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Monolithic Ceramic Foams for Ultrafast Photocatalytic Inactivation of Bacteria

Pinggui Wu^{†,a}, Rongcai Xie[†], Kari Imlay[‡], and Jian Ku Shang^{†,b}

[†]Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

[‡]Department of Microbiology, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

Abstract

Palladium-modified nitrogen-doped titanium dioxide (TiON/PdO) foams were synthesized by a sol-gel process on a polyurethane foam template. The TiON/PdO foam was tested for microbial killing using *Escherichia coli* cells as a target. Under visible-light illumination, the TiON/PdO foam displayed a strong antimicrobial effect on the bacteria cells in water. The antimicrobial effect was found to be dependent on the palladium content and the calcination temperature. In a flow-through dynamic photoreactor, the new photocatalyst efficiently inactivated *E. coli* within a short contact time (< 1 min), the shortest ever reported for photocatalytic killing of bacteria. The strong antimicrobial functions of the TiON/PdO foam were related to the charge trapping by PdO and to the high contact efficiency of the foam structure.

Keywords

Titanium Oxide; Foam; Antimicrobial; Water Disinfection

I. Introduction

Porous metal oxides have long been studied for applications in catalysis, micro- and optoelectronics, photovoltaics, and separation, etc. Such materials with uniform channel dimensions have a set of attractive properties, such as light weight, high specific surface area, large damping capacity, good chemical inertness, low dielectric permittivity, and low thermal conductivity. For example, macroporous supports account for optimal flow and improved efficiencies in catalysis and large molecule separation processes.¹ Porous materials are usually classified into three types according to the pore sizes: microporous (pores ≤ 2 nm), mesoporous (pores in the range 2–50 nm), and macroporous (pores > 50 nm). In the literature, microporous materials are usually the zeolite-type structures.

Mesoporous materials have been extensively researched over the past decade, including mesoporous silica, mesoporous titanium dioxide (TiO₂), mesoporous zirconium dioxide, and mesoporous manganese oxide, etc. These mesoporous metal oxides are usually synthesized via templating with surfactants or block copolymers. The fabrication pathways for macroporous structures have also been established, such as decomposition of foam agents, replication of polymer foams, and foaming of sol-gel solutions. Despite these processing methods for making macroporous ceramics, there are not many reports about the preparation

^bAuthor to whom correspondence should be addressed. jkshang@illinois.edu.

^aCurrent addr.: Peter R. Carney Tech Center, Superior Graphite Co., Chicago, IL 60632

of titanium dioxide monolith,^{1–3} in contrast to the extensive investigation on powders and thin films of this oxide.

Since the discovery of photoelectrochemical splitting of water on TiO₂ by Fujishima and Honda in 1972,⁴ TiO₂ has been intensively investigated as photocatalysts for energy conversion^{5–8} and environmental applications.^{7, 9–12} In most recent years, much effort has been devoted to the development of visible-light-activated photocatalysts by doping TiO₂ with either transition metals^{13–17} or nonmetal anions,^{18–23} and by codoping approach where synergetic sensitizing effect of a second element on anion-doped TiO₂ was used to enhance photo-activity.^{24–29} Liu and Gao²⁴ reported a (S,N)-codoped TiO₂ photocatalyst which has a better photocatalytic activity than S-doping and N-doping for degradation of methylene blue solution under visible-light. Sakatani *et al.*²⁷ successfully synthesized metal ion and nitrogen co-doped TiO₂, and used it for visible-light photocatalytic degradation of acetaldehyde. Our group reported enhanced visible-light photo-activity of palladium-modified nitrogen-doped titanium oxide.^{30–35} We found that PdO nanoparticles in a TiON/PdO thin film can be reduced to metallic palladium under visible-light illumination by optoelectronic interaction between TiON and PdO, enhancing the visible-light absorption of a TiON/PdO thin film.³⁰ The TiON/PdO nanopowders made by the sol-gel process have demonstrated enhanced photocatalytic activity over TiON in degradation of humic acid³¹ and TiON/PdO-embedded activated carbon/glass fiber (ACGF) materials exhibited effective antibacterial,^{32, 33} antiviral,³⁴ and anti-bacterial spore³⁵ properties. The enhanced photocatalytic effects of palladium modification have been studied and attributed to reduced electron-hole recombination.³¹

