Femtosecond laser deposition of TiO_2 nanoparticle-assembled films with embedded CdS nanoparticles*

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(Received 14 October 2013)

Based on the normal pulsed laser ablation method, femtosecond pulsed laser deposition (fs-PLD) is adopted in vacuum for the production of TiO_2 nanoparticle-assembled films. We study the morphology and electronic characteristics of TiO_2 nanoparticle-assembled films deposited at different oxygen background gas pressures from high vacuum (~10^{-4} Pa) to 100 Pa and different deposition time. Our results show that TiO_2 nanoparticle-assembled films obtained in high vacuum present both a mixture with rutile phase and anatase phase and a pure rutile phase. At the same time, there are more mesoporous structures in the film after annealing, which is beneficial for the enhancement of photocatalytic activity. In water splitting experiment, part of the TiO_2 nanoparticle-assembled films embedded with a small mass fraction of CdS nanoparticles (~5%) present an interesting photocurrent enhancement with a maximum value of ~0.2 mA/cm^2 under a solar simulator.

Document code: A **Article ID:** 1673-1905(2014)01-0043-4

DOI 10.1007/s11801-014-3196-6

Currently, femtosecond pulsed laser deposition (fs-PLD) in vacuum has been demonstrated to be a versatile tool for the preparation of metal and semiconductor nanoparticle films, as well as for the synthesis of innovative magnetic or electronic films[1-5]. TiO_2 is one of the most intriguing semiconductors for its various properties, such as large energy band width and controllable surface property[6-15]. Even if it is more popular to generate hydrogen (H_2) by using the nanotube arrays as electrodes[8-11], the mesoporous TiO_2 film also becomes another useful method for its easy preparation in water splitting reaction[12-15]. But most of the mesoporous TiO_2 films mentioned in previous reports are synthesized in solution. On the basis of our previous work about fs-PLD[1-3,16,17], in this paper, we research the morphology and electronic characteristics of TiO_2 nanoparticle-assembled films deposited by fs-PLD method in a vacuum chamber, at different oxygen background gas pressures from ~10^{-4} Pa to 100 Pa.

Fig.1 shows the schematic diagram of the device in fs-PLD method. The TiO_2 nanoparticles were produced by irradiating a rotating TiO_2 crystal target with 300 fs and 527 nm Nd:glass laser pulses at the incident angle of 45°. Lixia Sang et al[10] proved that the deposited CdS can enhance the charge-transfer properties of TiO_2 film. So here we select CdS nanoparticles with a minor mass percentage of ~5% to be embedded into the TiO_2 nanoparticles-assembled films with a dimension of 0.5 cm×0.5 cm on Ti substrate during deposition. All the experiments were carried out at the maximum laser output energy, and the laser fluence on the target was around 1.4 J/cm^2. The produced nanoparticles were collected on Ti substrates located at 35 mm away from the target surface in normal direction at room temperature, and the films were characterized by scanning electronic microscope (SEM) and X-ray diffraction (XRD).

* This work has been supported by the National Natural Science Foundation of China (Nos.11104201 and 51376013), the Open Fund of Key Laboratory of Opto-electronic Information Technology, Ministry of Education, in Tianjin University, and the China National Scholarship Fund.

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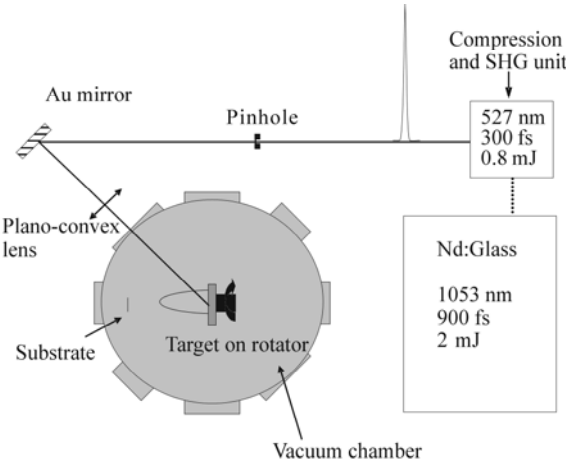


Fig.1 Schematic diagram of the device for fs-PLD

Photoelectrochemical measurements were performed in the photocell using a configuration with three electrodes shown in Fig.2, which consists of the prepared samples as working electrode, platinum gauze as counter electrode, a saturated Ag/AgCl electrode as reference, and Na_2SO_4 solution as electrolyte. A solar simulator (91160, Newport, USA) was used as light source. An AM 1.5 filter was used to obtain the sun light, which was illuminated on the photoanode with intensity of 100 mW/cm^2. All the data were scanned and collected three times to guarantee the reliability on an electrochemical analyzer (CHI 614C, CH Instruments).

