

Article

Photocatalytic Activity of Multicomponent TiO₂/SiO₂ Nanoparticles

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Abstract: Multicomponent TiO₂/SiO₂ nanoparticles with a diameter of 50–70 nm were generated using a liquid flame spray (LFS) nanoparticle deposition in a single flame. Here, we study the photocatalytic activity of deposited multicomponent nanoparticles in gas-phase via oxidation of acetylene into carbon dioxide that gives new insight about the multicomponent nanoparticle morphology. A small addition of SiO₂ content of 0.5%, 1.0% and 3.0% significantly suppressed the photocatalytic activity by 33%, 44% and 70%, respectively, whereas 5.0% SiO₂ addition completely removed the activity. This may be due to a formation of a thin passivating SiO₂ layer on top of the of the TiO₂ nanostructures during the LFS nanoparticle deposition. Surface wetting results support this hypothesis with a significant increase in water contact angle as the SiO₂ content is increased.

Keywords: photocatalysis; TiO₂; SiO₂; nanoparticles; liquid flame spray (LFS)



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1. Introduction

Accumulation of toxic compounds into ecosystem is a global and growing problem. Effective catalytic materials are needed to remove toxic, typically organic, compounds from wastewater to airborne pollution. Several technologies have been developed for solving this problem ranging from advanced oxidative technologies (AOT) [1] widely used in the wastewater management plants to solar-driven catalysis using novel multicomponent metal and metal oxide based photocatalysts [2]. Photocatalysis is a promising approach for heterogeneous catalysis in which chemical reactions can be accelerated by the excitation of a catalyst by incident photons. The photocatalytic activity depends on the ability of the photocatalyst to form electron-hole pairs, which produce free radicals, which participate in secondary reactions [2].

Nowadays the most studied photocatalyst is titanium dioxide (TiO₂). TiO₂ is a well-known, non-toxic and widely used white pigment with good photostability [3]. In anatase crystalline form the bandgap between the valence and the conduction band is 3.2 eV that corresponds to a photon wavelength of 387 nm in the ultraviolet A (UVA) range. Photons with shorter wavelength (and thus higher energy) can excite electrons from the valence band to the conduction band: the generated electrons and holes can diffuse onto the surface and facilitate various reduction and oxidation reactions, respectively. In the seminal work by Fujishima and Honda in 1972 [4], water splitting to hydrogen and oxygen was demonstrated by irradiating TiO₂ electrode with UVA light in a photochemical cell. The photocatalytic activity of TiO₂ has been widely investigated ranging from controlled wettability of surfaces to selective conversion of CO₂ into fuels (CH₄, CH₃OH, HCHO and HCOOH) [5] TiO₂ nanostructures can also be used to generate hydrogen from water [6] and decomposition of organic molecules (pollutants) [7]. Additionally, the photocatalytic activity of TiO₂ can be modified by doping TiO₂ nanostructures with metals and non-metals [8–10].

There exists also a large variety of TiO₂ based photocatalysts such as TiO₂/SiO₂, Al₂O₃-TiO₂ and TiO₂-zeolite. Introduction of additional elements in TiO₂ system can enhance the photocatalytic activity. For example, 2% Al₂O₃-TiO₂ nanocomposite [11] for selective degradation of imazapyr showed a two- to three-fold improvement of photocatalytic activity compared to mesoporous TiO₂, whereas TiO₂-zeolite photocatalysts from metakaolin and rice husk ash [12] showed an enhanced photoactivity compared to powder TiO₂. Alternatively, TiO₂/SiO₂/graphene oxide (GO) photocatalyst [13] demonstrated enhanced visible light photoactivity for self-cleaning surfaces resulting from synergetic action of TiO₂ and GO in which TiO₂ produces electron-hole pairs and GO quickly transfer them to the surface for redox reactions. Many reports have been devoted to doping TiO₂ doping with SiO₂ such as TiO₂/SiO₂ nanocomposite [14,15] for efficient removal of organic pollutants. However, a reduced photocatalytic response of TiO₂/SiO₂ system [16] has also been observed since SiO₂ can form blocking layer on top of TiO₂ nanoparticles preventing electron and hole transport onto the nanoparticle surface.

In this paper we use a liquid flame spray (LFS) nanoparticle deposition that is versatile tool for depositing a large range of metal and metal oxide nanoparticles on various substrates [17,18]. The LFS process contains a high velocity and high temperature hydrogen-oxygen flame in which an organometallic precursor is fed. The precursor evaporates, nucleates and forms solid nanoparticles that can be collected on various substrates. The LFS process parameters such as gas flows, precursor feed rate and burner to substrate distance can easily be modified for a deposition of nanoparticles with highly controlled size and amount. Typically, the LFS deposition produces a highly porous network of interconnected nanoparticles with porosity up to 95% [19].

LFS deposited TiO₂ nanoparticles are well suitable for photocatalysis. We have previously utilized LFS nanoparticle deposition for photocatalytic wettability conversion of TiO₂ nanoparticle coated paperboard [20]. A detailed surface chemical analysis was carried out using both X-ray photoelectron spectroscopy [21] and time-of-flight secondary ion mass spectroscopy [22] that confirmed the role of hydrocarbons and hydroxyl groups generated on the surface via photocatalytic activation. The LFS deposited nanoparticles adhere onto the surface via rather weak van der Waals forces and, therefore, the LFS deposited nanoparticles can easily be removed by wear as has been shown earlier [23]. Multicomponent nanomaterials can also be generated using LFS and Teisala et al. [24] showed that LFS generated binary particles sinter better when mixing some amount of SiO₂ into TiO₂. They showed that even a small fraction of SiO₂ will make the LFS deposited TiO₂ nanoparticles more stable, i.e., having more wear resistance. The reason for this is that the SiO₂ helps particle sintering (neck-forming) or, alternatively, the SiO₂ can coat or cover the TiO₂ nanoparticles and, thus, support the deposited structure.