It is known that use of the powder form TiO₂ presents a major challenge in a fluid media photocatalysis processes. So far most photocatalysis processes are based on TiO₂ aqueous suspensions,^{7, 9–12} where removal of the dispersed photocatalyst from the treated slurry often requires ultrafiltration or ultracentrifugation. To eliminate these needs, researchers have reported immobilized^{36–40} TiO₂ systems on various conductive or non-conductive supports, lightguides, glass microspheres, magnetic cores, and polyelectrolyte capsules.

In this study, visible-light-active macroporous titanium dioxide monoliths were prepared by a sol-gel process on polymer templates to take advantages of the unique structure of monolithic foam, and the antimicrobial properties of the foam structure were determined in a dynamic flow-through reactor using *E-coli* as the indicator. Compared to the slurry or immobilized powder form, the TiON/PdO foam has the advantages of high contact efficiency and low back pressure during flow-through water disinfection applications. By combining the macroporous structure of the open-cell shape and the mesoporous structure of the TiON/PdO walls, the contact efficiency of the bacterial cell with the photocatalyst was greatly increased. Ultrafast (killing times in less than 40 seconds) photocatalytic inactivation of *Escherichia coli* was achieved with visible-light illuminated TiON/PdO foams.

II. Experimental Procedure

(1) Materials System

Titanium tetraisopropoxide (TTIP, 97%, Sigma-Aldrich, St. Louis, MO), tetramethylammonium hydroxide (TMA, 25 wt.% in methanol, Sigma-Aldrich), and palladium acetylacetonate (Pd(acac)₂, 99%, Sigma-Aldrich) were used as precursors to serve as titanium, nitrogen, and palladium sources, respectively. Ethyl alcohol (EtOH, 100%, AAPER, Alcohol and Chemical Co., Shelbyville, KY) and dichloromethane (CH₂Cl₂, 99.6%, Sigma-Aldrich) were used as solvents. Polymer cushion foam purchased from McMaster (Catalog # 8643K518, very soft polyurethane foam) was used as the template in synthesis.

(2) Synthesis

The synthesis of TiON/PdO foam was carried out by combining a sol-gel process to obtain nanopowders³¹ with the use of a polymer template. A mixture of TTIP and TMA (mol ratio 4:1) was first made in EtOH. Then a proper amount of Pd(acac)₂ was dissolved in CH₂Cl₂, and added to the TMA/TTIP/EtOH mixture to achieve the desired total Pd content.

Hydrolysis of all precursors was initiated by exposure to the moisture in air. A cube of 1.0 g polyurethane cushion foam was soaked in the precursor mixture. The foam template was rapidly and completely infiltrated by the suspension through its pores, and was left to gelation process in the fume hood in air for 24 h. Following calcination at 500°C in air for 4 h, fine crystallites of TiON/PdO were formed on the template. Upon removing the template during calcination, a TiON/PdO solid foam was made with an interconnected pore structure.

