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Au/TiO\textsubscript{2} Hierarchical Nanofibers Heterostructure: Controllable Synthesis and Enhanced Photocatalytic Performances

Chao Pan\textsuperscript{1} and Li Dong\textsuperscript{2}

\textsuperscript{1}College of Science, Dalian Ocean University, Dalian, Liaoning
\textsuperscript{2}College of Science, Dalian Nationalities University, Dalian, Liaoning

\textsuperscript{1,2}China

1. Introduction

Titanium dioxide, because of its unique optical, electrical and chemical attributes, is a widely studied material. It is well-known for its use in photocatalysis, gas sensors and dye sensitized solar cells and batteries. (Fujishima & Honda, 1972, Garzella et al., 2000, Meng et al., 2003, Ohko et al., 1998) Titanium dioxide (TiO\textsubscript{2}) was extensively studied for its applications in high performance photovoltaics. Now, the greatest challenge in TiO\textsubscript{2}-based photocatalysis is obtaining a highly efficient catalyst. Many efforts have been made to enhance the activity and it is found that the morphology is one of the important factors influencing the activity, which may lead to interesting shape-dependent properties. (Li et al., 2007)

In various morphologies, the hierarchical 3D architectures have been regarded as the more interesting structures due to the greater number of active sites than other 2D or 1D architectures. (Wu et al., 2006, Hu et al., 2007) Therefore, Preparation of high-quality hierarchical TiO\textsubscript{2} nanostructure of desired morphology is of great fundamental and technological interest. Up to now, various methods, including hydrothermal, (Sinha et al., 2009) solvothermal, (Zhu et al., 2009) vapor deposition methods, (Wu & Yu, 2004) as well as electrochemical approaches, (Zhang et al., 2010) have been used to synthesize the TiO\textsubscript{2} materials with different morphologies and architectures, such as nanotubes, (Su et al., 2008) hollow nanospheres, (Li et al., 2006) nanofibers, (Pan et al., 2007) nanorods, (Xu et al., 2008) nanocolumn, (Li et al., 2008) and dandelion-structured spheres. (Bai et al., 2008) Though there are many effective ways to enhance the photocatalytic activity, this approach also has some disadvantage. In particular, direct fabrication of complex hierarchical nanostructures with controlled morphologies, crystalline orientations, grain size, and surface architectures is one of the most challenging topics because of their promising functions. To overcome the above inconvenience, many attempts have been made to effectively fabricate TiO\textsubscript{2} photocatalysts, for example, by electrospun Nanofiber-based hierarchically organized TiO\textsubscript{2} nanocomposite. Electrospinning is a process by which high static voltages are used to produce nano and microscale fibers, with the fiber diameter in the range from less than 10 nm to over several micrometers. The variety of materials and fibrous structures that can be electrospun allow for the incorporation and optimization of various functions to the nanofiber, either during
spinning or through post-spinning modifications. (Teo & Ramakrishna, 2009, Pan et al., 2010) Recent efforts have made this technique a new platform for fabricating complex nanostructures having controllable hierarchical features. For example, a number of groups have demonstrated that electrospinning allows one to maneuver the secondary structures of individual fibers as well as to increase their structural complexity. (Ostermann et al., 2006, T.S. He et al., 2010, Cao et al., 2010, Wang et al., 2008)

Here we demonstrate that electrospinning and sputter coating technique can be combined to provide a simple route to formed the 3D hierarchical structural Au/TiO$_2$ nanofibers. The structure of samples prepared at different Au depositing time were investigated. The relationship between photocatalytic activity and the structure is discussed in detailed.

2. Experimental

2.1 Materials

Poly (styrene-co-methacrylic acid) (SMAI) was synthesized by our group. Titanium tetraisopropoxide (Ti(OC$_4$H$_9$)$_4$), N,N-dimethyl formamide (DMF), tetrahydrofuran (THF) and acetic acid (HAc) were purchased from Shanghai Guanghua reagent Plant. These chemicals were used without further purification. Distilled water was used as hydrolysis agent. DW-P403-1AC High Voltage supply was obtained from Tianjin Dongwen High Voltage Power Supply Co. A TS2-60 multi-syringe pump was obtained from Baoding Longer Precision Pump Co., ltd.

