Article

Kinetics of highly active TiO₂ microspheres formation in a presence of ethylammonium nitrate ionic liquid

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Abstract: Spherical microparticles of TiO₂ were synthesized by the ionic liquid-assisted solvothermal method at different reaction time (3, 6, 12 and 24h). The properties of the prepared photocatalysts were investigated by means of UV-vis diffuse-reflectance spectroscopy (DRS), BET surface area measurements, scanning electron microscopy (SEM), X-ray diffraction analysis (XRD), and X-ray photoelectron spectroscopy (XPS). The results indicated that the efficiency of phenol degradation was related with a time of the solvothermal synthesis as determined for TiO₂_EAN(1:1)_24h sample. Microparticles of TiO₂_EAN(1:1)_3h formed during the only 3h of synthesis time revealed really high photoactivity under visible irradiation – 75%. This value increased to 80% and 82% after 12h and 24h, respectively. The photoactivity increase was accompanied by the increase of the specific surface area thus pores size, as well as ability to absorb UV-vis irradiation. The high efficiency of phenol degradation of IL-TiO₂ photocatalysts was ascribed to the interaction between the surface of TiO₂ and ionic liquid components (carbon and nitrogen).

Keywords: ionic liquids, ionic liquid-assisted solvothermal reaction, reaction time, titanium dioxide, heterogeneous photocatalysis, visible light

1. Introduction

A worth-mentioning number of recent studies explores photosensitized titanium dioxide photocatalysts' applications inter alia in solar cells, energy storage, hydrogen production via water-splitting process, photocatalytic degradation of organic pollutants for water/air purification [1-5]. Expected low-exploitation costs, prevalence in utility and safety creates motivation for intensified research in the field of solar to chemical energy conversion. Photoactive performance of the pristine TiO₂ nano- and microparticles is limited by its 3.2eV bandgap to the absorption of UV light. Since UV light range constitutes the total radiant energy in only as diminutive amount as 5%, harvesting greater range of solar spectrum is considered vital for achieving significant effectiveness of photocatalysis [5, 6]. Extension of the TiO₂ spectral response range to absorb photons under visible (43%) or/and near infrared (49% of solar spectrum energy) irradiation is crucial for this purpose. The TiO₂ photocatalytic properties can be controlled and its optical response expanded to absorb photons under visible or/and near infrared light irradiation by alteration of the TiO₂ bandgap via morphology engineering [7-10].
It was found that, after excitation, electrons and holes propagate to the nano- and microparticles surface, where they react with electron acceptors and donors, respectively [6, 9, 11, 12]. Additionally, it is noted that slower recombination rate and larger surface area account for more active adsorption/desorption reactions and surface transfer of photoexcited electrons [9, 12, 13], whereas the potential adverse effects that originate in highly defective site, typically developing with the growth of large surface area, may be rectified by higher crystallization of the particles [9].

Ionic liquids (ILs) gain increasing attention in terms of their assistance in TiO₂ synthesis as solvents and spatial and, perhaps, band structuring agents. Their high viscosity, dielectric constant, thus polarity and dispersal capacity are widely recognized as the properties responsible for the charge, steric, and viscous stabilization of small-sized slow-growing crystallites and hindrance of disadvantageous for photocatalytic activity particles aggregation and agglomeration processes [7, 10, 11, 14-23].

The synthesized in a presence of ILs nano- and microparticles are characterized by larger specific surface area, higher crystallization level and less crystalline defects [17]. Hence, in the assistance of ILs, formation of particles of beneficial surface reactivity is promoted, inducing more effective photons absorption, trapping and their migration to the surface. Moreover, energetically simplified pathway of excited electrons through an ionic liquid’s HOMO and LUMO orbitals [16], along with prolonged stabilized charge separation is revealed to result in formation of greater amount of reactive oxygen species (ROS) in the subsequent reaction of electrons and holes with oxygen and water, respectively. The generated reactive oxygen species (°OH and O₂•-) are crucial reagents in photodegradation of pollutants [16, 17, 24].

Notwithstanding, direct relation between the structure of ILs and size/morphology of nano- and microparticles of semiconductors, such as the TiO₂ photocatalysts, remains still ambiguous. Up till now, the following factors had been reported predominant in effectuating the structure, thus activity of said particles: (1) IL anion type (the number of atoms it is composed of, as well as its steric structure); (2) IL cation type (increasing length of alkyl substituents extends hindrance of particle growth; apart from this, π-π stacking of imidazolium cations promotes ILs role as templating agents); (3) cation – anion interaction energy – the frailer, the weaker cation-anion interactions, the firmer capping on growing TiO₂ particles and the more efficient inhibition/hampering of the unfavorable Ostwald ripening process; (4) type of overall interactions (π-π, van der Waals, Coulomb and electrostatic forces, hydrogen bonding) [15, 16, 21, 25].