Traditionally photocatalytic activity has been characterized using an indirect method based on a color transformation of an optical dye, such as methylene blue (MB) [25]. However, such an indirect method should not be used for photocatalytic activity measurements; this is especially true at visible wavelengths as the incident light itself can bleach the used dye and, therefore, induce an erroneous result [26]. Moreover, during the sample immersion in water solution nanoparticles may detach and migrate from substrate into the solution. Therefore, a much better alternative to measure photocatalytic activity is based on a gas-phase oxidation of small organic compounds such (e.g., methane, acetylene) due to their relatively simple structures which can be easily broken. The mineralization of carbon compounds into CO₂ can be directly and simply measured by monitoring the rate of CO₂ increase in the reaction chamber. Moreover, the gas-phase detection removes all mechanical stresses induced by liquid phase methods on the nanostructures.

In this work, we report a simple fabrication method for deposition of TiO₂/SiO₂ multicomponent nanoparticles in a single flame. The photocatalytic activity was characterized using an in-house built photoreactor based on decomposition of acetylene into CO₂ [27,28]. The multicomponent nanoparticles showed a small increase in the adhesion but increase of SiO₂ content even up to 5% completely reduced the photocatalytic activity. The observed

reduction of photocatalytic activity may be associated to a formation of a thin passivating layer on top of photocatalytically active TiO_2 that prevents the diffusion of the generated electrons and holes onto the surface. A thin passivating layer is also supported by the observed water contact angles that are significantly increased in the presence of SiO_2 .

2. Results and Discussion

Five photocatalysts were produced by the LFS method with different TiO_2 and SiO_2 content (pure TiO_2 and $\text{TiO}_2/\text{SiO}_2$ with ratios of 99.5/0.5, 99.0/1.0, 97.0/3.0 and 95.0/5.0, respectively). Surface morphology of all LFS nanoparticle deposited samples were analyzed by using scanning electron microscopy (SEM). Figure 1 displays the distribution of nanoparticles that is rather uniform for all depositions. Average nanoparticle diameter ranged from 40 nm to 80 nm with majority of particles within 50–70 nm range independent of the used precursor formulation that is in good agreement with our previous studies with similar LFS deposition parameters [20,21].

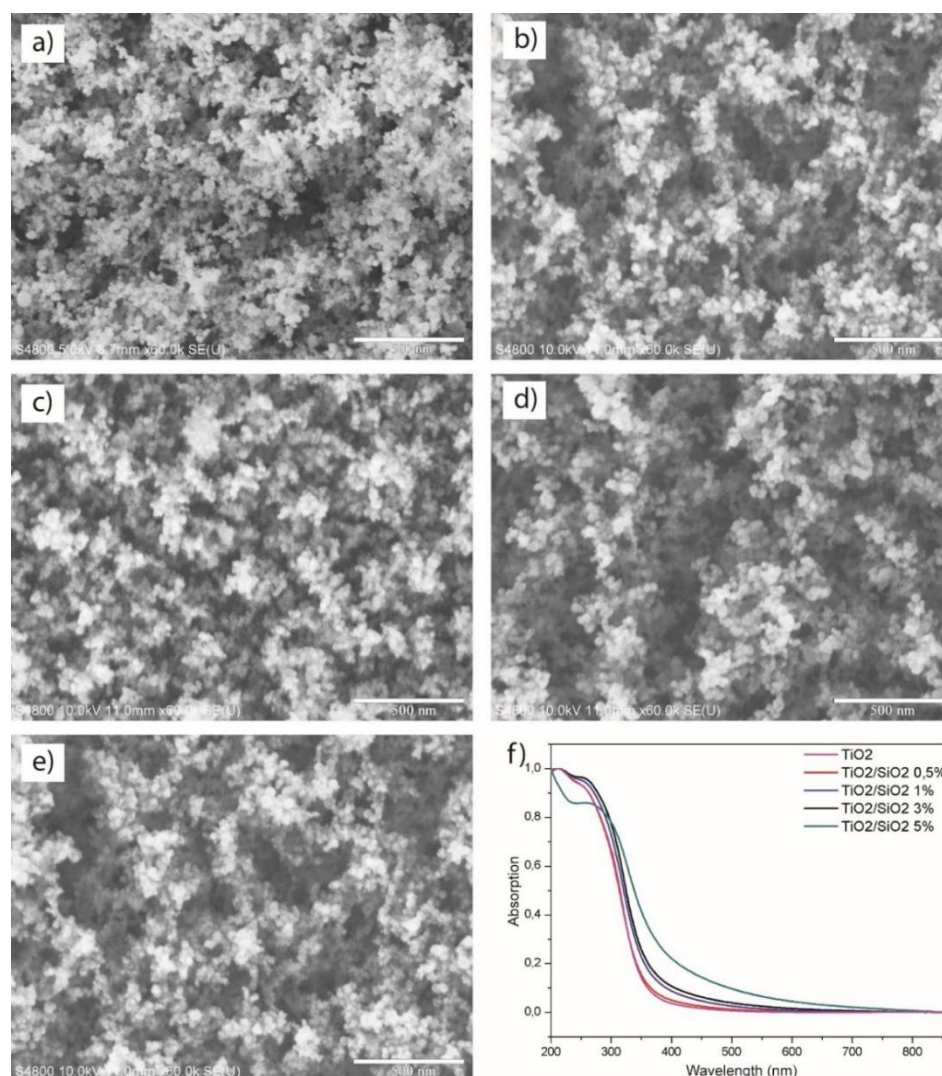


Figure 1. SEM images of (a) TiO_2 , (b) $\text{TiO}_2/\text{SiO}_2$ 99.5/0.5, (c) $\text{TiO}_2/\text{SiO}_2$ 99.0/1.0, (d) $\text{TiO}_2/\text{SiO}_2$ 97.0/3.0, (e) $\text{TiO}_2/\text{SiO}_2$ 95.0/5.0 and (f) UV-Vis absorption spectra of the corresponding samples.