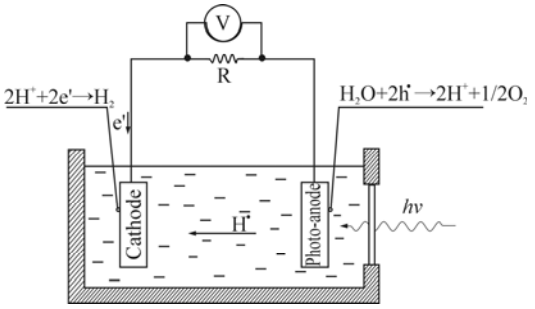


Fig.2 Schematic diagram of water splitting measurement experiment

Because the PLD vacuum environment can affect the crystalline quality of the film and the deposition time influences the film thickness[3], we change the vacuum chamber pressure by an oxygen injection from high vacuum (~10^{-4} Pa) to low pressure (100 Pa) at different fs-PLD time. The different conditions are listed in Tab.1.

Tab.1 Different deposition conditions of fs-PLD

Sample	#1	#2	#3	#4	#5
Pressure (Pa)	10	100	10^{-4}	10	10^{-4}
Time (h)	3	3	3	1.5	1.5

Here we just select three kinds of chamber pressures of 10^{-4} Pa, 10 Pa and 100 Pa to compare the effects of photocurrent generation, while the laser deposition time significantly changes the thickness of nanoparticle film. The annealing condition is set as the maximum temperature of 500 °C for 30 min.

Fig.3 shows the morphologies of sample 3 before and after annealing. From Fig.3, one can observe that there is no significant difference between the images before and after annealing. It can be seen from Fig.3(b) that more mesoporous TiO_2 structures are generated after annealing, which is quite beneficial to water splitting. For the other results of films prepared in different chamber pressures, the morphologies show too many differences.

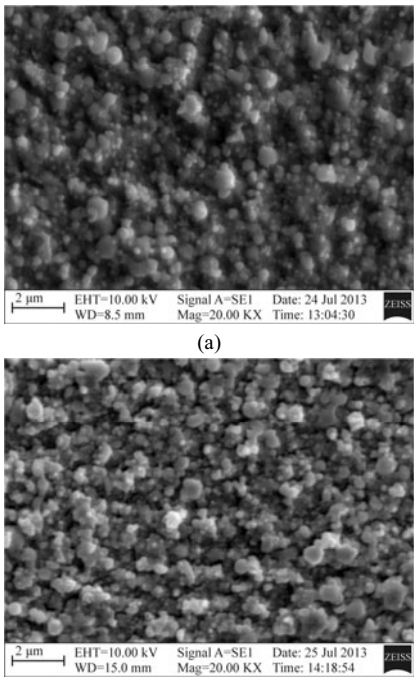
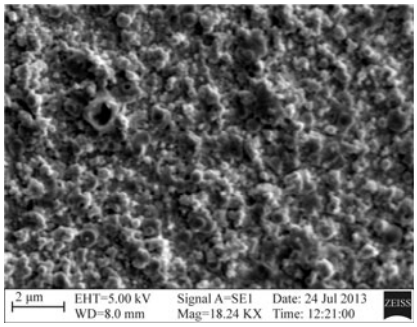
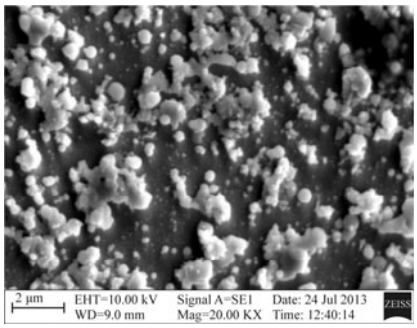


Fig.3 SEM images of sample 3 (a) before and (b) after annealing

Fig.4 shows the surface images of samples 1 and 2 before annealing. It can be seen from Fig.4 that the thickness of the nanoparticle film is reduced with the pressure from high vacuum (~10^{-4} Pa) to 100 Pa at fixed deposition time. In particular, the substrate surface can be seen in Fig.4(b). It means that the deposition rate of fs-PLD is significantly affected by the chamber pressure. From 10 Pa to 100 Pa, the deposition rate is decreased very sharply, which shows the same trend for TiO_2 film fabricated by Silvia Tuzi et al[17]. For Fig.4(a), the mesoporous structures in sample 1 are also less than those in sample 3, while the surface morphologies of samples 4 and 5 are similar to those of samples 1 and 3, respectively. Owing to the film scale of 0.5 cm×0.5 cm, very little amount of H_2 can be generated and collected by our experiment. So here we select samples 3 and 5 to analyze the solar photocurrent generation with water splitting measurement method shown in Fig.2.