Furthermore, the proposed fons et orgio of influences on TiO₂ photoactivity are tenable: (1) doping with N, C, F elements after ILs thermal decomposition; (2) directly sensitizing the TiO₂ particles; (3) affecting the transfer of photo-generated charges through the bulk of particles; (4) favoring oxygen vacancies and Ti³⁺ species formation during synthesis [26-28]. However, up to date kinetics of formation of TiO₂ particles during ionic liquid-assisted synthesis was not presented and discussed.

In this regard, in this study, TiO₂ particles had been synthesized solvothermally with the assistance of selected ionic liquid – ethylammonium nitrate [EAN][NO₃], one of the earliest reported in the literature protic ionic liquid [29, 30].

Apart from prevailing in studies topics of synthesis process and characterization of IL-assisted TiO₂ microparticles [22, 30-32], we focused on evaluating functional properties of obtained microparticles, namely – their photoactivity. Alongside the stated, we strive to infer the mechanisms of ILs assistance through exploration of influence of selected ILs, illustrated with the example of ethylammonium nitrate [EAN][NO₃] [29].

We place an emphasis on the essentiality of (1) researching Vis-light induced photoactivity – in comparison to already researched UV-induced photoactivity [19, 25, 33-35] and (2) conducting research in the presence of a model pollutant (2a) neutral in terms of photosensitization of TiO₂, (2b) proposing simple in its mechanism of degradation and mineralization and (2c) of low photosorption coefficient [27, 36, 37] – in contrast to common choice of organic dyes (methylene blue, methyl orange, rhodamine B) [7, 10, 13, 18, 19, 25, 38, 39], we applied phenol. What also is
imperative, we excluded the minor in facilitating the photocatalysis reaction active species, while exposing the substantial ones – through active species scavenger tests. In this article, we present the results of previously non-analyzed and non-reviewed comprehensively [EAN][NO3]-assisted TiO2 microparticles, which photocatalytic effect on degradation and mineralization of phenol in aqueous solution vastly exceeded our expectations, reaching as high as 82% of degradation rate in our tests, which are described below. Moreover for the first time we have examined kinetics of TiO2 microspheres formation in a presence of ethylammonium nitrite ionic liquid.

2. Results

First of all, a set of samples with selected IL to TBOT molar ratios were synthesized and characterized taking into account surface area and photoactivity. Sample labeling, the amount of ILs to precursor used during the preparation procedure, as well as the specific surface area, pore volume of the obtained photocatalysts and their photocatalytic activity under Vis irradiation are given in Table 1. On the basis of the photocatalytic effect we have chosen the sample with the highest activity to examine the kinetics of the TiO2 microspheres formation in a presence of ethylammonium nitrite ionic liquid, which is showed in Figure 1. As presented in Table 1, the effect of solvothermal synthesis duration (3, 6, 12 and 24h) on surface properties and photoactivity for IL:TBOT ratio equaled to 1:1 was also investigated.

Figure 1. The structure of ethylammonium nitrite [EAN][NO3] ionic liquid.

2.1. The BET surface area and SEM analysis

The results listed in Table 1 revealed the influence of the ionic liquid content on the specific surface area and pore volume of the synthesized samples. All the samples presented higher specific surface area in comparison with TiO2 synthesized without IL (184 m2.g-1), and also than that reported for commercially available P25 (50 m2.g-1)[40]. The values of the specific surface area for TiO2 prepared in a presence of [EAN][NO3] ranged from 190 m2·g-1 (sample prepared with the lowest IL:TBOT molar ratio - 1:10) to 233 m2·g-1 for the sample obtained with IL:TBOT molar ratio of 1:2. In this regard, the direct relation between the amount of the IL in the reaction mixture and the specific surface area for these photocatalysts was detected. However, further increase of the IL content taken to synthesis (up to IL:TBOT molar ratio of 1:1) resulted in a decrease of the pore volume, thereby specific surface area due to probably overloading of the TiO2 surface with organic salt. It might indicate that IL work like designer agent of microstructures’ physical and structural properties.

