Memory antibacterial effect from photoelectron transfer between nanoparticles and visible light photocatalyst

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A novel visible light photocatalyst system was developed, consisting of palladium oxide (PdO) nanoparticles well dispersed on a nitrogen-doped titanium oxide (TiON) matrix. Clear evidence of photoelectron transfer between PdO nanoparticles and the TiON matrix was obtained for the first time. The optoelectronic coupling between PdO and TiON introduces enhanced photocatalytic bacterial disinfection under visible light illumination by electron trapping on a PdO nanoparticle, and a unique catalytic memory effect on bacterial disinfection due to the discharging of trapped electrons on PdO nanoparticles in the dark when the illumination is switched off. Thus, a unique robust catalytic disinfection system is created, which is driven by solar/visible light illumination, enables the continuous operation in day and night, and could be adapted to a broad range of environmental applications.

Introduction

Photoelectron trapping has long been regarded as an effective mechanism to reduce the charge recombination on (and thus enhance the photocatalytic efficiency of) semiconductor photocatalysts. Numerous studies have suggested that fine particles of transition metals or their oxides, when dispersed on the surface of a photocatalyst matrix, can act as electron traps on n-type semiconductors such as TiO2. Indirect evidence of electron trapping on these fine particles had been demonstrated by the much longer characteristic decay times in these systems, compared with pure TiO2, with transient absorption decay spectra measurements. However, direct evidence of photoelectron transfer between the trapping particles and the photocatalyst matrix remains elusive.

Here we developed a novel visible light photocatalyst system consisting of palladium oxide (PdO) nanoparticles well dispersed on nitrogen-doped titanium oxide (TiON) matrix, hereafter referred to as TiON/PdO. Clear evidence of charge flow to/from PdO nanoparticles on the visible light photocatalytic TiON matrix were obtained by the AFM study of the surface charge distribution and in situ XPS analysis on palladium additive chemical status of TiON/PdO thin film samples both under visible light illumination and in the dark. The discharging of PdO nanoparticles following visible light illumination created a unique catalytic memory effect on bacterial disinfection in the dark, while photoelectron flow to the PdO nanoparticles enhanced photocatalytic disinfection efficiency under visible light illumination. The introduction of transitional metal ion modification as demonstrated with palladium in this study could be easily adapted to other transitional metal ions, and the charging/discharging on PdO nanoparticles may occur in other transitional metal ion-modified anion-doped TiO2 material systems. Thus, our work here could provide the basis for design of new generations of photocatalysts for a broad range of environmental applications.

Experimental

TiON/PdO thin film sample was prepared by the ion-beam-assisted deposition (IBAD) technique. The surface morphology of TiON/PdO thin film was examined by scanning electron microscopy (SEM) with a Hitachi S-4700 Scanning Electron Microscope. Prior to imaging, the sample was sputtered with gold for 15 s (Emitech K575 Sputter Coater). An FEI Tecnai G2 F30 electron microscope (FEI Company, Eindhoven, The Netherlands), operated at an accelerating voltage of 300 kV with a point resolution of 0.17 nm, was used to carry out high resolution transmission electron microscopy (HRTEM) observations. The atomic force microscopy (AFM) observations was conducted on the Asylum Research MFP-3D AFM (Asylum Research) with platinum/iridium coated conductive contact mode tips (SCM-PIC, Veeco Instruments). XPS measurements were made on a Physical Electronics PHI 5400 X-ray Photoelectron Spectrometer with an Mg K anode (1253.6 eV photon energy, 15 kV, 300 W) at a take-off angle of 45°.

