2020

Multilayer TiO2 Inverse Opal with Gold Nanoparticles for Enhanced Photocatalytic Activity

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American Chemical Society (ACS)

Tieteelliset aikakauslehtiartikkelit
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http://dx.doi.org/10.1021/acsomega.0c00833

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Multilayer TiO₂ Inverse Opal with Gold Nanoparticles for Enhanced Photocatalytic Activity

Abid Zulfiquar,* Filipp Temerov,** and Jarkko J. Saarinen

ABSTRACT: Three-dimensional highly ordered multilayer titanium dioxide (TiO₂) inverse opal (TIO) structures with two pore sizes were fabricated over a large surface using a self-convective method. The fabricated TIO multilayers were functionalized with gold nanoparticles (AuNPs) by immersing the samples in solution with gold nanoparticles. The photocatalytic activity of TiO₂ was enhanced by 85% via plasmonic activation of AuNPs that increased the lifetime of photogenerated holes and electrons. The improved photocatalytic activity was characterized with both UVA and visible light irradiation using an in-house built gas-phase photoreactor.

1. INTRODUCTION

Recently, semiconductor-based photocatalysts have attracted large attention due to their significant potential for solving environmental problems.1 Titanium dioxide (TiO₂) is a chemically and biologically stable, cost-effective, and nontoxic photocatalytic material that has several applications from oxidation of harmful organic compounds2-5 and production of hydrogen gas by photoelectrochemical dissociation of water.6 It can be used for purification of air and polluted water with self-cleaning of the surface.7 TiO₂ has found applications in optical filters for dielectric mirrors,6 dye-sensitized solar cells, and agriculture including the degradation and detection of pesticide residues, germination, and growth of plants by controlling different diseases.8,9 It also has applications in the surface-enhanced Raman scattering (SERS).10 However, the rather large band gap of TiO₂ limits its use as photocatalytic activation requires light in the UVA region (only 3–5% of the solar energy is in the UVA range). Additionally, recombination of photogenerated electrons and holes can reduce its quantum efficiency.

The concept of photonic crystals (PCs) was proposed by Yablonovich and John in 1987 with specific physical properties such as light localization,11 a slow light effect,12 and photonic band gap (PBG) properties.12 PBG inhibits the propagation of light with a specific wavelength due to the coherent Bragg diffraction. The slow light effect enhances the absorption of light by increasing the reflections of light inside the PCs. Many electron–hole pairs can be generated upon overlapping the slow photon wavelength and the TiO₂ electronic excitation wavelength for enhanced photocatalytic activity. Various structures have been studied for fabrication of PCs such as opal and inverse opal (IO) photonic crystal structures. Opal PCs can be prepared by self-assembly of colloidal particles, whereas IO PCs can be formed by filling the opal PCs with a material having a high refractive index followed by removal of the self-assembled particles. IO PCs are three-dimensional porous structures that have a large specific surface area and optical properties associated with PCs. PCs have an artificial periodic structure, which work for light in a similar manner as the semiconductor behaves for electrons.13 Because of these similarities, they have the characteristic band gap but in the photon wavelength range (photonic band gaps, PBGs). The presence of PBG permits the PCs to control the flow of light by inhibiting the transmission of light for a specific wavelength in one, two, or more directions within the PBG materials.14

TiO₂ IO (TIO) PCs can offer a large surface area for adsorbing the pollutant molecules.15 An alternative way to improve photocatalytic activity is to incorporate metal and nonmetal nanoparticles (NPs) and noble metal NPs such as gold and silver into the TIO structure.16-18 Loading TIO with noble metal NPs can significantly enhance the lifetime of photogenerated holes and electrons, which, as a result, increase the photocatalytic activity of TiO₂.19 The TiO₂ morphology and surface characteristics have also a significant role in the improved photocatalytic activity.20 Furthermore, noble metal NPs exhibit localized surface plasmon resonance (LSPR), which can couple visible light for photocatalytic activation of TIO.21

