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To cite this article before publication: Timofey Savchuk et al 2021 Nanotechnology in press https://doi.org/10.1088/1361-6528/ac317e

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Anodic TiO₂ nanotube arrays for photocatalytic CO₂ conversion: comparative photocatalysis and EPR study

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Received xxxxx Accepted for publication xxxxx Published xxxxx

Abstract

Titania (TiO₂) is a widely used semiconductor for the photocatalytic decomposition of organic impurities in air, water and the conversion of CO₂ into hydrocarbon fuel precursors. TiO₂ in the form of nanotubes arrays is the most attractive for practical use because of the morphological advantages providing more favorable diffusion of photocatalytic reaction products and a low recombination rate of photogenerated electrons and holes. We have carried out a comparative study of the photocatalytic activity of gas-phase conversion of CO₂ to hydrocarbon products and the defect properties of multi-walled and single-walled arrays of TiO₂ nanotubes. Methanol and methane have been detected in the CO₂ photoreduction process. The photocatalytic evolution rate of multi-walled TiO₂ nanotubes is twice as fast for methane as for single-walled TiO₂ nanotubes after four hours of irradiation and four times faster for methanol. The type and features of the structural defects have been investigated by EPR spectroscopy. For the first time, it has been shown that Ti³⁺/oxygen vacancy centers are mainly located inside the outer layer of nanotubes, while carbon dangling bonds have been observed directly on the surface of the inner layer. Carbon defects have been found to be the centers of adsorption and accumulation of photoinduced charge carriers. The results are entirely new; they clarify the role of different types of defects in the photocatalytic conversion of CO₂to hydrocarbon compounds and show good prospects for applying TiO₂ nanotube arrays.

Keywords: TiO₂ nanotube arrays, CO₂ photocatalytic conversion, EPR

1. Introduction

Due to rising global energy consumption and CO₂ levels in the atmosphere, in recent years, photocatalytic processes for the gas-phase conversion of CO₂ into hydrocarbon fuel

precursors have been intensively studied [1-4]. At present, the efficiency of most photocatalysts for practical applications is still very low [5]. Photocatalysts based on nanostructured TiO₂ with large specific surface area (nanoparticles, nanowires, nanotubes) have attracted researchers

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58 59 60 due to the chemical stability and photocorrosion resistance of the material and the material suitable band edge position [6,7]. In turn, anodic arrays of titania nanotubes (TiO₂ NTs), which can be described as vertically oriented nanotubes with large surface area, can promote more favorable mass diffusion of photocatalytic reaction products, directional charge transfer, and lower recombination rate of photoinduced charge carriers compared to TiO₂ nanoparticles [8–10].

Typically, highly ordered TiO₂ NTs arrays are formed by electrochemical oxidation of Ti in fluorine-containing electrolytes based on ethylene glycol and glycerol [11–13]. Such TiO₂ NTs are multi-layered and contain an inner layer of nanotubes (IL) enriched with ethylene glycol decomposition products, while the outer layer (OL) contains mostly pure TiO₂ [14,15]. Formed TiO₂ NTs have an amorphous structure and, therefore, low photoelectrochemical activity. The formed samples are annealed in air to obtain the TiO₂ crystal structure. After annealing, the inner layer of the nanotubes turns into a mesoporous structure with a mixture of anatase and rutile nanocrystals with an average size of ~7 nm. [16]. The outer layer of the nanotube is almost stoichiometric anatase [16]. Also, the presence of carbon in IL nanotube multi-walled TiO2 NTs after annealing in air has been described in [16, 17].

Only a few studies have investigated the photocatalytic activity of TiO_2 NTs arrays produced in ethylene glycol-based electrolytes during CO₂ conversion in the gas phase in the presence of water vapor. Zubair et al. described the photocatalytic properties of TiO₂ NTs modified with graphene quantum dots, disregarding the presence of carbon and the multilayer nature of the nanotube. [6]. Li et al. reported the effect of increasing the CH₄ production rate in a gas-phase photocatalytic CO₂ conversion process on the surface of TiO₂ NTs obtained in ethylene glycolbased electrolyte and modified with Cu₂O [18]. Low et al. showed a significant increase in the rate of CH₄ production from TiO₂ NTs modified with

Ag nanoparticles but did not indicate a multilayer structure [9]. They also failed to consider the role of the multi-wall structure of nanotubes [18, 9]. At the same time, Macak et al. showed that removing the inner layer of a nanotube leads to an increase in the photoactivity of TiO₂ NTs used as photoanode material for photoinduced water decomposition, compared to nanotube arrays with an inner layer [17]. In [19], Motola et al. reported improved photocatalytic activity of single-walled TiO₂ NTs in the photoinduced degradation of methylene blue dye.