It can be concluded from Figure 1 that it is difficult to see any significant effects in morphology caused by variation in the $\text{TiO}_2/\text{SiO}_2$ content. A small increase in the nanoparticle diameter (to 70–80 nm) with an increased aggregation tendency can be seen with increased SiO_2 content. Figure 1f shows UV-Vis absorption spectrum of the samples. Increased SiO_2

content is followed by a reduced TiO_2 absorption in wavelength range of 200–300 nm. This is expected as SiO_2 has a significantly lower absorption in the UV region compared to TiO_2 and, thus, increased SiO_2 content will reduce UV absorption of the multicomponent nanostructures.

To study the actual particle formation photocatalytic activity is a great tool as it is highly surface sensitive, i.e., even a thin SiO_2 layer on top of TiO_2 can prevent the generated electrons and holes to diffuse onto sample surface. Hence, the expectation would be that the samples with an increasing SiO_2 content will be photocatalytically less active in a linear manner than the pure TiO_2 . Therefore, it is crucial to determine the photocatalytic activity as a function of $\text{SiO}_2/\text{TiO}_2$ ratio but keeping the average particle size almost constant.

Figure 2 shows the measured photocatalytic activity of the multicomponent LFS nanoparticles deposited on a glass substrate. Two glasses were used in the reactor chamber to increase the active surface area for improved response from the CO_2 detector. Pure TiO_2 nanoparticle resulted in the highest photocatalytic activity with CO_2 increase of 26.2 ppm in 30 min. All multicomponent $\text{TiO}_2/\text{SiO}_2$ samples showed a lower photocatalytic activity compared to the pure TiO_2 sample. Additionally, increase of SiO_2 content was followed by a lower CO_2 increase. With 5.0% SiO_2 content, no photocatalytic activity was observed. This is in contrary to our previous work [29], with multicomponent nanoparticles used for controlled wettability on a paperboard in which up to 50% SiO_2 content was required to convert the initially superhydrophobic surface into a hydrophilic one.

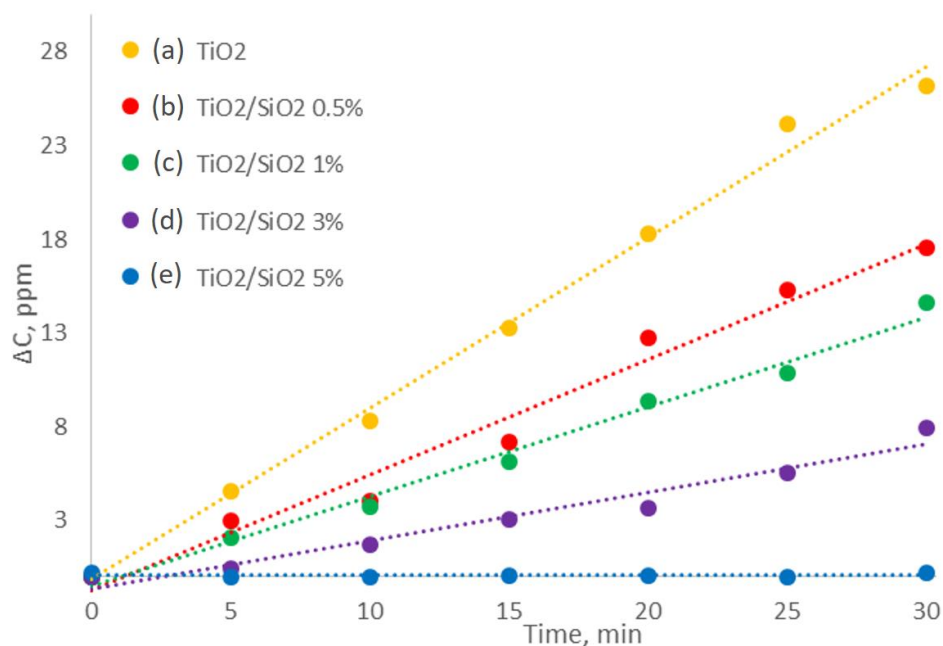


Figure 2. Measured photocatalytic activity of (a) TiO_2 100% and $\text{TiO}_2/\text{SiO}_2$ multicomponent nanoparticles with (b) $\text{TiO}_2/\text{SiO}_2$ 99.5/0.5, (c) $\text{TiO}_2/\text{SiO}_2$ 99.0/1.0, (d) $\text{TiO}_2/\text{SiO}_2$ 97.0/3.0 and (e) $\text{TiO}_2/\text{SiO}_2$ 95.0/5.0.