In the present study, TIO multilayers were produced using a crack-free method that was functionalized with gold NPs (AuNPs) for improved photocatalytic activity of TIO.
Generally, TIO structures can be fabricated in three sequential steps: (1) self-assembly of monodisperse colloidal particles, (2) infiltration of the assembled opal template with a TiO\textsubscript{2} precursor solution, and (3) calcination of the opal template.\textsuperscript{22} However, fabrication of TIO structures using conventional methods face several challenges. First, the TiO\textsubscript{2} precursor is sensitive to moisture, resulting in difficulties to control the degree of precursor infiltration. Second, the use of excess precursor amount can form overlayers on the surface of TIO since it is problematic to control the precursor infiltration, and these overlayers can decay the optical properties.\textsuperscript{19}

TIO were fabricated using a sol–gel precursor solution for the infiltration of interstitial spaces of a self-assembled polystyrene (PS) template.\textsuperscript{23} The problem with overlayers of precursor solution on top of TIO was solved using a lift-off technique. However, the lengthy procedure was not able to completely remove the precursor overlayers. A sandwich-vacuum method\textsuperscript{24} was used to remove the precursor overlayers. This was carried out successfully, but it also induced large cracks into the PS template. Hence, there is a clear demand for a more efficient method to fabricate high-quality crack-free TIO structures. Here, large-area, crack-free multilayer TIO structures were fabricated using the titanium-(IV)-bis-lactato-bisammonium dihydroxide (TiBALDH) precursor. The advantage here is a more uniform distribution of TiO\textsubscript{2} precursor solution in the interstitial spaces of opal PS that produces a high-quality ordered IO structure suitable for the fabrication of the uniform crack-free IO structure.

Photocatalytic activity of TIO has been traditionally measured by a color change using optical dyes such as methyl orange or methylene blue. However, the incident light itself can bleach the dyes, and these methods can generate an erroneous result.\textsuperscript{25} Furthermore, the NPs may detach from the surface of TIO and transfer into the solution during the sample immersion into the dye-containing solution.\textsuperscript{26} To overcome these barriers, a better way to evaluate the photocatalytic activity is by gas-phase mineralization of organic compounds such as acetylene (C\textsubscript{2}H\textsubscript{2}) oxidation into carbon dioxide (CO\textsubscript{2}). Additionally, gas-phase detection methods also remove all mechanical stresses from the micro- and nanostructures.

This paper summarizes the fabrication of TIO multilayers with AuNPs having an enhanced light absorption. The opal templates for TIO multilayers were fabricated by the deposition of one-size PS followed by a different-size PS using a crack-free method. TIO multilayers were obtained by calcinating the PS templates. The fabricated TIO multilayers were functionalized with AuNPs (Au-TIO) that were deposited both on the walls and cavities of TIO multilayers by vertically immersing the glass substrates containing the TIO into the AuNP solution. The photocatalytic activity measurement was carried out using the in-house built gas-phase photoreactor under both UVA and visible light activation.

**2. RESULTS AND DISCUSSION**

**2.1. Characterization of TIO Multilayers.** The PS colloidal spheres, in the presence of the TiO\textsubscript{2} precursor, were self-assembled as a face-centered cubic (FCC) form by using the vertical deposition method, as shown in Figure 1a. The samples were preheated at 100 °C before the deposition of the other-size PS colloidal particles to guarantee a contact between the assembled PS sphere and glass surface before the deposition of the second layer of PS. The deposition of the second layer, as shown in Figure 1, was partially uneven due to high surface tension between the first and second deposition of PS.\textsuperscript{24} Figure 2 presents an SEM image of 3D uniform TIO multilayers in the anatase crystalline phase that were obtained upon calcination of the opal templates.