(3) Photocatalyst Characterizations

A Rigaku RAX-10 x-ray diffractometer (Rigaku Corporation, Tokyo, Japan) was run at CuK α (0.15418nm) radiation at 45 kV and 20 mA to obtain XRD patterns. X-ray photoelectron spectroscopy (XPS) was performed on a PHI 5400 x-ray photoelectron spectrometer (Perkin-Elmer Corporation, Eden Prairie, MN) with an Mg K anode (1253.6 eV photon energy, 15 kV, 300 Watt) at a take-off angle of 45°. Multiplex XPS spectra of each individual element were recorded using a band-pass energy of 35.75 eV, corresponding to an energy resolution of 1.2 eV. Foams were observed with a Zeiss 62293 optical microscope using the transmitted beam. The foams' surface morphology was examined by a scanning electron microscope Hitachi S-4700 (Hitachi, Tokyo, Japan) at an acceleration voltage 5–15 kV. The analysis of surface area and pore size distribution was carried out with an Autosorb-1 apparatus (Quantachrome). Samples were outgassed at 200°C. Nitrogen isotherm results at 77 K in the appropriate relative pressure ranges were used for subsequent calculations. Specific surface area of the sample was determined using the standard BET equation. The pore size distribution was calculated from the desorption branch of N₂ adsorption-desorption isotherm using the conventional Barrett-Joyner-Halenda (BJH) method. The analysis of the data was completed using the built-in computer program supplied with the apparatus.

(4) Bacteria Culture and Viability Assay

Wild type *Escherichia coli* AN 387 was provided by Prof. J. A. Imlay at the Department of Microbiology, University of Illinois. Bacteria cells were inoculated each time from an agar plate into a 4 ml liquid Luria-Bertani (LB) medium, as detailed in Table 1. The cells were grown aerobically in the medium placed on a rotary shaker at 37°C for 18 h. Cells were harvested from overnight culture by centrifugation for 5 min at 277 K and 6000 rpm, washed twice using a phosphate buffer solution (0.05 M KH₂PO₄ and 0.05 M K₂HPO₄, pH 7.0), then resuspended and diluted in stock buffer solution prior to the use for sterilizing experiments. The initial cell concentration was in the magnitude of 10⁵ colony forming unit (cfu)/ml, determined by a viable count procedure on agar plates after serial dilutions. All solid or liquid materials have been autoclaved for 30 min at 121°C before use.

The experimental set-up used for a dynamic bactericidal testing is shown schematically in Fig. 1. At starting time, aliquot of 3 L bacteria suspension was laced in a sterile container. The amount of photocatalyst applied in each test was 1.00 $\pm$ 0.05 g, about 2 inches in flow-through length when inserted to the glass tube. Tube's diameter is about 1 cm. At the end of the tube, glass fiber stopper was used to prevent the foam from going away. The glass tube was illuminated by two 30 W fluorescent lamp, at intensity *ca.* 1.2 mW/cm² as measured by a Multi-Sense MS-100 optical radiometer (UVP, USA). The light intensity below 400 nm was < 0.01 mW/cm² as measured with the same optical radiometer. The flow rate of the bacteria suspension was adjusted to 5 ml/min with a controlling valve, and the collected cell

aliquots were withdrawn for cell viability assay. The one-time-through contact time was approximately 30-40 sec by calculations.

During cell viability assay, after appropriate dilutions in buffer solution, aliquots of 20 μ l cell culture together with 2.5 ml top agar was spread onto an agar medium plate and incubated at 37°C for 24 h. The number of viable cells in terms of colony-forming units was counted and survival ratio is determined as N_t/N_i (t-treated; i-initial). The data and conclusions were confirmed by replicate experiments. Control runs were carried out with the photocatalyst wrapped in dark while other conditions being equal. For comparison, purely light-illuminated cell suspension sample was also collected without passing a photocatalyst.

