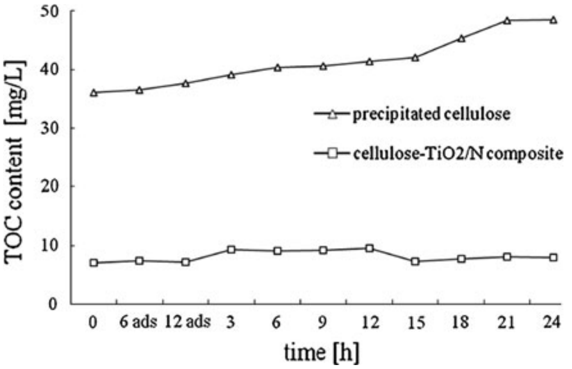

Fig. 6 Photostability measurements of precipitated cellulose and composite of cellulose and 10 wt% of TiO_2/N catalyst during RR 198 solution radiation by UV light

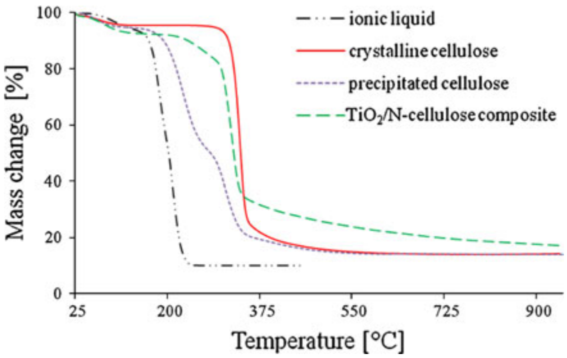

Fig. 7 Thermogravimetric (TG) curves of ionic liquid, crystalline cellulose, precipitated cellulose and composite of cellulose and 10 wt% of TiO_2/N catalyst under nitrogen atmosphere

It was noted that additive of TiO_2/N photocatalyst decreases the decomposition temperature of new composite. Some nanoparticles of cellulose could be present in water and that results in the increase of TOC value and that fact could not be excluded during the efficiency estimation of separation method.

Conclusions

The nanocrystalline anatase TiO_2/N (10 wt%) was introduced to crystalline cellulose by hydrogen bonding in ionic liquids environment. Under these conditions hydrogen bonding is more likely than the formation of a chemical bond. The obtained TiO_2/N-cellulose composite exhibited high UV–Vis light absorption. Additive of nitrogen modified titania in the cellulose matrix leads to enhancing water resistivity and thermal as well as photocatalytic stabilization of prepared cellulosic composite material. The properties of the obtained new composite are very promising for application as mechanical resistant material for protective coats or paper industry as well as the possibility of forming the desired shape.

Acknowledgments This work was supported by grant No. 7548/B/H03/2011/40 (National Science Centre, Poland) and grant No. MNiSW/DPN/4878/TD/2010 (National Science Centre, Poland). The authors wish to thanks to Adam Czyżewski for thermogravimetric analysis.

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References

Bubacz K, Choina J, Dolat D, Borowiak-Paleń E, Moszyński D, Morawski AW (2010) Studies on nitrogen modified TiO_2 photocatalyst prepared in different conditions. J Mater Res Bull 45:1085–1091. doi:10.1016/j.materresbull.2010.06.024

Chowdhury S, Scott JL, Mohan RS (2007) Reactivity of ionic liquids. Tetrahedron 63:2363–2389. doi:10.1016/j.tet.2006.11.001

Fan H, Li G, Yang F, Yang L, Zhang S (2011) Photodegradation of cellulose under UV light catalysed by TiO_2. J Chem Technol Biotechnol 86:1107–1112. doi:10.1002/jctb.2632

Janus M, Choina J, Morawski AW (2009) Azo dyes decomposition on new nitrogen-modified anatase TiO_2 with high adsorptivity. J Hazard Mater 166:1–5. doi:10.1016/j.hazmat.2008.11.024

Nagaoka S, Hamasaki Y, Ishihara S, Nagata M, Iio K, Nagasawa C, Ihara H (2002) Preparation of carbon/TiO_2 microsphere composites from cellulose/TiO_2 microsphere composites and their evaluation. J Mol Catal A: Chem 177:255–263. doi:10.1016/S1381-1169(01)00271-0