![Figure 1. SEM images of (a) top and (b) cross-sectional views of the self-assembled PS template.](image1)

![Figure 2. SEM images of (a, b) TIO 200/400 and (c, d) TIO 400/200 and cross-sectional images of (e) TIO 200/400 and (f) TIO 400/200.](image2)

Highly ordered multilayers were successfully fabricated in a large area (10 μm) with minor cracks, as shown in Figure 2a,c. Structures in larger area than 10 μm showed the cracks that were created during the calcination process with shrinkage of the IO structures. This may decrease the photocatalytic activity of the materials.\textsuperscript{27} Due to shrinkage, TIO 200/400 and TIO 400/200 after calcination showed air void diameters about 73 and 65% compared to the original 400 and 200 nm PS sphere diameters, respectively.

SEM images of TIO multilayers from 200 nm PS colloidal spheres as the bottom layer and 400 nm PS colloidal spheres as the top layer are presented in Figure 2a,b. Top view of TIO 200/400 shows that the surface has a pore size of 290 nm (Figure 2b), whereas the cross-sectional image (Figure 2e) further confirmed the fabrication of multilayer TIO 200/400. Similarly, Figure 2c,d and Figure 2f show the top and cross-sectional view of TIO 400/200, respectively. Top view of TIO 400/200 shows that the surface has a pore size of 130 nm (Figure 2d), confirming the fabrication of the upper layer IO

https://dx.doi.org/10.1021/acsomega.0c00833

ACS Omega 2020, 5, 11595−11604
structure from 200 nm PS particles. The cross-sectional images of both surfaces showed a 4.3 ± 2.0 μm thickness of the TIO surfaces, which depended on the used PS concentration (Figure 2e,f). A TiO₂ precursor solution with a volume ratio of 1:1.5:1 used for the fabrication of TIO was observed to be the best ratio for the synthesis of IO structures. Uniform IO structures were achieved without precursor overlayers.

The anatase crystalline form of TIO structures was further confirmed by Raman spectroscopy. The peak at 133 cm⁻¹ (Eg(1)) presented in Figure 3a corresponds to the bending vibration of the O−Ti−O bond, whereas the other peaks at 384 cm⁻¹ (B₁g), 504 cm⁻¹ (A₁g), and 631 cm⁻¹ (Eg(2)) indicate the Ti−O−Ti bending. The anatase crystalline phase of TIO multilayers was also studied using the XRD spectroscopy. The XRD pattern of TIO multilayers is presented in Figure 3b. Five diffraction peaks at 2θ angles of 25.5, 37.9, 48.0, 53.0, 55.0, 62.7, 68.7, 70.0, and 75.0° can be assigned to the crystal planes (JCPDS 21-12768) of (101), (004), (200), (105), (211), (204), (116), (220), and (215), respectively. The comparison of Raman and XRD spectra confirmed that the anatase crystalline form of TIO was formed upon calcination at 550 °C. The calcination temperature also affects the photocatalytic results of the material. IO structures obtained at low temperature possess the smaller crystallite grains due to a low degree of structure contraction. The smaller crystallite grains of IO structures can increase the photocatalytic activity of TiO₂ due to more catalytic active sites, large surface area, and their ability to reduce the chances of recombination of photogenerated holes and electrons.

2.2. Characterization of AuNPs. AuNPs were prepared using the hydrothermal reduction method. The size of the AuNPs can be controlled by varying the temperature, concentration of substances, and pH of the solution. AuNPs with an average size of 18 ± 2 nm were synthesized by
using 1% solution of sodium citrate as a reducing agent. The reducing agent solution was added to a dilute aqueous solution of HAuCl$_4$·3H$_2$O at 100 °C. Figure 4d shows the average diameter of AuNPs around 18 ± 2 nm that was measured using the STEM. Figure 6d confirms that AuNPs were prepared without any capping agent, i.e., by lowering the temperature, not only smaller-size particles were accumulated but also larger-size particles were produced with diameters ranging from 19 to 22 nm. Surface plasmon resonance (SPR) in AuNPs was analyzed by UV-visible (UV-vis) absorption spectroscopy. The normalized absorption spectrum of AuNPs is given in Figure 4b. The SPR absorption peak of synthesized AuNPs was observed around 520 nm in the visible range that depends on the size of particles. In the literature, Au nanoparticles with a diameter around 20 nm were observed to have a sharp absorption peak around 520 nm. This is also in agreement with our size distribution shown in Figure 4d. Larger nanoparticles have a larger optical cross section and scatter more light that results in the absorption spectrum shifts toward longer wavelengths (red shift). The synthesis of round-shaped AuNPs was confirmed by the STEM images and by a single peak in the UV–vis spectrum of AuNPs, whereas Au nanorods displayed two peaks in the UV–vis spectrum.