The scanning electron microscopy images of the pure TiO2 and IL-assisted TiO2 particles obtained for various molar ratios of IL:TBOT in a presence of [EAN][NO3] are presented in Figure 2. The pristine TiO2 exhibited smooth surface with average size from 0.5-4 µm. In the case of IL-TiO2 samples it is showed that the sample with the molar ration 1:1 and the sample with a low amount of IL (1:8) present a spherical structure and did not change in relation to pristine TiO2.
Table 1. Characteristics of TiO₂ particles obtained by [EAN][NO₃] – assisted solvothermal synthesis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time of synthesis</th>
<th>Molar ratio (IL:TBOT)</th>
<th>Specific surface area (m².g⁻¹)</th>
<th>Pore volume (cm³.g⁻¹)</th>
<th>Phenol degradation efficiency under 60 min of Vis irradiation (%)</th>
<th>Rate of phenol degradation under visible light (λ&gt; 420) [µmol·dm⁻³·min⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂ pristine</td>
<td>24</td>
<td>-</td>
<td>184</td>
<td>0.069</td>
<td>7</td>
<td>0.18</td>
</tr>
<tr>
<td>TiO₂_EAN(1:10)_24h</td>
<td>24</td>
<td>1:10</td>
<td>190</td>
<td>0.093</td>
<td>28</td>
<td>1.01</td>
</tr>
<tr>
<td>TiO₂_EAN(1:8)_24h</td>
<td>24</td>
<td>1:8</td>
<td>211</td>
<td>0.102</td>
<td>19</td>
<td>0.55</td>
</tr>
<tr>
<td>TiO₂_EAN(1:5)_24h</td>
<td>24</td>
<td>1:5</td>
<td>216</td>
<td>0.105</td>
<td>33</td>
<td>1.11</td>
</tr>
<tr>
<td>TiO₂_EAN(1:3)_24h</td>
<td>24</td>
<td>1:3</td>
<td>216</td>
<td>0.105</td>
<td>36</td>
<td>1.17</td>
</tr>
<tr>
<td>TiO₂_EAN(1:2)_24h</td>
<td>24</td>
<td>1:2</td>
<td>233</td>
<td>0.113</td>
<td>41</td>
<td>1.32</td>
</tr>
<tr>
<td>TiO₂_EAN(1:1)_24h</td>
<td>24</td>
<td>1:1</td>
<td>221</td>
<td>0.108</td>
<td>82</td>
<td>3.12</td>
</tr>
<tr>
<td>TiO₂_EAN(1:1)_3h</td>
<td>3</td>
<td>1:1</td>
<td>239</td>
<td>0.12</td>
<td>75</td>
<td>2.28</td>
</tr>
<tr>
<td>TiO₂_EAN(1:1)_6h</td>
<td>6</td>
<td>1:1</td>
<td>207</td>
<td>0.101</td>
<td>75</td>
<td>2.38</td>
</tr>
<tr>
<td>TiO₂_EAN(1:1)_12h</td>
<td>12</td>
<td>1:1</td>
<td>209</td>
<td>0.102</td>
<td>80</td>
<td>2.53</td>
</tr>
</tbody>
</table>

Figure 2. SEM images of TiO₂ obtained from IL-assisted solvothermal synthesis: TiO₂_EAN(1:8)_24h; TiO₂_EAN(1:1)_24h and reference TiO₂.
The experiments of the TiO\textsubscript{2}\_EAN(1:1)\_24h sample preparation performed in the different time regimes revealed that 3h of the solvothermal synthesis is enough to obtain the TiO\textsubscript{2} microspheres (see SEM images presented in Figure 3 below). However, the reaction yield was relatively low (only 19%) and increased with increasing reaction time (38% for 6h, 65% for 12h and 93% for 24h). Moreover, elongation of the synthesis time resulted at first in decrease of the specific surface area from 239 m\textsuperscript{2}.g\textsuperscript{-1} (after 3h) to 207 m\textsuperscript{2}.g\textsuperscript{-1} (after 6h), and then in the enlargement of the specific surface area to 221 m\textsuperscript{2}.g\textsuperscript{-1} (after 24h).

