Effect of Pd as Dopant on Photocatalytic Microbial Inactivation of TiO_2 Thin Film

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Introduction

TiO_2 thin film has excellent photocatalysi properties. Because of that it has various applications such as air clean-up, water purification, anti-bacteria, antifogging coating, gas sensors and so on[1,2].

When TiO_2 is exposed to light, by the absorption of ultra band gap light it can be excited and generate electron/hole (e^-/h^+) pairs in the conduction/valence band region. The electron/hole pairs move to the surface and convert oxygen to superoxide radicals ($O_2^{\cdot-}$) by reaction with the electrons and H_2O molecules to $OH^{\cdot}$ radicals by reaction with the holes; then this radicals can participate in the photodegradation process and oxidize the pollutant [3,4].

In spite of beneficial applications, there are some limitations for using this semiconductor. One of them is the necessity of photo activation of this layer with UV illumination. Another is charge carrier recombination that results in decreasing photocatalytic activity. Some metals such as iron, cobalt, and chromium have been used as dopants to overcome these limitations. Presence of these metals in the film decreases the recombination of electron/hole and acts as charge separator. The excited electrons are transferred from the conduction band of the semiconductor to the metal, thus preventing recombination [5].

This film had been prepared by different kinds of deposition techniques such as sputtering, chemical vapor deposition, sol gel processing and so on. Sol gel techniques have an ability for the production of homogeneous layers at a molecular level, ease and versatility of processing and lower crystallization temperature [1,4].

In this current study, we used Palladium for improving antibacterial properties of TiO_2 thin film. We prepared the TiO_2 thin film loaded with Pd, using particulate sol gel route on stainless steel 316 substrates, then Evaluating antibacterial activity of coating against S.aureus bacteria was done by static antibacterial tests.

Experimental part

The solution for TiO_2 thin film was prepared by adding hydrochloric acid (HCl) 37% (Merck) to titanium tetraisopropoxide(TTIP)(Merck). Then distillated water was added dropwise to the solution under stirring. The resulting solution was stirred at 50°C for at least 1 hour. The final molar ratio of TTIP:HCl:H_2O was 0.1: 0.2 : 53.3.

The preparation of Pd-TiO_2 sol was similar to that of TiO_2 sol. The only difference was that corresponding amount of palladium acetate(Merck) was added to TiO_2 sol to obtain 1%wt PdO in TiO_2 after calcination step.

Thin films of TiO_2 and Pd-TiO_2 were deposited over stainless steel 316. Plates were dipped into sols and after a few minutes withdrawn at the speed of 1mms^{-1}. They were allowed to dry at room temperature and baked at 100°C for 10 min. Finally they were annealed at 550°C for 1 hour.

These thin films were characterized by means of X-ray diffraction (XRD) and scanning electron microscopy (SEM).

The antibacterial assessment was carried out to ensure the effect of palladium doping on semiconductor photocatalytic properties of TiO_2. S.aureus --a gram-positive type of bacteria-- was cultivated in a nutrient broth (containing 10g/l beef extract, 10g/l peptone, 5g/l NaCl). Nano-structured samples were placed in a tube which contained solution. Then these tubes were put in the incubator, being exposed to UV light at 37°C.

Before coating the surface of stainless substrate with TiO_2, it was coated with a thin silica film. This thin film decreases the migration of substrate elements to TiO_2 coating that has a detrimental effect on photocatalytic activity of layer.

Results

FTIR analysis was used to identify the chemical changes which occurred in the solution. Wide and broad absorption peaks at about 576 Cm^{-1} and 3323 Cm^{-1} correspond to Ti-O-Ti and O-H surface vibration bands respectively. The absorption peak at about 1623 Cm^{-1} is related to H-O-H stretching vibration bands (figure 1).

Figure1:FTIR analysis of TiO_2 powder

XRD pattern of layer exhibited the presence of anatase crystalline phase. The peak at $2\theta=25.4$ corresponds to (101) reflections of the anatas phase, which has the greatest photocatalytic activity.

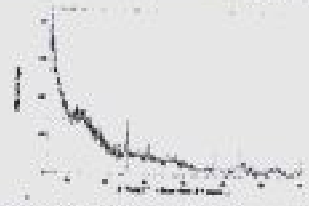

Figure 2: XRD pattern of TiO_2 coating at 550°C for 1 hour

Figure 3 illustrates SEM images of the layer that were ancaled at 550°C for 1 hour. (a) represents the layer without palladium doping and (b) represents the layer with 1% palladium content. The presence of palladium is shown with white separated particles in TiO_2 film. The radius of Pd^{2+} is larger than Ti^{4+}(r_{Pd2+}= 0.8Å; r_{Ti4+}=0.68Å), so it is unlikely that Pd^{2+} enter the TiO_2 lattice. Therefore Pd^{2+} is in direct contact with the TiO_2 nanoparticle.

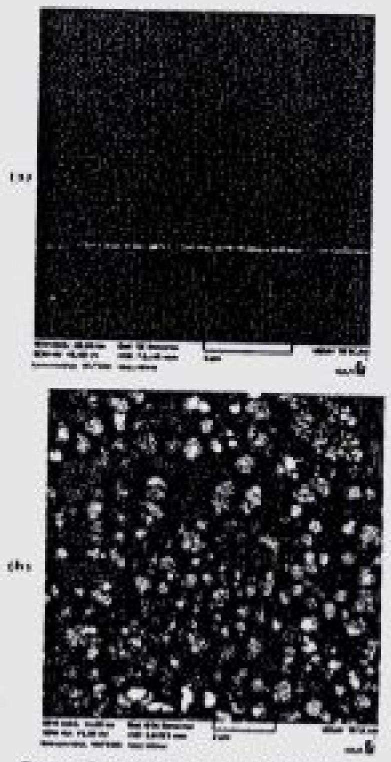

Figure 3. (a)SEM images of TiO_2 thin films (b) modified with 1% Pd content

Results of photocatalytic inactivation tests indicated that the samples which contained palladium show little photocatalytic activity without irradiation of UV light. These samples show high antibacterial activity for eliminating the S.aereus bacteria deposited after 2 hours' illumination with UV radiation. However, the relative number of bacteria which survived for TiO_2 coating is about 55% after 2 hours.

Conclusion

The doping with palladium enhances the photoactivation of semiconductor by UV. PdO-TiO_2 thin film indicated to be biocidally effective against S.aereus with a 100% kill in 2 hours.

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