The rapid decrease of the photocatalytic activity by the increase of SiO_2 content may be associated with the LFS nanoparticle formation process in the flame during deposition. Both precursor solutions were fed into the same flame simultaneously and the nanoparticle formation process with two precursors is not well understood [30,31]. It is possible that TiO_2 nanoparticles nucleate first while SiO_2 nanoparticles nucleate later [32]. Hence, the first formed TiO_2 nanoparticles can provide a nucleation center for rapid covering layer of SiO_2 . As a result, multicomponent LFS deposition may produce a nanocomposite consisting of a $\text{TiO}_2/\text{SiO}_2$ core-shell structure. Furthermore, SiO_2 may also act as bridging agent between multicomponent nanoparticles and between the substrate and the multicomponent nanoparticles. The bandgap energy of SiO_2 is 8.9 eV (corresponding to 139 nm in the deep

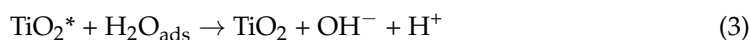
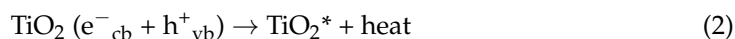
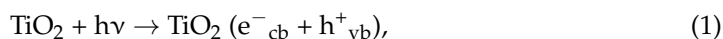
UVC range) that requires significantly more energetic photons for photocatalytic excitation than anatase TiO₂ with a bandgap of 3.2 eV (387 nm) in the UVA range. The observed photocatalytic activity results support the hypothesis of a core-shell particle formation with even a thin SiO₂ layer on top of TiO₂ nanoparticles that can prevent the diffusion of the excited electron-hole pairs onto the surface.

For a more detailed characterization of the multicomponent nanoparticles scanning transmission electron microscopy (STEM) was used with energy-dispersive X-ray (EDS) mapping. Figure 3 shows the STEM images with the corresponding EDS profiles of multicomponent TiO₂/SiO₂ nanoparticles. Figure 3a shows STEM images of pure TiO₂ nanoparticles on microscope glass with average diameter of nanoparticles in range of 40–70 nm. Majority of nanoparticles have a spherical shape. The corresponding EDS profile verifies that nanoparticles consist of TiO₂ (characteristic peaks at 4.5 and 5.0 keV). Signals of copper and aluminum originate from the sample holder grid (characteristic peaks at 0.9 and 1.4 keV). No SiO₂ was observed as expected. Figure 3b,c display STEM images of TiO₂/SiO₂ 99.5/1.5 and 99.0/1.0 samples, respectively. No significant changes were observed in the nanoparticle morphology but the EDS profile indicated presence of SiO₂ characteristic peak (1.7 keV). Figure 3d shows the STEM image of TiO₂/SiO₂ 97.0/3.0. The size of nanoparticles was in the same range (40–70 nm) but the EDS profile showed an increase of Si content. Finally, Figure 3e presents the STEM image of TiO₂/SiO₂ 95.0/5.0. A small increase in the average diameter of nanoparticles (50–80 nm) was observed and the EDS profile displayed the highest amount of Si in all samples.

A tribology test with a cotton cloth square tip was performed to test adhesion of multicomponent nanoparticles on glass substrate. The surfaces after tribological wear are presented on Figure 4 and show a more broken and smeared outlook with disordered nanoparticles. Agglomerated nanoparticles after tribological wear had a diameter of approximately 70–90 nm. Figure 4f shows the photographs of pure TiO₂ nanoparticle coated surface before and after tribological wear. The tribologically worn area is clearly seen in the center of image with photocatalytically active coating reduced approximately by 50%. Hence, the photocatalytic activity is expected to be reduced by a factor of two.

Figure 5 shows photocatalytic activity results of TiO₂/SiO₂ multicomponent nanoparticles after tribological wear. As shown on Figure 4f, approximately 50% of the active area was tribologically worn. The removal of the active area roughly by half reduces the photoactivity in average by two as shown on Figure 5 with remaining activity ranging from 52.6% (TiO₂ sample) to 46.5% (TiO₂/SiO₂ 97.0/3.0). The highest rate of photo oxidation of C₂H₂ was observed with pure TiO₂ photocatalyst. As the content of SiO₂ was increased, the photocatalytic activity was decreased to 8.9 ppm, 6.6 ppm, 3.7 ppm and 0 ppm SiO₂ content of 0.5%, 1%, 3% and 5%, respectively.

The photocatalytic activation of TiO₂ is facilitated by absorption of a photon with energy equal to, or greater than, the band gap of TiO₂ (3.2 eV). This results in a generation of an electron–hole pair that can easily migrate onto the surface of the TiO₂ nanoparticle (Equation (1)). The surface water molecules react with oxygen in Ti–O–Ti bond and form a hydroxyl ion and a proton (See Equation (3)). Electrons formed upon absorption of light can react with absorbed oxygen generating highly reactive oxygen species (ROS, Equation (4)) whereas holes can interact with hydroxyl ion producing hydroxyl ion radical (Equation (5)). Hydroxyl ion radicals react with absorbed acetylene that is followed by photodegradation into CO₂ and H₂O (Equation (6)). The overall reactions (1)–(6) are given below:



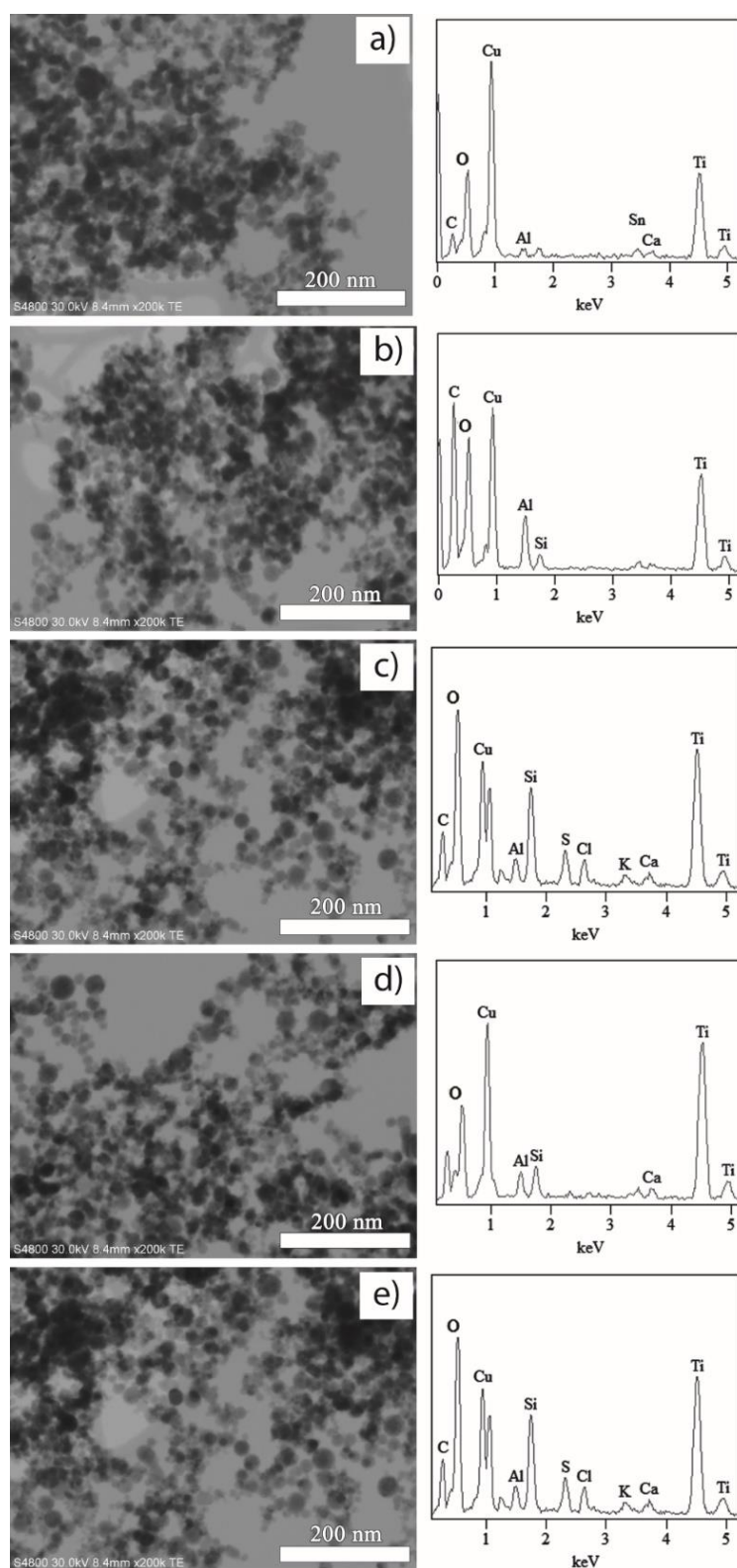
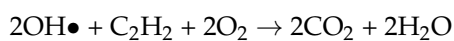


Figure 3. STEM images and EDS profiles of (a) TiO_2 100%, (b) $\text{TiO}_2/\text{SiO}_2$ 99.5/0.5, (c) $\text{TiO}_2/\text{SiO}_2$ 99.0/1.0, (d) $\text{TiO}_2/\text{SiO}_2$ 97.0/3.0 and (e) $\text{TiO}_2/\text{SiO}_2$ 95.0/5.0).