However, the effect of the inner layer on the photocatalytic conversion activity of CO₂ is still an open question. Electron paramagnetic resonance (EPR) spectroscopy can be a good solution for observing structural defects in nanotubes' outer and inner layers and comparing the differences with their photocatalytic properties [20]. Therefore, our work to aims study the photocatalytic properties of multi-walled and single-walled arrays of TiO₂ nanotubes for photoinduced conversion of CO₂ in the gas phase, their structure, and defect properties.

2. Methods

2.1 Samples preparation

Before anodizing, the titanium foil (50 µm thick, 99.7 % metal basis) was treated in acetone in an ultrasonic bath for 15 minutes, rinsed in deionized water (18.2 M Ω), and dried in an argon flow. Anodic TiO₂ nanotube arrays were formed by anodizing titanium foil at 60 V and 20 °C. A platinum ring was used as a counter electrode. The electrolyte for anodic oxidation was prepared by dissolving 0.3 wt. % NH4F and 2 wt. % deionized water in ethylene glycol. The anodization process was carried out in two stages. The duration of the first anodization stage was 30 minutes. The layer formed was then removed from the foil surface by cathodic polarisation in a 5% H₂SO₄ solution. The resulting pre-treated foil was then washed in deionized water and dried in an air flow. The duration of the second anodization stage was 60

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minutes. The obtained samples were cleaned in ethanol, dried in an air flow, and subjected to heat treatment in a muffle furnace at 450 °C for 1 h at a heating rate of 30 °C/minutes. As a result, calcinated arrays of multi-walled nanotubes (MW TiO₂ NTs) were prepared.

To produce arrays of single-walled nanotubes (SW TiO₂ NTs), a technique similar to that described in [17] was used. Freshly prepared MW TiO₂ NTs samples were pre-annealed in air at 200 °C for 1 h at a heating rate of 10 °C/minutes. The samples were then soaked in a solution of H₂SO₄ and 30 vol.% H₂O₂ in a 9:1 ratio for 4 minutes and then washed in water and ethanol. The thickness of the porous titanium oxide layers obtained was 4.2 μ m.

2.2 HAADF-STEM

Obtained MW and SW TiO₂ NTs samples were studied by electron diffraction and HRTEM using a Titan Themis 200 microscope (FEI, Netherlands). The methodology was described previously in [13].

2.3 EPR measurements

The EPR spectra were recorded on a Bruker ELEXSYS-E500 spectrometer (X-band, sensitivity 10^{10} spin/G). The measurement temperature was varied between 300 and 40 K using the Bruker ER 4112HV temperature control system. The concentration of paramagnetic centers was estimated using a CuCl₂×2H₂O monocrystal with a known number of spins as a standard. The g values were estimated using the MgO(Mn++) standard.

2.4 Optical investigation

Spectra of light diffuse reflection were recorded with the help of Perkin Elmer LS 55 spectrometer.

2.5 CO₂ conversion

The photocatalytic activity was measured in a flow reactor equipped with a cooling jacket and a quartz window. Three A-UV diodes (maximum intensity 370 nm) were used as the light source, and the power density was set to 40 mW/cm². The surface area exposed to the light was 7 cm² in the case of TiO₂ NTs samples. Comparison of the photocatalytic activity of TiO₂ NTs samples was attributed to the calculated specific surface area using SEM and TEM images.

The photocatalytic process was carried out under the following conditions: reaction temperature 30°C, reaction mixture 5% vol. H₂O/ 95% vol. CO₂, total gas flow 1.2 mL/minutes. The samples were placed in the reactor on a helium flow (3 mL/minutes) with water vapor for the night (10 h) before measurements to eliminate air from the chamber. The first points were taken in a helium flow in the dark after the measurements began. The samples were irradiated under a helium flow with recording photocatalytic degradation products to clear the surface of organic substances. With the system reaching a stable stance, the flow changed to CO₂. After 4 hours, the light irradiation was turned off. The analysis of the gas products was carried out using an HP PLOT/Q capillary column GC-FID. The yield of the organic compound was calculated using the following equation:

$$Y = \frac{J}{S * SPA} * 60$$

where Y is the product yield (nMol m⁻² h⁻¹), J is the molar flux rate (μ Mol/minutes), S is the sample surface area (cm²), and SPA is the calculated specific surface area (m²/cm²), 60 is the theoretical photocatalytic process time (minutes). SPA was calculated by SEM image analysis using the free software ImageJ. Calculation details are discussed in the Supplementary Material (Figure S1).