Explanation of this observation may be found in SEM images of microparticles prepared with the same amount of substrates (molar ratio of TBOT to ILs equaling to 1:1), however differing by the time of thermal treatment (3, 6, 12 and 24 hours) presented in Figure 3. In all the introduced variations, the majority of the particles lie within the scope of 1-3 µm for 3h (48%), 2-3µm for 6 (24%) and 24 hours (28%), and 3-4 µm for 12 hours (19%). Percentage contribution of the particles with diameter above 4 µm was rarely reached and never exceeds 15% for all the obtained samples. In the images sequence presented below, we noted that sample subjected to thermal treatment for 3 h is mainly composed of a large number of small spherical particles with a range of 1-3 µm. Nonetheless, between particles synthesized in 6, 12- and 24-hour regime, less of a difference was recognized. In this regard, high surface area of the particles prepared within 3h may be related to higher contribution of the smallest particles.

![SEM images of TiO\textsubscript{2}\_EAN(1:1) obtained in different synthesis time: 3h, 6h, 12h and 24h.](image)

**Figure 3.** SEM images of TiO\textsubscript{2}\_EAN(1:1) obtained in different synthesis time: 3h, 6h, 12h and 24h.

### 2.2. XRD analysis

PXRD patterns for the series of TiO\textsubscript{2}\_EAN are presented in Figure 4-5 All patterns looked similar since the samples contained only the anatase (TiO\textsubscript{2}) phase. The open circles represent experimental data points, a solid red line is a profile fitting (LeBail method) and vertical bars mark positions of the expected Bragg reflections for the used model (I 41/a m d, s.g. # 141). The LeBail fit given lattice parameters for TiO\textsubscript{2} that are gathered in Table 2. The lattice parameters are similar and are close to reported by I. Djerdj and A.M. Tonejc [41]. The PXRD reflections are broad which indicates small crystallite size that was estimated to be between 5,0 and 6,5 nm. However, no correlation was observed between the amount of ionic liquid taken for synthesis as well as preparation time and the crystallite size.
**Figure 4.** XRD pattern of TiO2-EAN prepared with different IL-TBOT molar ratio. A solid line is a profile fit to the experimental data (open circles). A Bragg reflections are marked by vertical bars.

**Figure 5.** XRD pattern of TiO2-EAN prepared with IL-TBOT molar ratio of 1:1 synthesized at different synthesis times. A solid line is a profile fit to the experimental data (open circles). A Bragg reflections are marked by vertical bars.
Table 2. Lattice parameters and average crystallite size of the TiO$_2$-EAN photocatalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>d (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$-EAN(1:1)_3h</td>
<td>3.8051(3)</td>
<td>9.554(2)</td>
<td>65</td>
</tr>
<tr>
<td>TiO$_2$-EAN(1:1)_6h</td>
<td>3.7907(7)</td>
<td>9.504(3)</td>
<td>50</td>
</tr>
<tr>
<td>TiO$_2$-EAN(1:1)_12h</td>
<td>3.7892(6)</td>
<td>9.507(3)</td>
<td>55</td>
</tr>
<tr>
<td>TiO$_2$-EAN(1:1)_24h</td>
<td>3.7890(6)</td>
<td>9.504(3)</td>
<td>50</td>
</tr>
<tr>
<td>TiO$_2$-EAN(1:2)_24h</td>
<td>3.7899(7)</td>
<td>9.499(3)</td>
<td>55</td>
</tr>
<tr>
<td>TiO$_2$-EAN(1:3)_24h</td>
<td>3.7926(8)</td>
<td>9.506(4)</td>
<td>60</td>
</tr>
<tr>
<td>TiO$_2$-EAN(1:5)_24h</td>
<td>3.7814(11)</td>
<td>9.472(6)</td>
<td>65</td>
</tr>
<tr>
<td>TiO$_2$-EAN(1:8)_24h</td>
<td>3.7953(9)</td>
<td>9.483(5)</td>
<td>55</td>
</tr>
<tr>
<td>TiO$_2$-EAN(1:10)_24h</td>
<td>3.7942(12)</td>
<td>9.476(7)</td>
<td>55</td>
</tr>
</tbody>
</table>

2.3. XPS analysis

The elemental surface composition of the selected ILs-TiO$_2$ specimens, evaluated by XPS, is shown in Table 3. The titanium, oxygen, carbon and nitrogen were detected and the corresponding high-resolution (HR) XPS spectra of Ti 2p, O 1s, C 1s and N 1s are presented in Figure 6. The chemical character of elements is identified in the deconvoluted spectra in Figure 6 and Table 3. The Ti 2p, O 1s and C 1s spectra exhibit features, characteristic for the ILs-TiO$_2$ specimens [16, 42]. The N 1s signal at 400 eV is commonly interpreted as the surface C-N bond. Only for the TiO$_2$-EAN(1:1) sample thermally treated for 24 h, the additional signal appears at about 402.8 eV, which may be assigned to oxidized nitrogen surface species.