2.2 Preparation of Au/TiO$_2$ nanofibers

2.2.1 Synthesis of copolymer SMAI

A brief of synthesis process is as follows: The boiling medium polymerization technique was used for the synthesis of a copolymer SMAI. 6 mL of MAA monomer, 600 mL water and 0.6 g KPS was added to the three-necked flask, and the stirring speed was set at 300 rpm. The mixture was raised to reflux, and the medium had boiled. The reaction was stopped after 2 h. A particular describe view the references. (Gu et al., 2007)

2.2.2 SMAI/ Ti(OC$_4$H$_9$)$_4$ nanofibres

In a typical procedure, 2.48 g of titanium tetraisopropoxide (Ti(OC$_4$H$_9$)$_4$) was mixed with 3 mL of acetic acid. After 30 min, this solution was removed from the glove box and added to 9.87 mL of THF/DMF=6:4 (wt) mixture containing 1 g of SMAI, followed by magnetic stirring for 1 h (with the solution held in a capped bottle). The mixture was immediately loaded into a plastic syringe (5ml) equipped with a 6 gauge stainless needle. The needle was connected to a high-voltage supply that is capable of generating DC voltages up to 15 kV. The feeding rate for the precursor solution was controlled using a syringe pump. A copper grid was placed 15 cm below the tip of the needle to collect the nanofibers. The as-spun nanofibers were left in air for 5 h to allow the hydrolysis of Ti(OC$_4$H$_9$)$_4$ to go to completion.

2.2.3 TiO$_2$ nanofibers

The SMAI/ Ti(OC$_4$H$_9$)$_4$ fibers were heated at 130 °C for 2 h and calcined at 450 °C for 2 h in air at a heating rate of 0.5 °C •min$^{-1}$ from 130 °C to 450 °C to completely eliminate the organics. After cooling to room temperature, TiO$_2$ fibers were obtained.
2.2.4 Au/TiO$_2$ nanofibers

A Cu plate with SMAI/ Ti(OC$_4$H$_9$)$_4$ composite nanofibers on it was clipped by a holder (Hitachi E-1010 Ion Sputter). The chamber was evacuated to 1.33 Pa ($10^{-2}$torr) by a mechanical pump, and the sputtering current was controlled with 15mA, for sputtering of Au started. The process time was adjustable at 5 sec, 40 sec, 2min, and 3 min. Finally, the SMAI was selectively removed from these nanofibers by treating them in air at 450 °C for 1 h and then cooled down to room temperature. The morphology and diameter of Samples were measured with SEM (S-3000 of Hitachi).

2.3 Photocatalytic activity measurements

The photocatalytic activities of the TiO$_2$: Au hybrid nanofibers for the photodecomposition of acetaldehyde gas were investigated. This was carried out at room temperature. An O$_2$(20%)-N$_2$ gas mixture adjusted to a relative humidity of 50% was used to fill a 500 mL Pyrex glass photocatalytic reaction vessel. Then 8mL acetaldehyde (1 vol% in N$_2$, Takachiho, Japan) were injected into the reactor using a syringe. After equilibrium in the dark for 2 h, the sample was irradiated with UV light with an intensity of 1 mW cm$^{-2}$, and the concentrations of CO$_2$ and acetaldehyde were followed by gas chromatography (GC-8A, Shimadzu). The sample size was 2.5×2.5 cm$^2$, and the weight of the Au-TiO$_2$ hybrid nanofibers was 5.3±0.1mg.

3. Results and discussion

3.1 Characterization of prepared TiO$_2$ nanofibers and Au/TiO$_2$ nanofibers

Figure 1a shows the SEM image of TiO$_2$/SMAI composite nanofibers electrospun from a DMF/THF solution. The average diameter of this sample was 470-500 nm. As the SMAI was selectively removed by burning the sample in air at 450 °C for 1 h, TiO$_2$ nanofibers with 200-300 nm and smooth surface were synthesized (Fig. 1b) The formation of the TiO$_2$ nanofibers is considered to involve the following steps during the fabrication. Firstly, when the Ti(OC$_4$H$_9$)$_4$ containing polymer solution was ejected from the orifice of the syringe, a composite fiber composed of SMAI and Ti(OC$_4$H$_9$)$_4$ forms. Then the Ti(OC$_4$H$_9$)$_4$ in the fiber was hydrolyzed to titania in the SMAI fibers by moisture in the air. The following calcination at 450 °C removes the polymer and crystallizes the titania. As a result, the TiO$_2$ fibers appear. Figure 1c shows the micrograph of TiO$_2$ nanofibers coated with Au and then annealed at 450 °C for 1hr. In the SEM micrographs, the sintering of Au nanoparticles takes place, resulting in organization. It is clear that the islands are formed by Au.
Fig. 1. (a) SEM image of TiO$_2$/SMAI nanofibers that were electrospun from an DMF/THF solution. (b) SEM image of the same sample after it had been calcined in air at 450 °C for 1 h. (c) SEM image of the same.