The EDS spectrum in Figure 4c verifies the presence of Au atoms in the solution and successful synthesis of AuNPs. A typical optical absorption band peak at 2.2 keV reflects the successful formation of AuNPs, whereas the other absorption band peaks were detected for copper grid that was used for the EDS analysis.

2.3. AuNP-Functionalized TIO Multilayers. Deposition of AuNPs into the TIO multilayers improved photocatalytic activity of TIO by enhancing separation of the photogenerated electron-hole pairs. Furthermore, AuNPs increase the absorption of visible light. The size of NPs has an effect on photocatalytic activity of the semiconductor material. Similarly, location of absorption peaks in the visible range also depends on the NP size. Both TIO samples were dipped in the same concentration of AuNP solutions. The same AuNP content was assumed in all samples as it is difficult to measure quantitatively the actual AuNP loading content from SEM and STEM images. This could be carried out using inductively coupled plasma (ICP) mass spectrometry or ICP-optical emission spectroscopy. The AuNPs were uniformly dispersed and firmly anchored on the walls and inside the pores of TIO structures, as displayed in Figure 5a. Large accumulated NPs were located inside the cavities of porous structures that were observed from SEM images in Figure 5b.

Au-TIO was characterized using STEM to confirm both the multilayer nature of IO structures as well as loading of AuNPs. Figure 6a clearly shows a uniform fabrication of TIO with two different diameters corresponding to 200 and 400 nm PS spheres. EDS mapping of Au-TIO confirms the coexistence of Ti and O in the sample (blue and red in Figure 6b,c, respectively).

The presence of AuNPs inside the porous TIO was confirmed by the STEM and EDS spectrum. Figure 7a shows a distribution of AuNPs inside the pores and on the surface of TIO, which can be clearly seen in a high-magnification STEM image shown in Figure 7b. The EDS spectrum in Figure 7c of Au-TIO verified the existence of Ti, O, and Au.

2.4. Photocatalytic Activity. Figure 8 presents a schematic for photocatalytic activity mechanisms of TiO$_2$ loaded with AuNPs upon the absorption of photons. The photocatalytic reaction in a pure semiconductor starts when a photon with energy equal or higher than the semiconductor band gap is absorbed. TiO$_2$ has a band gap around 3.2–3.3 eV that corresponds to 390–400 nm within the UVA range. Electron paramagnetic resonance (EPR) studies have confirmed that the photoexcited electrons from the conduction band (CB) and photogenerated holes from the valence band (VB) get separated from each other and trap at different atomic sites.

Electron–hole recombination (EPR) studies have also suggested the role of O$_2$· and H$_2$O$_2$. The presence of O$_2$· and H$_2$O$_2$ radicals in the adsorbed organic molecules or their intermediates results in direct oxidation or alternatively via formation of hydroxyl radicals with the reaction to water molecules.

Detailed mechanisms of hydroxyl radical formation have been debated in the literature: both direct hole oxidation and electron scavenging involving oxygen molecule reduction to superoxide anion radicals (O$_2$·$^-$) have been discussed. Therefore, TiO$_2$ can be used for generating reactive oxygen species for oxidation of organic molecules. In our case, we used acetylene as a target molecule. Adsorption of alkenes and alkynes is typically poor on the oxide surface, and hence, an intermediate is probably formed that binds on the oxide surface. Based on redox potential of the organic molecules, they may convert to the product through cation radical formations by the reduction of h$. Water or hydroxyl ions (–OH) may also reduce the h$ and convert to hydroxyl radicals (–OH), which can then oxidize C$_2$H$_4$ molecules.