TiON/PdO fibers were synthesized by a sol–gel process with the ACGF template, and details can be found in ref. 10 and 11. TiO2 and TiON fibers were also synthesized for comparison purpose with similar procedures, just without adding nitrogen or palladium precursors. Wild type Escherichia coli (E. coli) AN 387 (ATCC 15597, the American Type Culture Collection) were used for the photocatalytic inactivation experiment. After overnight culture, the cells were diluted to a cell suspension (ca. 0.5 cfu ml−1) in buffer solution (0.05 M KH2PO4 and 0.05 M K2HPO4, pH 7.0) prior to use for photocatalytic inactivation. All solid or liquid materials have been autoclaved for 30 min at 121 °C before use. For E. coli disinfection under visible light illumination,
a metal halogen desk lamp was used, which has a glass filter to provide zero light intensity below 400 nm. The light intensity striking the cell suspensions was at ca. 1.0 mW cm$^{-2}$, as measured by a Multi-Sense MS-100 optical radiometer. For *E. coli* disinfection in the dark, TiON/PdO fiber samples were first illuminated by the same lamp for ~10 h to simulate the day-time illumination, then the lamp was shut off and fiber samples were put into dark environment for 0 h, 3 h, 8 h, and 24 h, respectively, before they were used to conduct the disinfection experiment in the dark. The aerobic experiment was conducted in air, while the anaerobic experiment was conducted in an enriched N$_2$ atmosphere. At the starting time, an aliquot of 3 mL *E. coli* cell suspension was pipetted onto a sterile 60 x 15 mm Petri dish with the TiON/PdO fiber sample placed in the bottom. A fixed concentration of ~1 mg photocatalyst mL$^{-1}$ *E. coli* solution was used in this study. At regular time intervals, 20 μL of aliquots of the TiON/PdO-treated cell suspensions were withdrawn in sequence. After appropriate dilution in buffer solution, aliquots of 20 μL together with 2.5 mL top agar were spread onto an agar medium plate and incubated at 37 °C for 18 h. The number of viable cells in terms of colony-forming units was counted. Analyses were in duplicate and control runs were carried out each time under the same experimental conditions, but without any photocatalytic materials.

**Results and discussion**

Nano-sized TiON/PdO photocatalytic thin film and fiber samples were prepared and investigated in this study. Fig. 1(a) shows the scanning electron microscopy (SEM) image of a TiON/PdO photocatalytic thin film sample synthesized by the IBAD technique. The film has a dense surface and the grain size in the film is ~30 nm. The high resolution transmission electron microscopy (HRTEM) image of TiON/PdO thin film in Fig. 1(b) revealed that palladium additives in TiON/PdO exist as crystallized PdO nanoparticles (several nanometres in diameter) well dispersed in the TiON anatase crystal matrix. Thus, PdO nanoparticles should reside on the surface and in the grain boundary areas in the interior of the sample. This observation is in accordance with our previous XRD analysis results on this photocatalytic material system.9–11

Under visible light illumination, electron-hole pairs are expected to be produced in the TiON matrix and on the catalyst surface due to the nitrogen-doping effect.12–14 Without nitrogen-doping, no visible light adsorption effect could be observed on the TiO$_2$/PdO thin film sample,9 and subsequently no significant bactericidal effect was observed with TiO$_2$/PdO fiber samples even under visible light illumination.15 To examine the surface charge distribution on a TiON/PdO thin film under these conditions, an atomic force microscopy (AFM) study was conducted in the contact mode as the TiON/PdO film was exposed to visible light. Fig. 2 shows the electric current distribution on TiON/PdO thin film surface under visible light illumination without applying the external electric voltage. The image was produced by superimposing the current profile on the 3D image of the height profile created by the MFP-3D software (Asylum Research). While the 3D height image reveals the surface morphology, the yellow-hot color displays the current value at different points on the semiconductor surface. Most parts of the surface have the same red color, while much stronger electric current signal was recorded at dispersed spots on the surface (bright yellow color). Without the external voltage, the electric current signal can only come from the photoelectrons on the surface which flow into the conductive AFM tip and travel through the external circuit. These bright yellow spots are

**Fig. 1** (a) SEM image of TiON/PdO thin film surface morphology. (b) High resolution transmission electron microscopy (HRTEM) image of the TiON/PdO thin film.

**Fig. 2** AFM 3D height image with the yellow-hot color displaying the electric current value of the TiON/PdO thin film surface under visible light illumination. (Note that white arrows point out some places with stronger electric current signal in dispersed spots on the surface to guide eyes.)

**Fig. 3** In situ XPS high-resolution scans over Pd 3d peaks on TiON/PdO thin film originally in the dark for 5 h, under visible light illumination, and in a dark environment for 1 h, 2.5 h and 3.5 h after the visible light is off. (Note that the red dashed curve fits Pd$^0$ 3d peaks, while the blue dashed curve fits Pd$^{2+}$ 3d peaks.)
observed among the grain boundary areas, where most of PdO nanoparticles reside in TiON/PdO, indicating an enrichment of photoelectrons on PdO nanoparticles following visible light illumination of the photocatalyst.