III. Results and Discussion

(1) Composition of Sol-Gel TiON/PdO Foam

XPS survey spectrum of the representative TiON/PdO foam, as shown in Fig. 2, demonstrates the existence of N, O, Pd and Ti in the foams. Multiplex high resolution scans over the N1s and Pd3d spectral regions are included in Fig. 3. The spectrum of Pd3d is shown in Fig. 3a. The peak around 336.8 eV is assigned to Pd3d_{5/2} in PdO form, which means Pd is oxidized.³⁰ An increase in the Pd3d band intensity was observed when samples were prepared with higher amounts of Pd precursor ranging from 10 to 90 mg. A semi-quantitative analysis of the TiON/PdO foam composition was estimated by taking the average intensity ratio from multiplex scans of N1s, O1s, Ti2p and Pd3d using the method adopted previously.²¹ The concentration of PdO determined by XPS is listed in Table 2. When only 10 mg palladium precursor was added to the sol-gel mix, the resultant solid TiON/PdO foam contains just about 0.2 wt.% PdO. Gradually, the amount of PdO incorporation was increased to 0.5 wt.% when 20 mg palladium precursor was added, or 0.8 wt.% PdO in the product when 30 mg palladium precursor was added. The highest added amount of 90 mg palladium precursor in the mix resulted in 1.8 wt.% PdO in the solid foam. It indicates that the higher amount of palladium precursor in the synthesis mixture, the higher content of palladium in the solid foams.

As the calcination temperature was increased in the range between 400 and 700°C, a substantial decrease in band intensity of N1s was observed, as shown in Fig. 3b. The appearance of an N1s band at 399–400 eV indicates that nitrogen was doped into the titanium oxide lattice and remained in the foam after calcination at 400°C and 500°C. The N1s peak was barely visible after calcination at 640 and 700°C, indicating that nitrogen as-doped during sol-gel synthesis was replaced by the oxygen in air through the high-temperature oxidation process. The concentration of nitrogen (i.e. the intensity ratio of N1s band) after calcination was also determined by the XPS technique. After calcination at 400°C, the TiON/PdO foam normally contains 1.9 ± 0.1 wt.% nitrogen, and after calcination at 500°C, nitrogen incorporation in the monolithic TiON/PdO foam decreases to 1.2 ± 0.1 wt.%. At 640°C and 700°C calcination, the concentration of N was too low to be reasonably measured with the XPS technique.

(2) Structure of Sol-Gel TiON/PdO Foam

Fig. 4 shows the typical x-ray diffraction pattern of a PdO/TiON foam when the calcination temperature varied in the range between 400 and 700°C. It can be seen that these foams exhibit a dominating anatase-TiO₂ phase. Typical XRD peaks of the anatase structure are marked in the spectra, including (101), (004), (200), (105), (211), (204), and (116). However, rutile-TiO₂ phase started to be seen when calcination temperature was at 640°C and above. It suggests that for the best crystalline quality of 100% anatase phase, a calcination temperature between 400 and 500°C is optimal. Crystallinity control of PdO/

TiON foam is of significance in photocatalysis application because many former studies have indicated a better photocatalytic property of anatase-TiO₂ phase than that of rutile-TiO₂ phase.^{41, 42}

The morphology of the foam was observed with optical and electron microscopy. Fig. 5 shows the open-cell morphology of the foam observed with an optical microscope. It is seen that the polymer foam-templating method produced TiON/PdO foams with pentagonal pore shapes and broad pore size distributions. The foam has an open network of large pores of average 100–200 μm in dimensions. The center-to-center average distance between the pores is about 100 μm and the average wall thickness of the pores is around 5 μm . As discussed by Wang et al.,¹ fabrication of metal oxides via the hydrolysis reaction of alkoxides usually results in a great deal of shrinkage and cracking of the materials, when large amount of water and alcohol are removed during drying and heat treatment. Such shrinkage and cracking of our materials was seen in the optical micrograph. It is also noted that the pores of these TiON/PdO foams are obviously larger than those macropore structures reported in the literature. Those previously reported macroporous materials, even fabricated with polymer foam as the template, produced sub-micron pores.^{1, 2} Larger macropores are more attractive for antimicrobial application in current communication. Rod-shaped *E. coli* cells are typically 0.5 μm in diameter and 1–3 μm in length. Since the pore dimension is much larger than the size of bacteria cells, these large pores are desirable both for improving the contact efficiency between the bacteria and the photocatalyst, and for reducing the pressure drop across the foam in a dynamic reactor. The pores may also allow light penetration inside the foam cubes during photocatalytic inactivation of bacteria.