Photocatalytic activities of all samples under UVA irradiation were evaluated by the rate of CO$_2$ production through
photodegradation of $\text{C}_2\text{H}_2$, and the results are shown in Figure 9a. Photocatalytic activities of AuNP-loaded multilayers were compared to multilayers without AuNPs as well as with single-layer IO structures. All samples displayed photocatalytic activity under UVA irradiation. TiO$_2$ 200, TiO$_2$ 400, TiO$_2$ 400/200, Au-TiO$_2$ 400/200, and Au-TiO$_2$ 200/400 produced CO$_2$ with rates of 1.31, 1.35, 1.95, 2.16, 2.11, and 2.42 ppm/min, respectively. Loading with AuNPs increased the photocatalytic activity by 8 and 12% for Au-TiO$_2$ 400/200 and Au-TiO$_2$ 200/400 compared to samples without AuNPs, respectively.

Photocatalytic activities of AuNP-loaded samples were also evaluated under visible light irradiation as AuNPs absorb visible light (Figure 4b) and can excite the Au-TIO composite. Samples without AuNPs under visible irradiation did not have photocatalytic activity since TiO$_2$ requires UVA light activation due to a large band gap. Figure 9b shows the photocatalytic activities of Au-TiO$_2$ 400/200 and Au-TiO$_2$ 200/400 under visible light that produced CO$_2$ with rates of 0.21 and 0.27 ppm/min, respectively. It can be concluded that IO structures with larger pores on top (200/400 samples) with and without AuNPs showed a larger photocatalytic activity compared to IO structures with small pores on top (400/200 samples) both under UVA and visible light. It is known that larger-size IO structures are more stable and have a higher efficiency for photocurrent compared to smaller-size IO structures. Furthermore, multilayer IO structures loaded with AuNPs displayed photocatalytic activity under visible light via the plasmonic coupling of AuNPs with visible light. Finally, reproducibility and stability of the results were confirmed for Au-TiO$_2$ 200/400 with UVA light irradiation shown in Figure 9c. The results confirm that the Au-TIO 200/400 photocatalyst was stable with no catalyst deactivation after three cycles. The cyclic photodegradation of $\text{C}_2\text{H}_2$ confirmed that pore structures were stable, and the response was unchanged during the process. It was also confirmed from the SEM image that AuNPs remain intact to IO structures after the cyclic degradation, as presented in Figure 9d.

SEM, TEM, and EDS analyses together with photocatalytic activities of Au-TiO$_2$ confirmed the deposition of AuNPs into the TiO$_2$ multilayers. There was a significant difference in the photocatalytic activities of TiO$_2$ multilayers with and without AuNPs.

The AuNPs play a significant role in enhanced photocatalytic activity of the IO structures by increasing the separation of photogenerated holes and electrons. The energy diagrams of the Au-TIO structure are presented in Figure 8. Absorption of photons by the metal NPs can excite plasmonic electron oscillations in which hot electrons can transfer into the CB of the semiconductor via the formed Schottky barrier followed by extra electrons in the CB of the semiconductor. Typical Schottky barrier heights in the Au-TiO$_2$ interface are in the range from 0.23$^5$ to 1.0 eV,$^{56}$ depending on the sample morphology and crystalline structure.

**Figure 7.** (a) STEM image of Au-TIO, (b) high-magnification STEM image of AuNPs inside the cavity of TiO$_2$, and (c) EDS spectrum of Au-TIO.