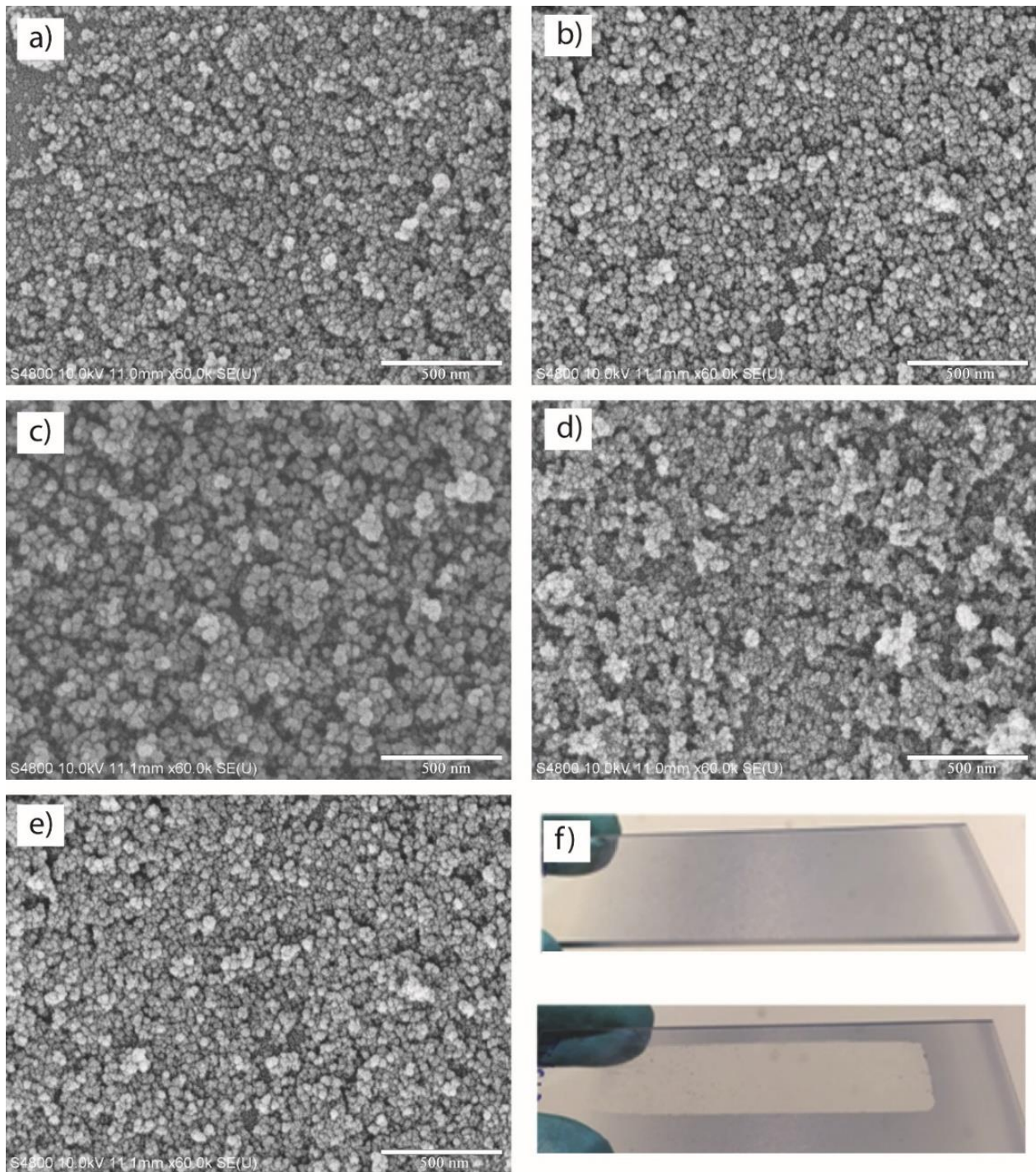


Figure 4. SEM images of (a) TiO₂, (b) TiO₂/SiO₂ 99.5/0.5, (c) TiO₂/SiO₂ 99.0/1.0, (d) TiO₂/SiO₂ 97.0/3.0 and (e) TiO₂/SiO₂ 95.0/5.0 after tribological wear. Photographs of the nanoparticle deposited microscope glass before and after the tribological wear are shown in (f).

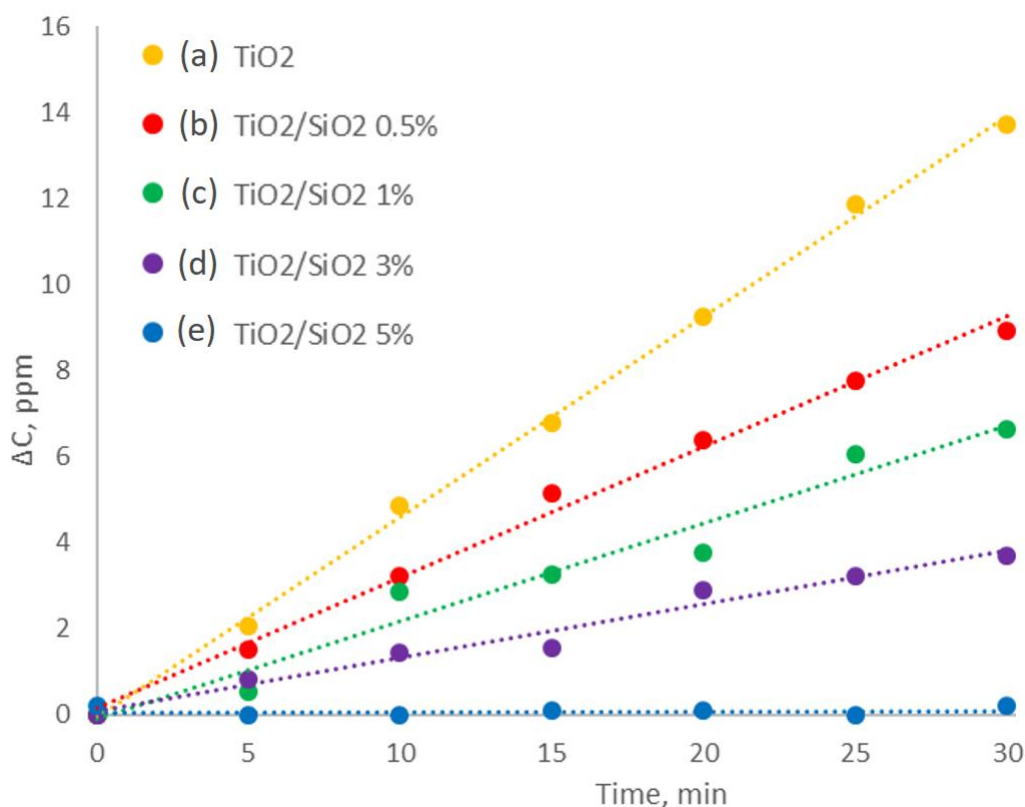


Figure 5. Measured photocatalytic activity of (a) TiO₂ 100% and TiO₂/SiO₂ multicomponent nanoparticles with (b) TiO₂/SiO₂ 99.5/0.5, (c) TiO₂/SiO₂ 99.0/1.0, (d) TiO₂/SiO₂ 97.0/3.0 and (e) TiO₂/SiO₂ 95.0/5.0 after tribological wear.

The surface chemistry of the deposited multicomponent nanoparticles was also characterized by water contact angle (WCA) measurements. Figure 6 shows the measured WCA values of the TiO₂/SiO₂ multicomponent nanoparticles deposited on glass. For multicomponent nanoparticles, the lowest value of 11.8° was observed with 0.5 silica content that was increased up to 34.1° with 5% SiO₂ content. These observations are in agreement with literature [33] of sol-gel deposited TiO₂/SiO₂ films that displayed a lower contact angle and increased photocatalytic degradation of MB with increased content of TiO₂ phase. The observed increase in the WCA supports the formation of a thin passivating SiO₂ layer on top of photocatalytically active TiO₂ particles. Capillary water absorption coefficients [34] can provide additional information about the wettability of multicomponent nanoparticle coated surfaces and we plan to return to this issue in a future communication.