3.2 Characterization of the Au–TiO$_2$ nanofibers surface
Figure 2 shows the XPS spectra for nanofibers of TiO$_2$ with Au. The peaks are marked with the figure to which they correspond. Figure 2a shows prominent peaks at

Fig. 2. a: Wide scanning XPS spectra; b: High energy resolution XPS of Au4f.
400.0 (N1s) and 284.8 eV (C1s). The peaks at 360 eV (Au4d3) and 345 eV (Au4d5), which are well visible, and small peaks at 84 eV (Au4f7/2) and 88 eV (Au4f5/2) indicate the presence of gold. (Database) The Au4f gold doublet size is on the order of the noise but is distinguishable at higher energy resolution (see 2b). Figure 2b show the high energy resolution XPS spectra of the Au–TiO2 nanofibers described above. The Au4f doublet at 84 (Au4f7/2) and 88 eV (Au4f5/2) is clearly resolved. The characteristic doublet at 84 (Au4f7/2) and 88 eV (Au4f5/2) together with the peaks at 360 (Au4d3) and 345 (Au4d5) eV, respectively, confirm the presence of metallic gold. (Ting et al., 1994) This indicates that that metallic gold was successfully converted into TiO2 nanofibers surface.

3.3 The influence of the ion beam sputtering time on the morphology of fibers and the amount of Au loading

To investigate the influence of deposition time on the morphology of the nanofibers, 5s, 40s, 2min, and 3min of ion beam sputtering time were adjusted, respectively and the SEM images were shown in Figure 3.

The electric conductivity of TiO2 nanofibers was not good. As shown in Fig. 3a, there was a charging phenomenon because the content of Au loading after 5sec was not enough to conduct the electrons. The charging phenomenon was reduced with the increasing of Au
deposition time, Figs. 3 (b) and (c). Meanwhile, some islands were formed on the surface. The Au islands became more with increasing of time. The Au islands were stacked with the clusters of the Au nanoparticles. The Au nanoparticles were implanted into TiO$_2$ nanofibers with a long sputtering time such as 3min (Fig. 3 d). The Au islands were in contact with each other, and heating process provided the energy for self-diffusion. Compared with Fig. 3b-c, there are fewer voids on the TiO$_2$ surface. Additionally, this clearly indicates that the morphology of the Au/TiO$_2$ nanofibers is dependent on the sputtering time. Simultaneously, we can see obviously that the content of Au loading increased with increasing of sputtering time.

The above results of Au deposition could be explained by a thin-film growth mode. (Kasuga et al., 1998; Lahav et al., 2003) As shown in Fig. 4, the period experienced two stages: (a) island, and (b) layer. When the smallest stable clusters are deposited on the TiO$_2$ surface and grow in three dimensions to form islands, it is called island growth mode, and the deposited atoms or molecules are more strongly bound to each other than to the TiO$_2$ surface. This usually happens in the system of Au on insulators. In our system, Au nanoparticles are stable to bind to each other, and TiO$_2$ nanofibers are insulating substrate. For the beginning there were many Au nanoparticles formed on the surface as show in Fig. 4(a), this is Au island form stage. Then the particles became larger and stacked with each other when the time of deposition was increased to 3 min as show in Fig. 4 (b). And the stacked layer became much thicker, this is Au layer form stage.