Olivier-Bourbigou H, Magna L, Morvan D (2010) Ionic liquids and catalysis: recent progress from knowledge to applications. Appl Catal A: Gen 373:1–56. doi:10.1016/j.apcata.2009.10.008

Pernak J, Syguda A, Janiszewska D, Materna K, Praczyk T (2011a) Ionic liquids with herbicidal anions. Tetrahedron 67(26):4838–4844. doi:10.1016/j.tet.2011.05.016

Pernak J, Borucka N, Walkiewicz F, Markiewicz B, Fochtman P, Stolte S, Steudte S, Stepnowski P (2011b) Synthesis, toxicity, biodegradability and physicochemical properties of 4-benzyl-4-methylmorpholinium-based ionic liquids. Green Chem 13:2901–2910. doi:10.1039/c1gc15468k

Pernak J, Wasiński K, Praczyk T, Nawrot J, Cieniecka-Rołonkiewicz A, Walkiewicz F, Materna K (2012a) Sweet ionic liquids-cyclamates: synthesis, properties, and application as feeding deterrents. Sci China Chem 55(8):1532–1541. doi:10.1007/s11426-012-4631-9

Pernak J, Praczyk T, Kardasz P, Jakubiak A, Syguda A, Materna K (2012b) Herbicidal ionic liquids with 2,4-D. Weed Sci 60(2):189–192. doi:10.1614/WS-D-11-00171.1

Pernak J, Syguda A, Materna K, Janus E, Kardasz K, Praczyk T (2012c) 2,4-D based herbicidal ionic liquids. Tetrahedron 68(22):4267–4273. doi:10.1016/j.tet.2012.03.065

Pernak J, Kordala R, Markiewicz B, Walkiewicz F, Popławski M, Fabiańska A, Jankowski S, Łożyński M (2012d) Synthesis, properties of ammonium ionic liquids with cyclohexyl substituent and dissolution of cellulose. RCS Adv 2(22):8429–8438. doi:10.1039/c2ra21502k

Petkovic M, Seddon KR (2008) Applications of ionic liquids in the chemical industry. Chem Soc Rev 37:123–150. doi:10.1039/b006677

Randorn C, Wongnawa S, Boonsin P (2004) Bleaching of methylen blue by hydrated titanium dioxide. Sci Asia 30:149–156. doi:10.2306/scienceasia1513-1874.2004.30.149

Stark A, Seddon KR (2007) Ionic liquids. In: Seidel A (ed) Kirk-Othmer encyclopaedia of chemical technology. Wiley, New Jersey, pp 836–920

Tang S, Baker GA, Zhao H (2012) Ether- and alcohol-functionalized task-specific ionic liquids: attractive properties and applications. Chem Soc Rev 41:4030–4066. doi:10.1039/c2cs15362a

Tsumura T, Kojitani N, Izumi I, Iwashita N, Toyoda M, Inagaki M (2002) Carbon coating of anatase-type TiO_2 and photoactivity. J Mater Chem 12:1391–1396. doi:10.1039/B201942F

Wada M, Sugiyama J, Okano T (1993) Native cellulose on the basis of the two crystalline Phase (Iα/Iβ) system. J Appl Polym Sci 49:1491–1496. doi:10.1002/app.1993.070490817

Wang H, Gurau G, Rogers RG (2012) Ionic liquid processing of cellulose. Chem Soc Rev 41:1519–1537. doi:10.1039/c2cs15311d

Wasserscheid P, Welton T (2008) Ionic liquids in synthesis. Wiley-VCH, Weinheim

Wawrzyniak B, Morawski AW (2006) Solar-light-induced photocatalytic decomposition of two azo dyes on new TiO_2 photocatalyst containing nitrogen. Appl Catal B: Environ 62:150–158. doi: 10.1016/j.apcatb.2005.07.008

Zeng J, Liu S, Cai J, Zhang L (2010) TiO_2 Immobilized in cellulose matrix for photocatalytic degradation of phenol under weak UV light irradiation. J Phys Chem C 114: 7806–7811. doi:10.1021/jp1005617

Zhou J, Liu S, Qi J, Zhang L (2006) Structure and properties of composite films prepared from cellulose and nanocrystalline titanium dioxide particles. J Appl PolymSci 101: 3600–3608. doi:10.1002/app.22650