Fig. 6 displayed the SEM micrographs of the interconnecting wall of the prepared monolith, the TiON/PdO particles calcined under 500 and 700°C, respectively. The micrograph of 500°C-calcined foam consists of small, densely packed TiON/PdO particles with an average diameter of 12 nm. It was noted that the higher the calcinations temperature, the larger particle size of the TiON/PdO particles. The average diameter of TiON/PdO particles after 700°C-calcination is 25 nm. In these micrographs, the mesoporous characteristics of the TiON/PdO particle-based walls made by the sol-gel process are observed. The duality of the foam porosity with both macropore and mesopore is ideal for high photocatalytic efficiency in flow-through operations. Macropores result in a low back pressure at elevated flow rates while mesopores provide large surface areas. Additional characterization of the porous feature of the as-formed photocatalytic foam is shown in Fig. 7. Nitrogen adsorption-desorption measurement results in the isotherm in Fig. 7a, where a large hysteresis between adsorption and desorption, characteristic of mesopores, is observed. The pore size distribution of the TiON/PdO wall is given in Fig. 7b. It indicates that the main pore diameter is 3.9 nm, and a secondary peak diameter is 16.8 nm. Thus, the TiON/PdO wall of the monolithic foam consists of mesopores, most with a diameter below 20 nm.

(3) Photocatalytic Disinfection of *E. coli*

Conventionally, bactericidal data are presented as changes in the survival ratio. Here we use N_t/N_i , N_i and N_t are defined as the number of colony-forming units per milliliter in the control and irradiation treatment, respectively. Control is the cell culture that runs through the foam and glass fiber stopper in dark. The effect of photocatalysis on cell viability is introduced under visible-light irradiation. The cell culture was let run for a sufficient ‘stabilization time’ before the cell suspension aliquots were collected for viability assay, in order to minimize the effect of physical filtration. The bactericidal results in Fig. 8 revealed the impact of metal ion loading on the killing effect of TiON/PdO foam. Each displayed data point is the average of duplicate/triplicate viability tests, with the given error bar. It has been discussed in Table 2 that the greater amount of palladium precursor, the higher palladium loading in the resulted TiON/PdO monolithic foams. Data in Fig. 8 indicated that the

palladium addition is an effective enhancer to the photocatalytic performance of monolithic foams. The treatment on TiON (i.e. 0% Pd) foam led to 89% survival ratio. With other conditions being equal, treatments on 500°C-calcined TiON/PdO foams led to lower survival ratios. However, when the concentration of Pd was too high, the enhancement effect of PdO was impaired: with *ca.* 0.2 wt.% PdO, the survival ratio was 60%; with *ca.* 0.5 wt.% PdO, the survival ratio was 65%; with *ca.* 0.8 wt.% PdO, the survival ratio reached the lowest of 32%; and then with *ca.* 1.8 wt.% PdO, the survival ratio rebounded to 77%. With higher and higher Pd concentrations, it was noticed that the resultant foams exhibited a gradual loss in mechanical strength. Eventually with 1.8 wt.% PdO, the resultant foam is weak and contains more structural cracks. The loss of pore-structure integrity can contribute to the lower photocatalytic effect. The decreased enhancement effect of higher Pd loading may also be associated with the phenomenon of PdO agglomeration, similar to what Gracia *et al.*¹⁶ observed in other $M_2O_n/TiO_{2-x}N_x$ materials (M is a metal, n is its valence and x is the content of nitrogen). Among the metal ions in M^{n+} -TiO₂ thin films (Cr, V, Fe, Co), Gracia and colleagues found that the extent of partial segregation of the cation in the form of M_2O_n is associated with the type and concentration of cations. In a review article about the effect of transition metal ions on photocatalysis, Litter¹⁴ has also noted that the rate and efficiency of photocatalytic reactions is strongly dependent on the type and concentration of the metal ion. The increase in photooxidation rates by addition of palladium ions has previously been attributed to the ability of this metal ion to scavenge electrons on the TiO₂ surface and consequently increase the lifetime of charge carriers.^{30, 31} Agglomeration of the palladium ions could weaken the scavenging efficiency.