The XPS data collected in Table 4 revealed the surface chemical composition of the TiO$_2$-EAN(1:1)_24h samples to be different than the sample of lower amount of TiO$_2$-EAN(1:8)_24h. For the last one the contribution of the Ti$^{3+}$ fraction is about 30% smaller and the nitrogen amount is evidently lower than for TiO$_2$-EAN(1:1)_24h sample. These observations confirmed higher amount of IL on the TiO$_2$-EAN(1:1)_24h sample surface (analogous relation was observed also for carbon atom). In the series of TiO$_2$-EAN(1:1) samples, differing by the time of thermal treatment, we noted systematic decrease of the oxygen Ti-O$_{surf}$ fraction with increasing time of thermal treatment from 6 h to 24 h and significantly smaller surface concentration of nitrogen for 24-hour synthesized sample (Table 4). Moreover, for the last sample the oxidised form of nitrogen species appears in addition to the main nitrogen N-C$_{surf}$ fraction (Figure 6). These observations indicated the surface transformation of IL-assisted TiO$_2$ in prolonged time of thermal treatment.

To elucidate the effect of phenol-degradation processing on the chemical composition of TiO$_2$-EAN photocatalyst, we analyzed both the sample after 3-cycles of photocatalytic processing and the same sample washed with deionized water. The results are compared in Figure 6 and Table 3. One can see nitrogen atom s concentration is similar for both samples. However, the water washed sample exhibits significantly larger surface amount of titanium fraction Ti$^{3+}$ and relatively higher contribution of -OH surface species (see O 1s and C 1s fractions in Table 3).
Figure 6. High resolution XPS spectra of elements detected in the surface layer of [EAN][NO₃]-modified TiO₂ particles.
<table>
<thead>
<tr>
<th>Sample label</th>
<th>Ti 2p\textsubscript{3/2} fraction (%)</th>
<th>O1s fraction (%)</th>
<th>C1s fraction (%)</th>
<th>N1s fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\sum \text{Ti} (\text{at.%}))</td>
<td>(\text{Ti}^{3+})</td>
<td>(\text{Ti}^{4+})</td>
<td>(\sum \text{O} (\text{at.%}))</td>
</tr>
<tr>
<td>(\text{TiO}_2_\text{EAN} 1:1_6h)</td>
<td>63.55</td>
<td>21.43</td>
<td>3.27</td>
<td>11.77</td>
</tr>
<tr>
<td>(\text{TiO}_2_\text{EAN} 1:1_12h)</td>
<td>68.33</td>
<td>18.98</td>
<td>8.50</td>
<td>3.28</td>
</tr>
<tr>
<td>(\text{TiO}_2_\text{EAN} 1:8_24h)</td>
<td>74.56</td>
<td>15.33</td>
<td>7.72</td>
<td>2.39</td>
</tr>
<tr>
<td>(\text{TiO}_2_\text{EAN} 4\text{-cycles})</td>
<td>70.46</td>
<td>21.06</td>
<td>8.75</td>
<td>1.73</td>
</tr>
<tr>
<td>(\text{TiO}_2_\text{EAN} 4\text{-cycles (washed)})</td>
<td>67.42</td>
<td>21.84</td>
<td>8.15</td>
<td>2.59</td>
</tr>
</tbody>
</table>
2.4. UV-Vis spectrum

The UV-vis adsorption spectra of TiO$_2$ synthesized with various molar ratio of [EAN][NO$_3$] to TBOT are presented in Figure 7. Pristine TiO$_2$ is only photoactive under the UV region (λ<400 nm). The addition of the ionic liquid to the TiO$_2$ synthesis environment increased the absorption range of IL-TiO$_2$ being noticeably photoactive at above 420 nm. The absorption properties of the samples prepared with IL were superior in comparison with pristine TiO$_2$ in the visible light range, whereas all samples showed similar UV absorption. Generally, higher IL amount used for synthesis resulted in the enhancement of the Vis light absorption by the IL-TiO$_2$ photocatalysts.

![UV-vis adsorption spectra of TiO$_2$ synthesized using various molar ratio of [EAN][NO$_3$] to TBOT.](image)

**Figure 7.** UV-vis adsorption spectra of TiO$_2$ synthesized using various molar ratio of [EAN][NO$_3$] to TBOT.

Interesting results were also obtained for the experiments where the influence of the reaction time was taken into account (Figure 8). When increasing the reaction time the enhancement of visible light absorption by IL-TiO$_2$ was observed. Thereby, the sample prepared during 24h was characterized by the significantly broader absorption and the highest red shift of the absorption edge, thereby higher effectiveness to create electron–hole pairs.