**Figure 8.** Schematic diagram for the separation of charges in TiO$_2$ IO with AuNPs.
AuNPs, due to the SPR effect, interact with visible light leading to the production of photogenerated metal ions (M⁺) and excited electrons (Figure 8). The photoexcited electrons then transfer from AuNPs to the CB of the TiO₂ surface (eq 2). The transfer of photoexcited electrons to TiO₂ structures is followed by separation of photoexcited electrons and M⁺ (Figure 8). The injected electrons can be used for conversion of molecular oxygen into superoxide anion radicals (O₂⁻) (eq 3), and the protonation of O₂⁻ radicals leads to the formation of H₂O₂ radicals (eq 4). The combination of trapped electrons on the surface of TiO₂ structures and H₂O₂ radicals produces the H₂O₂ that forms the hydroxyl radicals (·OH) (eqs 5 and 6). All these active species and M⁺ play their role in the oxidation of C₂H₂ (eq 7). It is worth emphasizing the role of three holes in eq 7 that are required for the reaction to take place, as demonstrated by Imanishi et al.58

\[
\begin{align*}
\text{MeNPs} + h\nu & \rightarrow \text{MeNPs}^* \quad (1) \\
\text{MeNPs}^* + \text{TiO}_2 & \rightarrow \text{MeNPs}^{*+} (h^\nu) + \text{TiO}_2 (e^-) \quad (2) \\
\text{TiO}_2 (e^-) + \text{O}_2 & \rightarrow \text{TiO}_2 + \text{O}_2^- \quad (3) \\
\text{O}_2^- + \text{H}^+ & \rightarrow \text{H}_2\text{O}_2 \quad (4) \\
\text{H}_2\text{O}^+_2 + \text{H}^+ + e^- & \rightarrow \text{H}_2\text{O}_2 \quad (5) \\
\text{H}_2\text{O}_2 + e^- & \rightarrow \cdot\text{OH} + \cdot\text{OH} \quad (6) \\
\text{MeNPs}^{*+} (3h^\nu) + 2\text{OH}^- & \rightarrow 2\text{C}_2\text{H}_2 + 2\text{O}_2 \\
& \rightarrow \text{MeNPs} + 2\text{CO}_2 + 2\text{H}_2\text{O} \quad (7)
\end{align*}
\]

A detailed reaction mechanism is given below by eqs 1–7

3. CONCLUSIONS
High-quality TiO₂ multilayers were fabricated in a large area using a convective self-assembly method for enhanced photocatalytic activity of TiO₂. Light absorption was increased by functionalizing TiO₂ multilayers with AuNPs that further improved photocatalytic activity by extending the lifetime of excited holes and electrons. Under UVA irradiation, up to 85% increase in the photocatalytic activity was observed compared to TiO₂ structures. The TiO₂ functionalized with AuNPs displayed photocatalytic activity also in visible light that was nonexistent with conventional solutions due to the TiO₂ band gap in the UVA range.
The fabricated TiO2 multilayers can extend the applications of photocatalysis from differential drug release and solar cells to optical filters. It was observed that photocatalytic activity of TiO2 can be tuned by changing the pore size of IO structures by using a combination of different pore sizes in IO periodic structures. Finally, functionalization with AuNPs can extend photocatalytic activity into the visible wavelengths, opening new avenues for the TiO2 applications with enhanced performance.

4. EXPERIMENTAL SECTION

4.1. Materials. Styrene (99%, Acros Organics), ammonium persulfate (APS, 98%, Sigma-Aldrich), and sodium dodecyl sulfate (SDS as a capping agent, 98.5%, Sigma-Aldrich) were used for the preparation of polystyrene (PS) spheres. A Millipore water purification system was used for deionized water. Ethanol (99.5%, ETAX Aa), titanium(IV)-bis-lactato-bisammonium dihydroxide (TiBALDH, 50% aqueous solution, Sigma-Aldrich), and hydrochloric acid (37%, VWR Chemicals) were used for the preparation of TiO2 precursor solution. Gold(III) chloride trihydrate (HAuCl4·3H2O, ≥99.9%, Alfa Aesar) and sodium citrate (TSC, ≥99%, Sigma-Aldrich) were used for the formation of gold nanoparticles. Glass plates (Thermo Scientific) were used as a substrate for the fabrication of TiO2-IO multilayers.