3. Results and discussion

The morphology of the resulting TiO_2 NTs samples was studied using a HAADF-STEM (Figure 1 a, b). In reference to Figure 1, the removal of the inner layer of TiO_2 NTs increases the inner diameter of the nanotubes. The average

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inner diameters of multi-walled and single-walled nanotubes are $d_{MW} \sim 48$ nm, $d_{SW} \sim 100$ nm, respectively. After the removal of the inner layer, the wall thickness of the outer layer of the nanotube approaches 12 nm. The calculated geometric specific surface area of MW and SW TiO₂ NTs samples was ~ 0.0054 and 0.0097 m²/cm², respectively.

The fine structural features of the investigated TiO₂ NTs samples were determined by electron microdiffraction. The electron microdiffraction patterns of MW and SW TiO₂ NTs are shown in Figure 1c.



Figure 1. HAADF-STEM images obtained with MW TiO₂ NTs (a) and SW TiO₂ NTs (b), and both sample radial intensity distribution profiles of electron microdiffraction patterns (c)

As can be seen, peaks of anatase $\{011\}$, $\{020\}$, $\{121\}$, $\{220\}$ are presented for both samples. However, the rutile peak $\{210\}$ was only detected for the MW TiO₂ NTs sample, which may indicate that rutile crystallites can only be found in the inner layer of the nanotube. Additional information on phase structure of the samples can be found in the Supplementary Material (Figure S2). We have conducted a study of the samples optical properties. Spectra of diffuse reflection (Figure 2) were used to determine an optical band gap of the samples.



Figure 2. Normalised spectra of the light diffusely reflected from MW and SW TiO₂ NTs films

The Kubelka–Munk theory is generally used to analyse diffuse reflectance spectra obtained from nontransparent highly scattering samples. This theory is well described in literature. And we have many times successfully used it for TiO₂ analysis earlier (see for example [21]). The analysis of the diffuse reflection provide the optical band gap value of 3.20 ± 0.05 eV for MW and 3.10 ± 0.05 eV for SW NTs (Figure 3).

The difference in the light diffusely reflected from the samples provides a possibility to compare light absorption of MW and SW NTs in visible region. Figure 4 shows the relative difference of the light absorption by MW and SW TiO₂ NTs.



Figure 3. Results of Kubelka–Munk theory calculations



Figure 4. Relative excess absorption of MW TiO₂ NTs film compared to SW NTs film

One can see from Figure 4 that MW NTs are absorbing more light than SW NTs in the region from 400 to 700 nm.

The results of gas-phase photocatalytic conversion of CO_2 in the presence of water vapor on the prepared samples are shown in Figure 5. The main product of the photocatalytic conversion process was methanol, and traces of methane were also recorded. Details of photocatalytic measurements, the selectivity of the photocatalysis process, and conversion paths of CO₂ to methane and methanol for TiO₂ NTs are discussed in the Supplementary Material (see Figures S2, S3 and accompanying text).

When illumination was turned on under a helium flow, products of the photocatalytic degradation and desorption processes (including methane, methanol, acetaldehyde, ethanol, acetone, and traces of formic acid and acetic acid) of adsorbed organic substances were recorded. After 150 minutes, the flow was changed to CO₂. Only two substances, methane, and methanol increased in the presence of carbon dioxide in the reactor. This can indicate the onset of photocatalytic conversion. The methane production rate increased sharply 60 minutes after the opening of the CO₂ inlet for the MW TiO₂ NTs sample, after which it decreased for the next 180 minutes. SW TiO₂ NTs sample was less active than the MW TiO₂ NTs in methane production and close to zero activity (Figure 5a). The methanol production rate increased rapidly with an intense peak for the MW TiO₂ NTs sample at the 120th minute after the opening of the CO₂ stream, after which it began to decrease for 150 minutes before the lights were turned off.



Figure 5. Photocatalytic rates of methane (a) and methanol (b) evolution over a specific area using MW and SW TiO₂ NTs samples under A-UV irradiation

The SW TiO₂ NTs sample showed more stable methanol production rate behavior compared to the MW TiO₂ NTs sample, but 4 times less activity after 4 hours of illumination. For both samples, the production rate dropped closer to zero when the lights were turned off. The unstable kinetics for MW sample TiO₂ NTs can indicate the passivation of surface active sites during photocatalytic stability conversion. Differences in and photocatalytic activity between the two types of samples can be attributed to different types of active sites (surface defects) and can be detected by EPR spectroscopy (Figure 6).