2.5. Photocatalytic activity of IL-TiO$_2$ in phenol decomposition model reaction

The photocatalytic activity of the IL-TiO$_2$ samples was evaluated by the degradation of phenol model compound under visible light (λ>420 nm) irradiation. The obtained results are summarized in Table 1 and presented in Figure 9. As it was mentioned above, before illumination, the solution was stirred for 30 min in the dark to establish molecular adsorption equilibrium. Pristine TiO$_2$ synthesized by the solvothermal method without addition of the ionic liquid was used as the reference sample.
Figure 8. UV-vis adsorption spectra of TiO$_2$ EAN(1:1) photocatalyst prepared in 3, 6, 12 and 24h.

Figure 9. Efficiency of phenol degradation under visible light ($\lambda>$420 nm) in the presence of TiO$_2$ prepared in [EAN][NO$_3$].

It was found that the TiO$_2$ EAN microparticles exhibited higher photoefficiency than pristine TiO$_2$, which is consistent also with higher BET specific surface areas and enhanced optical properties. After 60 min of photocatalytic process, 7% of phenol was degraded using unmodified TiO$_2$, however the TiO$_2$ EAN efficiency was higher and strongly influenced by the amount of ILs used during the synthesis. For example, up to 82% of phenol was degraded in the presence of photocatalyst TiO$_2$ EAN(1:1)$_{24h}$, where molar ratio of [EAN][NO$_3$] to TBOT taken for synthesis was 1:1. This value is about 5.5 times higher compared to pristine TiO$_2$, indicating its excellent photocatalytic activity. This observation was correlated with the UV-vis adsorption spectra, where TiO$_2$ EAN(1:1)$_{24h}$ sample showed the highest extension of the absorption edge to the visible light region. It was found that the samples prepared with IL:TBOT molar ratio 1:10...
and 1:8 revealed the lowest photoactivity among the photocatalysts obtained in the presence of ethylammonium nitrate IL. In this regard, the photodegradation efficiency increased with increasing the quantity of ionic liquid taken to synthesis (thereby IL present at the TiO2 surface).

Moreover, the efficiency of phenol degradation was also related with time of the solvothermal synthesis as determined for TiO2_EAN(1:1) sample. Microparticles of TiO2_EAN(1:1)_3h formed during only 3h of synthesis time revealed really high photoactivity under visible irradiation – 75%. This value increased to 80% and 82% after 12h and 24h, respectively. The photoactivity increase was accompanied by increase of the specific surface area thus pore sizes as well as ability to absorb UV-vis irradiation. Additionally, based on the XPS measurements it was concluded that the increase in the visible light absorption and the enhancement of the photocatalytic activity may be related to the highest quantity of carbon and Ti(+3) defects at the TiO2 surface.

To investigate the degradation/regeneration capacity and the structural stability during the entire process, we performed the stability tests for the sample characterized by the best photocatalytic activity under Vis light irradiation. In the stability tests, the same sample was repeatedly used in the phenol photodegradation reaction for 3 times. As shown in Figure 10, the significant drop of the phenol removals from 84% to 33% was found.

![Figure 10. Phenol removals in the photodegradation using the TiO2 microspheres in a cycled mode.](image-url)

In order to further clarify the possible mechanism of phenol degradation, reactive species trapping tests were designed. Controlled photoactivity experiments using different radical scavengers (ammonium oxalate as scavenger for h+, AgNO3 as scavenger for e-, benzoquinone as scavenger for O2•− radical species, and tert-butyl alcohol as scavenger for •OH species) were carried out similarly to the above described photocatalytic degradation process. The only exception was that the radical scavengers were added to the reaction system. The addition of ammonium oxalate and AgNO3 had weak inhibition efficiency of phenol degradation, indicating that h+ and e− had negligibly small effect on the mechanism of photocatalytic degradation. The photocatalytic conversion falls by approximately half when the tert-butyl alcohol (TBA) as the scavenger for hydroxyl radicals was used. As shown in Table 4 when benzoquinone as the trapping agent of O2•− was added into phenol solution under visible irradiation the photodegradation of phenol significantly declined to about 7%. These results clearly suggested that the photocatalytic degradation of phenol under Vis irradiation in the presence of TiO2_EAN(1:1) was mainly intimate with the photogenerated superoxide radical species. Secondly, the photogenerated OH radicals were also involved in the decomposition of phenol.
Table 4. Effect of scavengers’ addition on phenol degradation efficiency under Vis irradiation.