Antibacterial performance of the TiON/PdO foams with *ca.* 0.8 wt.% PdO calcined at different temperatures was also studied. The bactericidal results in Fig. 9 revealed the effect of calcination temperature on the killing property of TiON/PdO foams. The survival ratios of *E. coli* cells were 20%, 32%, 48% and 54% for calcination temperatures of 400, 500, 640 and 700°C, respectively. This decreased rate of killing with increased temperature of foam-processing may be a result of multiple factors. Better photocatalytic performance can be attributed to the desirable amount of N%, the pure anatase crystalline phase and the smaller particle size of TiON/PdO obtained from 400°C-calcination.

Up to here, we have successfully demonstrated a type of visible-light-active macroporous titanium dioxide monolith for photocatalytic application. In the open literature, most of the TiO₂-disinfection experiments were conducted in a stationary photoreactor, where the bacterial suspension was contained in a receptacle in the presence of TiO₂-based photocatalysts. After being irradiated for certain time period, the cell aliquots were taken for viability assay. Published results showed that a range of 5–45 minutes of irradiation time (named contact time or residence time in flow-through processes) are needed to reach *E. coli* survival ratio < 50% on a UV/TiO₂ system^{12, 43–45} or on a Visible/TiON system.^{26, 46} In very few reported flow-through photoreactors, liquid containing *E. coli* was circulated for nearly 60 min under UV to obtain survival ratio < 50% with an immobilized TiO₂ layer.³⁶ Although a direct comparison between the photocatalytic efficiency of TiON/PdO foam and the published results is difficult due to the lack of standardized conditions, here the non-circulated *E. coli* suspension runs through the photoreactor (Fig. 1) with 40 sec contact time or less. For such a short treatment time, the survival ratio of bacteria cells treated by our TiON/PdO foam with 0.8 wt.% PdO is 20% (equivalent number of inactivated *E. coli* cells 80,000). Compared to other photocatalytic studies where an inactivation at this level was normally reached after 5–45 minutes of treatment, the antimicrobial rate of TiON/PdO monolith is “ultrafast”.

This ultrafast behavior is the result of multiple factors: Firstly, nitrogen and palladium co-doping significantly enhances the quantum yield upon visible-light irradiation. The

synergetic effect of N and Pd doping in TiO₂ has been confirmed in published results.^{30–35} Palladium cation has a positive effect on the optical property of TiON. The band gap value of TiON/PdO was found to be lower than that of TiON when a narrow range of Pd concentrations is present.³⁰ Palladium cation is also known to act as an electron trap and increase the quantum yield of reactive oxygen species during photocatalysis.^{31–35} On the UV-activated TiO₂, photocatalytic killing has been linked to the membrane damage or loss of metabolic activities by reactive oxygen species. We believe that similar mechanism also works here for the enhanced visible-light disinfection on TiON/PdO foams. As former study indicated, the trace amount of palladium does not directly kill the bacteria.³² It indirectly contributes to the killing by serving as electron trap which prevents electron-hole recombination, so that more hydroxyl radicals can be generated on the irradiated TiON/PdO photocatalysts.³³ Secondly, characterization has shown that the monolithic foam has a bi-model pore structure: wide-open macropores and mesoporous TiON/PdO particle walls. These pores contribute to higher specific surface area of the light weighted foams. A linear relation between the rate of photocatalytic reaction and amount of substrate(s) adsorbed on the surface of photocatalyst has been previously reported.⁴⁷ A large surface area of a constant surface density provides a larger number of surface sites surrounding the e⁻-h⁺ pairs, which leads to faster rate of e⁻ and h⁺ reaction with the substrates. Thirdly, the monolithic foam provides full contact between the bacteria cells and the photocatalytic TiON/PdO walls owing to the 100 μm open structure. The open-cell structure simultaneously permits better illumination penetration. From the photocatalytic testing results, there is a reason to anticipate the monolithic foam structure to have a great potential in photocatalytic applications.