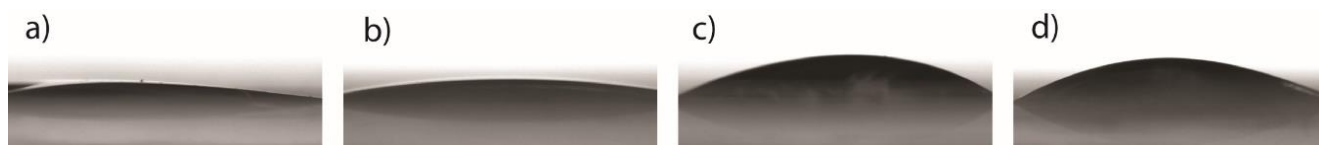


Figure 6. Water contact angle images of (a) TiO₂/SiO₂ 99.5/0.5, (b) TiO₂/SiO₂ 99.0/1.0, (c) TiO₂/SiO₂ 97.0/3.0 and (d) TiO₂/SiO₂ 95.0/5.0. 100% TiO₂ sample completely wetted the surface with WCA close to 0.

The observed results are in contrast to our previous work with wettability of multicomponent TiO₂/SiO₂ nanoparticles on paperboard [29] that showed wettability conversion approximately at 50% SiO₂ increase, whereas here on glass even a 3% SiO₂ content resulted in a significant increase of the WCA. It is worth emphasizing here that our previous study was carried out on a paperboard in which the deposited nanoparticles collect volatile hydrocarbons evaporated from the deposited paperboard substrate. On paperboard the wettability formed an S-shaped curve as a function of the TiO₂ fraction (in fact, the ratio of

Ti/(Si + Ti) content in the used precursor for LFS) when scanned through all the SiO₂/TiO₂ compositions. This meant that 0% and 10% of TiO₂ deposits collected the least amount of hydrocarbons, whereas 90% and 100% of TiO₂ deposits collect the most hydrocarbons. This was followed by the observed S-curve behavior from highly wetting state to highly non-wetting state around 50% TiO₂ content. In this study, no volatile organic compounds were present as glass was used as a substrate.

3. Materials and Methods

3.1. Liquid Flame Spray (LFS) Multicomponent Nanoparticle Deposition

Functional multicomponent nanoparticles were generated using a liquid flame spray (LFS) nanoparticle deposition that allows a cost-efficient deposition of various metal and metal oxide nanoparticles in atmospheric conditions for large areas [17,18] as shown schematically on Figure 7a. LFS contains a high temperature and a high velocity flame in which an organometallic precursor evaporates, nucleates and forms solid nanoparticles of the final material. LFS multicomponent nanoparticle deposition was carried out using single nozzle type burner and the microscope glass samples were attached in a rotating carousel for the nanoparticle deposition. The nozzle was placed 6 cm away from the sample surface. Hydrogen and oxygen were used for the combustion gases with gas flow rates of 50 L/min and 15 L/min, respectively. The precursor feed rate was set to 12 mL/min. As the combined total concentration of titanium and silicon was fixed to 50 mg/mL, this resulted in production rate of 600 mg of TiO₂/SiO₂ nanoparticles in minute. Ratio of Si was varied between 0 and 5% and a total of 5 different TiO₂/SiO₂ ratios were used.

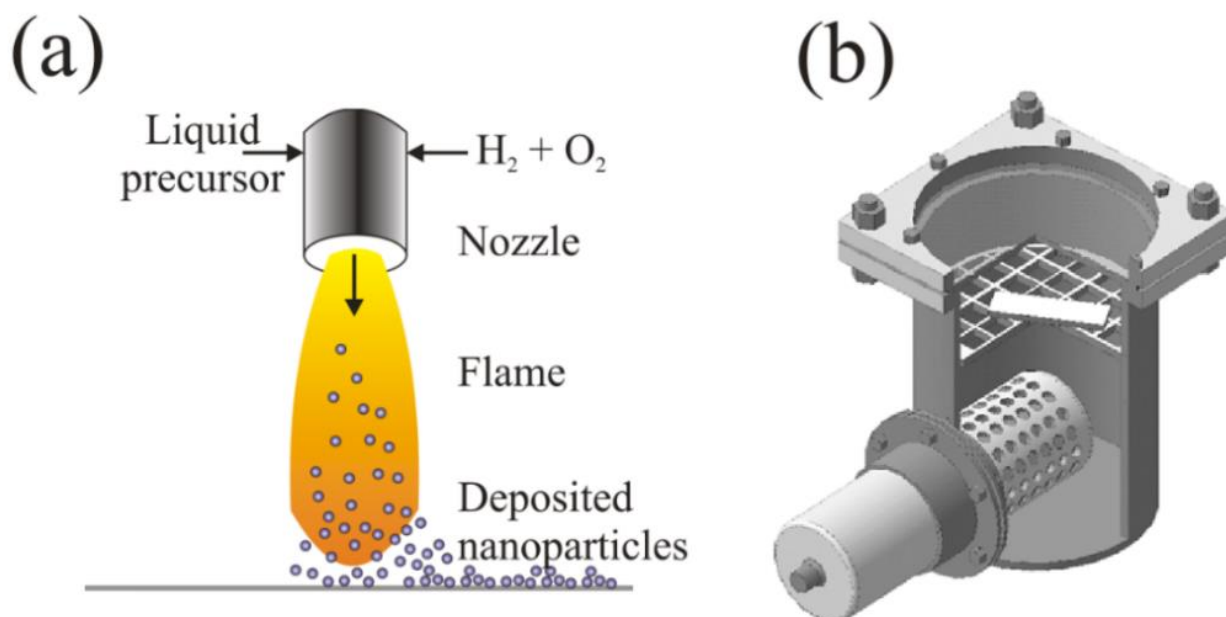


Figure 7. Schematic picture of (a) LFS nanoparticle deposition and (b) the used gas-phase detector for photocatalytic activity characterization.