4.2. Synthesis of PS Spheres. Synthesis of polystyrene spheres was carried out using the procedure by Erola et al.59 with minor modifications. The synthesis of 200 nm PS spheres was carried out in the first step and used as seeds for the synthesis of 400 nm PS spheres. For the synthesis of 200 nm PS spheres, 160 mL of distilled water was added in a reaction vessel followed by an addition of 200 mg of SDS as a capping agent. The reaction solution was stirred at 70 °C using an anchor-like stirrer at 500 rpm. The reaction mixture was stirred for another 30 min at the same temperature after the addition of 20 g of styrene. An initiator was prepared by dissolving 200 mg of APS in 20 mL of deionized water and added into the reaction mixture. The reaction was proceeded for 20 h under a nitrogen atmosphere. For the preparation of 400 nm PS spheres, the polymerization reaction was proceeded by adding 30 mL of prepared 200 nm PS colloidal spheres and 150 mL of distilled water in a three-neck round flask followed by an addition of 25 mg of SDS. The temperature of the reaction mixture was raised up to 70 °C under the nitrogen atmosphere, and 28 mg of APS solution in 20 mL of deionized water was poured into the reaction mixture. Styrene (21.6 g) was slowly injected into the flask once the solution temperature reached 70 °C that took approximately 10 min. The reaction mixture was allowed to polymerize at 70 °C for 20 h after the injection of styrene.

4.3. Preparation of Crack-Free TiO2 Multilayers. Fabrication of high-quality TiO2 multilayers was carried out in two steps: (1) convective self-assembly of PS colloidal crystals (CCs) using the TiO2 precursor solution and (2) calcination of self-assembled PS CCs to remove PS and to convert the TiO2 into anatase crystalline phase with the highest photocatalytic activity among the other crystalline phases of TiO2.60 PS with average diameters of 200 and 400 nm were used in this study. In the first step, for convective self-assembly of PS CCs, the TiO2 precursor solution was freshly prepared 30 min before use. The hydrolyzed TiO2 precursor solution was prepared by mixing the TiBALDH, ethanol, and 0.1 M HCl with a volume ratio of 1:1.5:1, respectively, and stirred for 30 min. The deposition of PS CCs was performed using the vertical deposition method. Four hundred fifty microliters of 200 nm PS spheres and 25 mL of water were added in a beaker followed by the addition of 200 μL of precursor solution. The mixture of PS and precursor solution in water was ultrasonicated for 30 min. The glass substrates prewashed with ethanol followed by deionized water were vertically suspended inside the beaker, containing the ultrasonicated PS and precursor solution. The deposition of PS/TiO2 CCs on glass substrates was allowed by evaporating the solvent in the oven at 68 °C for 40 h. After the deposition of 200 nm PS/TiO2 CCs on glass substrates, the samples were preheated at 100 °C for 1 h to make a strong binding between the PS template and glass slide by partially melting the PS. After preheating, 450 μL of 400 nm PS spheres was deposited on top of the bottom layer using the same approach as for 200 nm PS sphere deposition. In the second step, the deposited PS/TiO2 CCs were calcined for the fabrication of inverse opal multilayers. The deposited films were calcined in air from room temperature to 250 °C in 250 min that was kept constant for 120 min. The temperature was further increased from 250 to 550 °C in 300 min and retained for 300 min to fully remove the PS spheres and to convert TiO2 into the anatase crystalline phase (Figure 10). TiO2 200/400 multilayers were obtained upon cooling the samples to room temperature. TiO2 400/200 multilayers with the bottom layer from 400 nm PS spheres and the upper layer from 200 nm PS spheres were also prepared using the same protocol but deposited with reversed order.

4.4. Synthesis of AuNPs. AuNPs were synthesized using a hydrothermal reduction method. For a typical process, 10 mL aqueous solution of HAuCl4·3H2O (0.1%) was dissolved in 100 mL of deionized water that was boiled. Solution of sodium citrate (1%, 2 mL) was mixed with the first solution and stirred for 15 min. The AuNPs were synthesized in solution upon cooling the reaction mixture to room temperature.