(a)

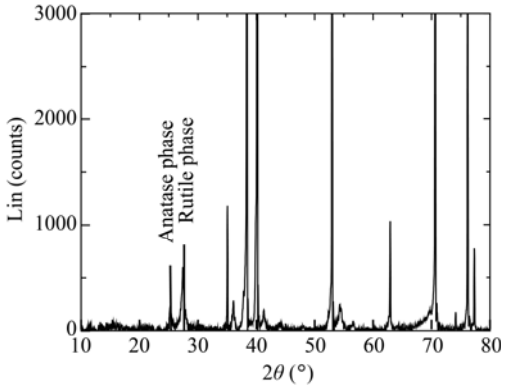


(b)

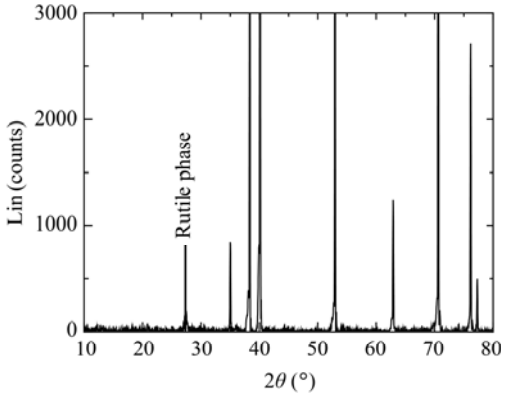
Fig.4 SEM images of (a) sample 1 and (b) sample 2 before annealing

Fig.5(a) and (b) show the XRD results for samples 3 and 5, respectively. It can be seen from Fig.5 that sample 3 shows a mixture with rutile phase and anatase phase, which is much better for application in water splitting measurement under a solar simulator, while sample 5 only shows the rutile phase, but CdS crystalline phase cannot be found in either sample 3 or 5. One possible reason is that CdS is too little and is embedded in the TiO_2 nanoparticle film, and XRD method can not scan them or isn't sensitive enough to find them from the surface of film.

The photocurrent measurement results for samples 3 and 5 illuminated by the solar simulator are shown in Fig.6. One surprising thing is that the photocurrent of sample 5 (0.2 mA/cm^2) is much higher than that of sample 3 (0.14 mA/cm^2), even if the thickness of sample 5 is much thinner. Following the deposition rate obtained by Silvia Tuzi et al [15], the thicknesses of samples 3 and 5 are just about 160 nm and 80 nm, respectively. A possible reason is that the photoelectron transmission mechanism is quite different from the TiO_2 tube film reported in Refs.[8]–[11], where the solar light can arrive at the bottom of the nanotube film directly or through diffuse scattering. But for our mesoporous structured TiO_2 nanopaticle films, this is not so easy. So the diffusion lengths for the two cases are quite different. For TiO_2 tube film, the thicker the film, the better the solar light absorption. But for mesoporous structured TiO_2 nanopaticle film, when the thickness is larger than the diffusion length (maybe between 80 nm and 160 nm at some points), the thicker nanoparticle TiO_2 would be a block for the photocurrent transmission. So the photocurrent of sample 3 is much lower than that of sample 5. But both of the two samples above present a higher photoelectron transmission rate based on the previous nanotube TiO_2 results[10]. For the further analysis on this point, we will discuss this in detail based on the further experiment from the crystalline chemical reaction and theory analysis in the near future.



(a) Sample 3



(b) Sample 5

Fig.5 XRD spectra of samples 3 and 5

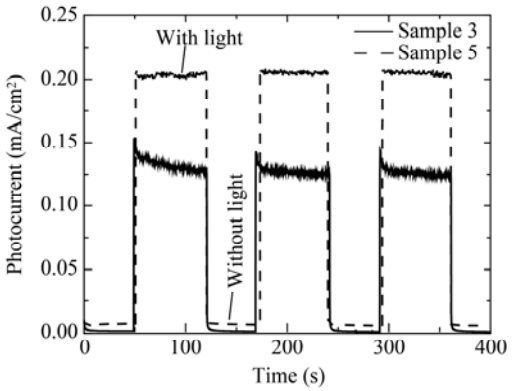


Fig.6 Photocurrent measurement results for samples 3 and 5

In conclusion, we show a method to prepare TiO_2 nanoparticle-assembled films with embedded CdS nanoparticles by fs-PLD. Our results show that the films deposited in high vacuum present a better mesoporous structured morphology with agglomerates of nanoparticles deco-

rated with smaller particles, thus improving the effective surface of the system. After annealing, the crystalline samples show a mixture with rutile phase and anatase phase or a pure rutile phase. We observe that the TiO_2 nanoparticle films embedded with a small mass fraction of CdS nanoparticles (~5%) present an interesting photocurrent enhancement and higher photoelectron transmission rate. But the thickness of TiO_2 nanoparticle film is limited by the light diffusion length, otherwise thicker nanoparticle film will be a block for the photocurrent transmission. The preliminary results show that the nanoparticle-assembled film produced by fs-PLD is promising as an important field of application for water splitting.

Acknowledgements

The authors thank Professor Antonio Vecchione for helpful discussion.

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