![Fig. 4. Basic modes of Au thin-film growth: (a) island, and (b) layer.](image)

3.4 Photocatalytic activity

We investigated the photocatalytic decomposition of acetaldehyde on the Au/TiO$_2$ (3min) complex nanofibers photocatalyst. A typical result for the photodecomposition of acetaldehyde is shown in Figure 5a.
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Fig. 5. a: Plot of concentration versus irradiation time for the degradation of acetaldehyde photocatalyzed by a TiO$_2$: Au nanofibers (3min). The sample area was 6.25 cm$^2$, and the light intensity was 1 mW cm$^{-2}$. b: Time courses for UV photodegradation of acetaldehyde. Curve a: Without photocatalyst; b: TiO$_2$ nanofibers; c: Au/TiO$_2$ nanofibers (40s); d: Au/TiO$_2$ nanofibers (2min).

The concentration of acetaldehyde dropped slightly in the dark but decreased quickly as a function of irradiation time. The decrease in acetaldehyde concentration could be fitted with a first-order kinetic model, which is a common phenomenon in diffusion-controlled photocatalytic processes.(Gibson et al., 2001) A parallel increase in the concentration of CO$_2$ was observed. There were no traces of acetaldehyde (in the photoreactor) after about 70 min reaction. Accordingly, the expected stoichiometric CO$_2$ concentration was generated. Indicating the complete mineralization of acetaldehyde on the TiO$_2$: Au fibrous photocatalyst under UV illumination. Figure 5b shows the change of concentration of acetaldehyde gas over time under UV irradiation in the presence of different TiO$_2$ materials. Control experiments indicated that the photocatalytic reaction hardly proceeded in the absence of TiO$_2$ (curve a). After 70 min, up to 54% (curve b) of the gaseous acetaldehyde was degraded in the presence of TiO$_2$ nanofibers. For the Au/TiO$_2$ nanofibers, we studied the influence of the Au depositing time on the photocatalytic decomposition of acetaldehyde. For 40s of the Au depositing time (curve c), after 70 min, up to 69.4% of the gaseous acetaldehyde was degraded. For 2 min of the Au depositing time, ca. 94% gaseous acetaldehyde was degraded to CO$_2$ and H$_2$O under the same conditions (curve d). This indicates that the Au depositing time influenced the photocatalytic effect, the speed of decomposition increased with the increasing of the Au depositing time. The photocatalytic activity of the Au/TiO$_2$ nanofibers was higher than TiO$_2$ nanofibers. The main reasons for that change are as following: Firstly, the open 3-D structure of the nanofibers photocatalyst has a beneficial effect on its activity.(Pan et al., 2009) Secondly, the Au cluster deposited on TiO$_2$ surface functions as the electron trap center, and the perimeters between Au and TiO$_2$ act as the active site for acetaldehyde decomposition. Thirdly, the effect of Au nanoparticles covered the surface of TiO$_2$ nanofibers enhanced as function of the sputtering time. This process inhibited ulteriorly the recombination rate of the photo-produced electrons and holes, as shown in Scheme 1. The three reasons complementary promoted the photocatalytic effect of the Au/TiO$_2$ nanofibers.
4. Conclusions

In conclusion, Au/TiO$_2$ nanofibers were successfully produced by a combination of electrospinning and sputter coating technique. The Au morphology on the obtained TiO$_2$ nanofibers is dependent on the depositing time, the Au surface becomes more compact and the wall-structure seems more complete with increasing Au depositing time from 40s to 3min. The thin-film growth mechanism of Au on TiO$_2$ nanofibers can be explained in terms of islands mode which is usually applied to the systems of metal on insulator. Photocatalytic results showed that the photocatalytic activity of the Au/TiO$_2$ nanofibers was higher than TiO$_2$ fibers. In addition, the interconnected Au/TiO$_2$ nanofibers structure also opens up the opportunity of Dye-sensitized Solar Cells and photocatalytic functions in the same material.

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Scheme 1. Interfacial charge transfer process of Au-doped TiO$_2$ nanocomposites under the irradiation of UV light.
5. References


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As an important one-dimensional nanomaterial, nanofibers have extremely high specific surface area because of their small diameters, and nanofiber membranes are highly porous with excellent pore interconnectivity. These unique characteristics plus the functionalities from the materials themselves impart nanofibers with a number of novel properties for advanced applications. This book is a compilation of contributions made by experts who specialize in nanofibers. It provides an up-to-date coverage of in nanofiber preparation, properties and functional applications. I am deeply appreciative of all the authors and have no doubt that their contribution will be a useful resource for anyone associated with the discipline of nanofibers.

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