4.5. Deposition of AuNPs into TiO2 Multilayers. An aqueous solution of the prepared AuNPs was diluted by adding 2 mL aqueous solution of AuNPs in 20 mL of deionized water and ultrasonicated for 30 min. After the ultrasonication, the
glass substrates with TIO multilayers were vertically immersed into the AuNP solution. The solvent was allowed to evaporate for 40 h at 65 °C. As a result, AuNPs were deposited into the pores of TIO multilayers, as shown in Figure 11.

Figure 11. Schematic illustration for deposition of AuNPs in TIO multilayers.

4.6. Characterization. The morphology and structure of TIO multilayers and Au-TIO multilayers were recorded using a Hitachi S-4800 field emission scanning electron microscope (FE-SEM). Cross-sectional images of the TIO multilayer were taken by scratching a small surface from glass substrates and dispersing that on a carbon tape.

The absorption spectrum of AuNPs was recorded using a PerkinElmer Lambda 900 UV/Vis/NIR spectrometer. The crystalline phase and morphology of Au-TIO were further analyzed by a scanning transmission electron microscope (STEM). The elemental identification of AuNPs and Au-TIO was recorded using energy-dispersive X-ray spectroscopy (EDS) with NORAN System SIX (NSS) software. The size distribution of AuNPs was measured using the STEM. The samples for STEM and EDS were prepared by drying the diluted aqueous solutions of AuNPs and Au-TIO on a copper grid coated with a lacey carbon film. A Raman microscope (Renishaw inVia) programmed with WiRE 3.4 software using an excitation laser of 785 nm with a 1 mW power with an integration time of 10 s with a measurement range of 100–800 cm⁻¹ was used to confirm the presence of anatase TiO₂.

The crystalline nature of the TiO₂ material was characterized with a Bruker AXD D8 Advance device using Cu Kα as the radiation source. The diffraction pattern was measured between 2θ and 90° at the 2θ scale with a step size of 0.3°/min.

4.7. Gas-Phase Photocatalytic Activity Measurement. Photocatalytic activity of TIO 200 (from 200 nm PS), TIO 400 (from 400 nm PS), TIO 200/400 (200 nm followed by 400 nm), TIO 400/200 (400 nm followed by 200 nm), Au-TIO 400/200, and Au-TIO 200/400 were evaluated by oxidation of acetylene (C₂H₂) into carbon dioxide (CO₂). Such an approach has been demonstrated for the characterization of photocatalytic activity. The photocatalytic activity of C₂H₂, ethylene, and propane are present in automobile exhaust gases, which can be removed by photocatalytic oxidation. Hence, the photodegradation of C₂H₂ was selected for this work to measure the photocatalytic efficiency of the TIO multilayer.

The photocatalytic activities were measured using an in-house built (University of Eastern Finland, Department of Chemistry, Joensuu campus) gas-phase photo reactor, as described in detail in ref 52. It was assumed that all samples had the same surface area. TIO samples on glass substrates (3.3 × 2.6 cm) were placed into the reaction chamber, and a constant concentration of CO₂ was maintained by purging the mixture of C₂H₂ and technical air through the reactor system. The samples were excited using a 450 W xenon lamp (OSRAM). A filter composed of PMMA glass was used to block the UVA portion of incident light with a cutoff filter (λ < 400 nm removed). The visible light source was fixed 10 cm above the reactor chamber. The photocatalytic activity was evaluated by the production rate of CO₂. It is noteworthy that photodegradation of C₂H₂ can also produce other compounds in small number, which can be detected by gas chromatography (GC) and thermal analysis techniques. CO₂ concentration was measured using an optical CO₂ detector (Vaisala GMP343) fixed into the reactor chamber.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

F.T. wishes to thank the Finnish Cultural Foundation for a research grant. J.J.S. acknowledges the Faculty of Science and Forestry at the University of Eastern Finland for the financial support (grant no. 579/2017).

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