<table>
<thead>
<tr>
<th>Scavenger type</th>
<th>benzoquinone</th>
<th>AgNO₃</th>
<th>Tert-butyl alcohol</th>
<th>Ammonium oxolate</th>
<th>Without scavenger</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active species</td>
<td>O₂⁻, e⁻, OH⁻, h⁺</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Vis &gt;420 nm filter</td>
<td>6.89</td>
<td>78.94</td>
<td>33.56</td>
<td>81.38</td>
<td>86.35</td>
</tr>
</tbody>
</table>

In order to explain what might have contributed to the increase in the photoactivity of TiO₂-ILs, the decomposition level of ionic liquid cations has been investigated by using chromatography techniques. It has been demonstrated that the ethylammonium nitrate ionic liquid was degraded in 97% after 24h solvothermal reaction. Therefore, it was probably that TiO₂ could be doped with nitrogen and carbon or/and surface-modified by carbon species. However, based on the XPS analysis, the Ti-N interactions between released nitrogen atoms, resulting from IL’s thermal decomposition, and TiO₂ matrix have not been observed. Thus, although we could expect incorporation of nitrogen and carbon atoms in a crystalline lattice of TiO₂, performed analysis did not confirm it. Nevertheless, it should be remembered that due to the low ionic liquid content on the TiO₂ surface, a low level of XPS detection (d.l. = 0.1 at.%) could affect the results. According to the literature, it could be generally stated that if TiO₂ particles grow in the presence of N and C precursors and under elevated temperature conditions, usually N and C atoms are incorporated into crystal lattice of semiconductors [43-45].

In order to identify the origin of visible light – induced activity, phenol degradation rate was plotted depending on the surface area values as well as carbon and nitrogen content in the surface layer. Data presented in Figure 11 suggested that the observed increase in photoactivity could be most interpreted by presence of nitrogen in the surface layer. Although the origin of photoactivity is not clear at this moment, it is crucial to note that preparation of highly active TiO₂ spheres was developed.

**Figure 11.** Dependence of the (a) surface area, (b) total carbon content, (c) C-C content and total nitrogen content on the photocatalytic activity.
3. Materials and Methods

3.1. Materials

For the aforementioned synthesis’ purpose the following reagents have been applied: (1) titanium(IV) butoxide (TBOT) – as the TiO₂ microparticles direct precursor and (2) 36% hydrochloric acid (HCl) – as a pH stabilizer, sourced from Sigma–Aldrich; (3) anhydrous ethyl alcohol (99.8% ethanol) – as the reaction medium (from POSCH S.A.); (4) ethylammonium nitrate (from IOLITEC, purveyed with ≥97% of purity) – the assisting ionic liquid and (5) deionized water provided locally.

3.2. Preparation of IL-assisted TiO₂ particles

The preparation of TiO₂ microparticles was carried out emulating the method reported in [16], of the following summary: (1) TBOT was dispersed in ethanol through dropwise pouring, under constant vigorous stirring; (2) HCl, deionized water and the due amount of IL – adequate to the applied molar ratio of TBOT to IL – were dissolved under unchanged conditions to the point of attaining a pellucid solution. Afterwards, the ensuing mixture was transferred into an inner Teflon and an outer stainless-steel autoclaves to be incubated at 180°C for 24h (for various TBOT to IL molar ratios) and for 6, 12 and 24h (for 1:1 TBOT to IL molar ratio) for the purpose of kinetics of crystal growth evaluation. Subsequently, the autoclaves were cooled down to the room temperature and obtained precipitate was cleansed through numerous washings with deionized water and ethanol, and then dried at 60°C during 4h. The preparation ended with the 2-hour calcination of plateau at 200°C, that was being reached at the 2°C/min slope. For reference, pristine TiO2 was as-synthetized – with the exception of the IL presence.