3.2. Photocatalytic Activity Characterization by Gas-Phase Oxidation of Acetylene

An in-house built gas-phase reactor for photocatalytic activity characterization was constructed from stainless steel with a shell diameter of 145 mm and volume of 15.4 cm³ as shown on Figure 7b. A removable lid consists of UV transparent glass and flange connection with reactor shell. The reactor was equipped with CO₂ detector (Vaisala GMP343, Vantaa, FI), temperature and humidity sensor (Thorlabs TSP01, Newton, NJ, US) and pressure meter (Wika PGT10, USB mode, Klingenberg, DE). All detectors were USB connected to the PC for a real-time measurement [27,28].

The photocatalytic activity measurement was carried out using acetylene (C_2H_2) and technical air that were supplied to the mixing chamber. The technical air played a role as a carrier of acetylene to the reaction chamber and proportion of technical air to acetylene was set to 3:1. Only gas-phase constituents were utilized in photocatalytic activity detection and there is no need for a buffer solution in gas-phase detection in contrast to cyclic voltammetry. The gases flow inside the reactor was continuous until the CO_2 concentration becomes constant. Once the concentration of CO_2 was stabilized, the valves were shut down and the concentration increase of photogenerated CO_2 was monitored (a batch type reactor). The ultraviolet A (UVA) lamp (UVP Black-Ray[®] B-100AP High Intensity, Cambridge, UK, 100 W) with peak emission at 365 nm and intensity of approximately 20 mW/cm^2 was located 17 cm above the reactor lid.

The detection method is based on oxidation of acetylene into CO_2 and H_2O . The main parameters of the photocatalytic reaction such as pressure and humidity during photocatalytic reaction did not change significantly and were assumed to be constant (40–50% and atmospheric pressure). An external ventilation was applied to remove excess heat from the UVA lamp and the overall temperature was kept in the range of 27–30 °C. After completion of the measurement, the valves can be opened and the reactor can be filled with technical air to remove all reaction components before the subsequent measurements. All photocatalytic activity results are an average of three, almost overlapping, parallel measurements that verifies the stability and reproducibility of both the used measurement system and the multicomponent photocatalysts with no mechanical stresses induced on the nanostructured surface during the gas-phase detection.

3.3. Tribological Wear of the Nanoparticle Coated Microscope Glasses

Tribological wear test was performed using a tribometer (CSM+ Instruments Tribometer TRN S/N 18-347, Needham, MA, USA). The tribometer with a square tip (area of $1 \times 1 \text{ cm}^2$) covered with a cotton layer by double-side tape was used with two cycles with a 3 N force during 10 s. The tribologically worn area was approximately 50% of the deposited nanoparticle area as displayed on Figure 4. The friction data was collected with a ModelIX software (CSM+ Instruments, Needham, MA, USA).

3.4. Scanning and Scanning Transmission Electron Microscope (SEM/STEM) Imaging

The morphology and average structural sizes of TiO_2 nanoparticles were observed with Hitachi S-4800 FE-SEM (field emission scanning electron microscope, Tokyo, Japan). Scanning electron microscope (SEM) images were acquired after cutting microscope slide to small squares ($2 \times 2 \text{ cm}^2$).

3.5. Absorption Spectrum

A PerkinElmer Lambda 900 UV–vis/NIR spectrometer (Waltham, MA, USA) with a 150 mm integrating sphere was used to measure the absorption spectra of the multicomponent nanoparticles.

3.6. Wettability Characterization

Water contact angle (WCA) measurements were carried out using a KSV Cam 200 (KSV Instruments Ltd., Helsinki, Finland) contact angle goniometer with 4 μL deionized water droplet at a room temperature. A Young–Laplacian fitting protocol was utilized to calculate the WCA value from the measured droplet profile.

4. Conclusions

We investigated LFS deposited TiO_2/SiO_2 multicomponent nanoparticles for photocatalytic activity. The addition of SiO_2 content did not improve nanoparticle adhesion but significantly reduced the photocatalytic activity, with the TiO_2/SiO_2 95.0/5.0 sample showing no photocatalytic activity. During a simultaneous deposition in the LFS flame, SiO_2 was probably deposited on top of TiO_2 nanoparticles, followed by significantly reduced

photocatalytic activity. The deposition of SiO₂ on top of TiO₂ was also supported by the changes in the surface wettability.

Our future studies will involve multicomponent metal (Ag or Au) combined with photocatalytic metal oxide (TiO₂ or ZnO) nanoparticles in which even a visible light can activate the photocatalysis via plasmonic activation of the metallic nanomaterials. For improved adhesion of TiO₂ nanoparticles on glass surface, a precursor layer will be studied. We believe that multicomponent nanomaterials will find many applications in solar-driven photocatalysis and chemistry in future.

Author Contributions: F.T. carried out the photocatalytic measurements, data analysis and wrote the first draft of the manuscript. J.H. performed the LFS nanoparticle depositions. J.M.M. supervised the LFS nanoparticle depositions. J.J.S. coordinated the joint research and finalized the manuscript. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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