IV. Concluding Remarks

In this study, the porous foam photocatalysts were made by templated growth of TiON/PdO nanocrystallites in the pore system of polyurethane packaging foam, followed by removal of the polyurethane. The TiON/PdO foams demonstrated ultrafast photocatalytic inactivation of *Escherichia coli* under visible-light irradiation. The addition of PdO nanoparticles effectively enhanced the disinfection activity of nitrogen-doped TiO₂ under visible-light. An optimal PdO loading was found to be 0.8 wt.%. Calcination temperature affected the crystalline phase, nitrogen content and grain size. In combination of these factors, low temperature (400°C to 500°C) calcination was found to have an advantage. In a flow-through reactor, the form of this novel monolithic photocatalyst saves the extra cost associated with the recovery of catalyst particles, and TiON/PdO can be efficiently activated by interior visible-light or the solar energy, these are merits of TiON/PdO foams as an alternative antimicrobial solution to water disinfection.

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Figure 1.

The experimental set-up used for photocatalytic measurements in the foam: 1) contaminated water; 2) regulating valve; 3) TiON/PdO foam; 4) glass fiber stopper; 5) 2×30 watt fluorescent lamp; 6) glass tube.

Figure 2.
Typical XPS survey spectra of palladium-modified nitrogen-doped titanium oxide foams.

(a)

(b)

Figure 3.

XPS multiplex high resolution scans: (a) the Pd 3d spectral regions where increase in band intensity was observed with 1) 10; 2) 20; 3) 30; 4) 90 mg palladium precursor added; (b) the N 1s spectral regions where decrease in band intensity was observed with higher calcination temperatures ranging from 400 to 700°C.

Figure 4. XRD patterns of the TiON/PdO foam after calcination at different temperatures of 400, 500, 640 and 700°C, respectively.

Figure 5.
Optical microscopy showing the open cells (macropores) of the porous TiON/PdO foams.

Figure 6. SEM images of a porous TiON/PdO wall of the foams after calcination at temperatures (a) 500°C; and (b) 700°C. The scale bar is 500 nm.

Figure 7.
 (a) The nitrogen adsorption-desorption isotherm of a TiON/PdO foam; (b) Pore size distribution obtained from BJH method.

Figure 8.

Survival ratio of *E. coli* cells treated by TiON/PdO foams with varying amounts of palladium loading 1) 0%, i.e. an TiON foam; 2) 0.2 wt.%; 3) 0.5 wt.%; 4) 0.8 wt.%; 5) 1.8 wt.%, all foams were subject to 500°C-calcination.

Figure 9.

Survival ratio of *E. coli* cells after photocatalytic treatment on TiON/PdO foams calcined at various temperatures 1) 400; 2) 500; 3) 640; and 4) 700°C.

Table 1

Compositions of the nutrient media (per liter) for bacterial viability assay.

	<i>E. coli</i> AN387 (wild-type)
Liquid medium	LB (pH=7.0): 10 g bactotryptone 5 g yeast extract 10 g NaCl
Plate	Liquid medium + additional 15 g bactoagar
Top agar	Liquid medium + additional 8 g bactoagar

Table 2

XPS data of the series of TiON/PdO foams

Pd precursor amount (mg)	PdO wt.% from XPS measurement
10	0.2 ± 0.05
20	0.5 ± 0.1
30	0.8 ± 0.2
90	1.8 ± 0.2