3.3. Surface properties characterization

The Brunauer-Emmett-Teller (BET) surface area was calculated by N₂ absorption-desorption isotherms at 77K on a Micromeritics Gemini V200 Shimadzu analyzer (equipped with the VacPrep 061 Degasser). The morphology of TiO₂ microparticles were studied by scanning electron microscopy (SEM) analysis, performed under a Hitachi TM-1000 microscope. The chemistry of the surface was researched by X-Ray photoelectron spectroscopy (XPS), the results were obtained with a PHI 5000 VersaProbeTM(ULVAC-PHI) spectrometer of monochromatic Al Kα radiation (h=1486.6 eV). Phase purity of the samples was determined by powder X-ray diffraction (PXRD) using a PANalytical X’Pert Plus diffractometer with Cu Kα radiation. To determine the unit cell parameters, profile fits were performed on the powder diffraction data through the use of the HighScore program using Thompson–Cox–Hastings pseudo-Voigt peak shapes. The average crystallite size was calculated using the Scherrer equation.

The decomposition level of ionic liquid cations was analyzed by using Dionex ICS 1100 liquid chromatograph. Deionized water containing 0.21 % (v/v) of methanesulfonic acid (Sigma Aldrich) was used, as a mobile phase. The separation was carried out isocratically with using Dionex ION PAC, CS16 column (3 x 250 mm Dionex) at 35°C. The flow rate was 0.36 mL min⁻¹. Each sample (before and after solvothermal reaction) was measured in triplicate. The decomposition level was calculated as:

$$\eta_{IL}(\%) = 100 \times \frac{C_0 - C}{C_0}$$

where: C₀ – is the initial concentrations of cations of ILs; C – is the concentrations of cations of ILs after the solvothermal reaction.

3.4. Evaluation of photocatalytic activity

The photocatalytic activity was measured through the phenol decomposition rate under visible-light irradiation. For this aim, we dispersed 0.125 g of obtained photocatalyst in the 25 ml of phenol solution.
aqueous solution (C₀ = 25 mg/l) inside a cylindrical reactor with a circular quartz window. In use there was a reactor fitted with a cooling jacket, during the reaction cooled by the constant flow of water at ≤10°C, supplied in aeration at 5 dm³/h. The reactor’s quartz–windowed side was exposed to illumination of intensity equaling to 3 mW/cm² (by 1000 W Xenon lamp, 6271H Oriel; optical filter >420 nm, GG 420).

In order to establish the absorption-desorption equilibrium between phenol and photocatalyst prior to the reaction, the suspension was allocated to 30-minutes long stirring in the dark, preliminarily to the photo-initiation of the catalysis. About 1 ml of the suspension was sampled from the reactor, then. During the irradiation – the samples were taken in 3, 20–minute intervals. Each sample was filtered through syringe filters (⌀=0.2 µm) for the removal of photocatalyst microparticles, anterior to the due evaluation. The concentration of the remaining phenol was measured colorimetrically (λmax = 480 nm), after the derivatization with diazo-p-nitroaniline, with UV-Vis spectrometer (Evolution 220, Thermo-Scientific).

5. Conclusions

This study is the first step towards enhancing our understanding of effect of ethylammonium nitrate ionic liquids on surface properties of TiO₂ spheres formed in the solvothermal synthesis. In summary, the TiO₂ microspheres with a superior visible-light photocatalytic activity were prepared in the presence of the ethylammonium nitrate ionic liquid by using a solvothermal method followed by calcination process. It should be highlighted that the most active TiO₂ samples formed in the presence of [EAN][NO₃] possessed almost the same activity induced by visible light than P25 TiO₂ under UV radiation. Phenol degradation rate equaled to 3.12 µmol/dm³/min for TiO₂_EAN/Vis system, while it was 3.46 µmol/dm³/min for P25/UV system. In this paper, kinetics of highly active TiO₂ microspheres formation in a presence of ethylammonium nitrate ionic liquid has been examined. The obtained results revealed that, the microparticles of TiO₂_EAN(1:1)_3h formed during only 3h of synthesis time revealed really high photoactivity under visible irradiation – 75%. This value increased to 80% and 82% after 12h and 24h, respectively. However, the reaction yield for the 3h synthesis time was relatively low (only 19%) and significantly increased with increasing reaction time (38% for 6h, 65% for 12h and 93% for 24h). The photoactivity increase was accompanied by increase of the specific surface area thus pore sizes as well as ability to absorb Vis irradiation.

The effective interactions between ionic liquid components mainly: carbon, nitrogen and microparticles surface of TiO₂ were clearly demonstrated by the XPS analysis. This factor could result in an excellent visible-light photocatalytic activity for the IL-TiO₂ samples prepared. The radicals trapping experiments revealed that O₂•− and OH• were the main active species during the degradation process.

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References