A direct consequence of the electron flow to PdO nanoparticles is that the PdO is reduced chemically, as the in situ XPS analysis revealed (see Fig. 3). The XPS analysis was focused on potential changes in the valence states of Pd additives with/without visible light illumination. The TiON/PdO thin film sample was first placed in the dark for 5 h right before an XPS high-resolution scan over the Pd 3d peak in the dark. Then, XPS scans were performed simultaneously with visible-light illumination on the sample. Differences in the Pd 3d peak shape and position were observed between scans in the dark and under visible-light illumination. In the dark, the binding energy of Pd 3d_{5/2} is \( \approx 336.20 \) eV, indicating that Pd additives exist as PdO. Under visible-light illumination, however, Pd peaks are broadened and the binding energy of Pd 3d_{5/2} is shifted to \( \approx 335.30 \) eV. The broadened Pd 3d_{5/2} can be best fit as a combination of Pd^{2+} 3d_{5/2} (peak at 336.2 eV) and Pd^0 3d_{5/2} (peak at 335.2 eV), which clearly demonstrates that a large portion of the PdO semiconductor nanoparticles in the TiON/PdO thin film has been reduced to metallic Pd^0 under visible-light illumination due to the electron enrichment of these Pd additives as demonstrated in Fig. 2. Thus, these photo-electrons are trapped on Pd additive sites. Both the AFM current map and the change in the valence state of Pd additives provide clear evidence that photoelectrons produced by visible light illumination of TiON matrix have flown from the TiON matrix to PdO nanoparticles.

When the visible light was switched off, the photoelectron production process stopped and no additional photoelectrons flew to the PdO nanoparticles. Instead, the direction of the charge transfer was reversed. As shown in Fig. 3, the portion of Pd^0 3d_{5/2} in the overall Pd 3d_{5/2} peak steadily decreased as the dark time increased. After several hours, most of the trapped electrons disappeared from the PdO nanoparticles, as indicated by the disappearance of the Pd^0 3d_{5/2} XPS peak. Thus, previously trapped electrons were released when the visible light was shut off. Fig. 4 schematically illustrates the process of photoelectrons flowing to PdO nanoparticles on TiON matrix under visible light illumination and the process of discharging of PdO nanoparticles after the visible light is switched off. Under visible-light illumination, the TiON matrix can produce \( e^-/h^+ \) pairs. The electrons can flow from TiON to PdO nanoparticles and are locally trapped at PdO nanoparticles, as demonstrated by the valence state change of Pd from +2 to zero. The trapping of charge carriers could decrease the \( e^-/h^+ \) pair recombination and subsequently increase the lifetime of charge carriers, beneficial to improving the photoactivity. When the visible light is switched off, these trapped electrons could be released, and these released electrons may flow back into the TiON matrix or react with oxygen/water to produce radicals if those species are available on the surface.

While the initial reception of photoelectrons by PdO will largely increase the lifetime of highly reactive holes, and thus enhance photocatalytic oxidation of organic and biological species, the subsequent release of the electrons in the dark may trigger the following reactions with oxygen or water:

\[
O_2 + e^- \rightarrow O_2^-
\]

\[
2O_2^- + 2H^+ \rightarrow 2 \cdot OH + O_2
\]

The production of \( \cdot OH \) radicals was recently verified by spin trapping EPR measurements. As long as the photoelectron discharge process carries on, catalytic oxidation would continue even after the illumination is turned off, thus creating a post-illumination catalytic memory effect.

Here, catalytic studies were performed on TiON/PdO fibers using \( E. coli \) as indicators. The fibers were synthesized by growing nano-sized TiON/PdO catalyst in the pore system of an activated carbon glass fiber (ACGF) template. On the individual glass fiber, a thin layer of TiON/PdO photocatalyst was immobilized. The immobilization of photocatalytic TiON/PdO onto the fiber template removes the need for recycling of photocatalysts in the powder form from the aqueous environment, and the fiber network provides increased contact efficiency for microorganism disinfection in water. Wild type \( E. coli \) AN 387 were used in this study as a model pathogen for both photocatalytic disinfection (under visible light illumination) and post-exposure disinfection (in the dark) experiments. Photocatalytic disinfection of \( E. coli \) was conducted by exposing the cells suspended in buffer solution with TiON/PdO fiber under visible light (\( \lambda > 400 \) nm) for varying time intervals. The buffer solution itself can keep \( E. coli \) alive up to 2 weeks. The survival ratio of \( E. coli \) were determined by the ratio of \( N_t/N_0 \), where \( N_0 \) and \( N_t \) are the numbers of colony-forming units at the initial and each following time interval, respectively.