Figure 6. EPR spectra of MW and SW TiO₂ NTs samples

As it is known, the EPR method detects the absorption of microwave energy by defects in a sample placed in a constant external magnetic field. The position of the absorption signal in the EPR spectrum depends on the type of defect and is characterized by the Lande spectroscopic splitting (g-factor). The absorbed energy factor is proportional to the concentration of defects in the sample. The analysis of EPR spectra showed that the EPR spectrum of MW TiO2 NTs samples is a superposition of two EPR signals, one of which has a g-factor equal to 2.0027±0.0005 and the two-component other has a g-factor g1=1.9961±0.0005 and g2=1.9697±0.0005 (Figure 6). The g values were estimated using the

MgO(Mn++) standard. EPR signals with such parameters, according to literature data, can come from the dangling bonds of carbon [22] and of Ti³⁺/oxygen vacancy centers [20], respectively. The carbon-related EPR signal is not observed for the SW TiO₂ NTs sample (compare EPR spectra of both samples, Figure 6). SW TiO₂ NTs samples are characterized only by an EPR signal with $Ti^{3+}/oxygen$ vacancy centers (Figure 6). This means that carbon defects are in the volume of the IL nanotube, which is removed by etching. These carbon dangling bonds can play different roles in photocatalytic material. Carbon defects can increase light absorption in the visible range [17, 23]. Moreover, carbon centers can contribute to the adsorption of CO₂ on the photocatalytic material [24, 26] (Figure 7). Defects are also known to serve as trap centers of charge carriers, reducing the surface charge concentration [24]. However, TiO₂ nanotube structures offer morphological advantages due to the short diffusion distance between the electron/hole generation sites and the material surface, limiting electron/hole recombination. Therefore, the role of carbon defects in the samples studied is favorable. We also calculated the concentration of spin centers in the samples examined. The MW TiO₂ NTs sample has $1,2\cdot10^{15}$ g⁻¹ carbon defects and $6\cdot10^{14}$ g⁻¹ Ti³⁺/oxygen vacancies. The SW TiO₂ NTs sample has 1.10^{15} g⁻¹ Ti³⁺/oxygen vacancies. This can indicate that most oxygen vacancies are found in the OL nanotube. These oxygen vacancies can be adsorption-active sites for CO₂ molecules [26–28] (Figure 7). However, since the photocatalytic activity of the SW TiO2 NTs is worse than that of MW TiO₂ NTs, it can be concluded that a significant proportion of oxygen vacancies are located in the bulk of the SW TiO₂ NTs. Therefore, the reason for the higher activity of the MW TiO₂ NTs sample compared to SW TiO₂NTs could be the presence of these carbon dangling bonds directly on the IL surface. In addition, the presence of the rutile phase in IL can improve the photocatalytic activity of the MW TiO₂ NTs

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sample by separating the photogenerated charge carriers at the anatase/rutile junction [30, 31]. Therefore, carbon defects can probably serve as the most active sites for CO₂ adsorption and contribute to the accumulation of photoinduced charge carriers [32-34].





4. Conclusions

A comparative study of the photocatalytic activity of gas-phase conversion of CO₂ to hydrocarbon products and EPR analysis of singleand multi-walled TiO2 NTs was carried out for the first time. The main product of the CO_2 photoreduction process was methanol, methane was also detected in trace amounts. The rate of photocatalytic evolution on the specific area using MW TiO₂ NTs sample is 2 times higher for methane than SW TiO₂ NTs after 240 minutes irradiation time and 4 times higher for methanol. Furthermore, the nature and concentration of the structural defects were evaluated by analyzing the EPR spectra. According to the comparison of photocatalysis and EPR spectroscopy results, the Ti³⁺/oxygen vacancy centers are mainly located in the volume of the OL nanotube. Carbon dangling bonds were only observed on the surface of the IL nanotube. The existence of carbon defects can contribute to the photocatalytic conversion of CO₂ on the surface of MW TiO₂ NTs compared to SW TiO₂ NTs. Indeed, these defects absorb light in the visible spectrum and are centers of adsorption and

accumulation of photoinduced electrons and holes. The results obtained are quite original and can help understand the difference in photocatalytic properties of multi-walled and single-walled TiO₂ NTs and the role of different types of defects in such photocatalysts. This information is essential for the development of photocatalysts for the photocatalytic conversion of CO₂ to hydrocarbon compounds.

Acknowledgements

TEM and electron microdiffraction studies were supported by the State assignment 2020-2022 N $_{\odot}$ FSMR-2020-0018. Photocatalytic measurements and electron paramagnetic resonance presented in the work were supported by a grant from Russian Science Foundation N $_{\odot}$ 21-19-00494, https://rscf.ru/en/project/21-19-00494/.

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