Fig. 5(a) shows the \( E. coli \) survival ratio under visible light illumination with various treatments. Without photocatalysts or just with TiO_2 fiber photocatalysts, no clear bactericidal effect was observed. Similar tests had been conducted on pure PdO, and pure PdO by itself showed no bactericidal effect. With TiON, the bacterial concentration decreased with light exposure time but very slowly at a rate of about 50% reduction in bacterial concentration in 1 h, which could be attributed to its visible-light-induced photocatalytic capability by nitrogen-doping into TiO_2. TiON/PdO fiber photocatalysts show a much faster bacteria-killing kinetics. After only one hour of visible light illumination, the \( E. coli \) survival ratio drops to \( \approx 10^{-4} \). The much faster killing rate reflected the role of PdO nanoparticles in reducing electron–hole pair recombination rate so that holes had longer lifetimes to kill bacteria.
visible light for 10 h, TiON/PdO fiber samples were put into a dark atmosphere (open symbol), respectively. After being illuminated under visible light (>400 nm) for 10 h, TiON/PdO fiber samples were firstly illuminated by the same lamp for ~10 h. Then, the lamp was shut off and fiber samples were stored in a dark environment for 0 h (■), 3 h (□), 8 h (▲), and 24 h (×), respectively, before they were used to conduct disinfection experiments in the dark. This series of pre-experiment holding times were designed to examine how long the possible post-illumination disinfection could last. Disinfection of \( E. coli \) was conducted under the same experimental set-up as the photocatalytic disinfection experiment described above, only without the light illumination. Fig. 5(b) shows the \( E. coli \) survival ratio in the dark after holding in the dark for various times. The overall trend in the reduction of the \( E. coli \) survival ratio shows clearly that TiON/PdO fibers do possess the post-illumination disinfection capability. With the increase of the pre-experiment holding time (from 0 h to 24 h), their bactericidal efficiency drops gradually. After being kept in the dark for 24 h following the visible light illumination, they lost most of their bactericidal capability. Neither TiON/PdO nor TiON without light is known to be toxic to \( E. coli \) bacteria. Our observation here suggests clearly that their demonstrated post-illumination bactericidal effect is not just from the material system itself, since otherwise, the pre-experiment holding time could not have such a dramatic effect on the \( E. coli \) survival ratio. The post-exposure disinfection replies on the memory of the visible light illumination prior to the dark environment, which starts the cycle of charge flow to the PdO nanoparticles and the subsequent electron release. We must point out that the duration of post-illumination bactericidal effect is mainly dependent on the electron release rate from PdO nanoparticles after the visible light illumination is turned off, which is influenced by the surrounding environment. Under the current experimental conditions, the duration of the post-illumination bactericidal effect could last for more than 10 h, while it may be shortened when the air humidity increases.

If the electron release from the PdO nanoparticles is essential for the post-exposure catalytic memory effect, oxygen should have a strong effect on the dark disinfection rate because oxygen could react with the released electrons and produce highly reactively radicals as suggested in the reactions (1) and (2) above. To test this hypothesis, we compared the post-exposure disinfection efficiency of TiON/PdO fiber on \( E. coli \) in either air or in an enriched \( N_2 \) environment, respectively. Fig. 5(c) clearly demonstrates that the post-exposure disinfection efficiency of TiON/PdO fibers was much slower in the enriched \( N_2 \) environment. Since the only difference between those two experiments was the oxygen concentration in the environment, Fig. 5(c), when combined with the return of the valence state from zero to +2 in Fig. 3, provides strong support to the notion that the catalytic memory effect is closely related to the electron release from PdO nanoparticles. On the pure TiON, no post-exposure effect was observed.

**Conclusions**

In summary, clear evidence of charge transfer to and from PdO nanoparticles was observed on TiON/PdO photocatalysts. The illumination of TiON/PdO composite photocatalyst system sets in motion a cycle of electron flow from the TiON matrix to the PdO nanoparticles and the subsequent discharge when the light is switched off. In first half of the cycle, electrons are stored in the PdO particles, allowing holes produced by light illumination to be more effective in photocatalytic oxidation of bacteria. In the second half, release of electrons results in a catalytic memory effect, lasting up to 24 h in the dark, to limit bacterial growth. The enhanced photocatalytic effect from photoelectron trapping and the catalytic memory effect from electron release overcome two of the most critical limitations of the current photocatalysts, inadequate photocatalytic disinfection efficiency and lack of the activity in the dark. Although the post-exposure disinfection efficiency in the dark is not as high as the photocatalytic disinfection efficiency under visible light illumination, it enables the continuous operation of a unique robust catalytic disinfection system driven by solar/visible light illumination. The approach demonstrated with TiON/PdO in this study may occur in other transitional metal ion-modified anion-doped TiO\(_2\) material systems, and could provide the basis for design of new
generations of photocatalysts for a broad range of environmental applications.

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