

The study on photochromism activity of Ag-TiO₂ aerogel

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Ag loaded TiO₂ aerogels were synthesized by sol-gel and supercritical drying methods. Anatase-TiO₂ phase was obtained after post-annealed at 400°C for 4 hrs in air. AFM image revealed that post-annealed sample at 400°C consisted by the rod-like particles with several hundreds nanometer. The colorless sample changed to dark brown after the UV irradiation, and returned to the initial state after the white light irradiation. The absorption spectra exhibited a little red shift after the UV irradiation, which may attribute to the appearance of metal Ag particles in TiO₂ matrix. Due to the poor crystal quality and no aggregation for Ag⁺ during post-annealed process, no big wavelength tuning had happened as speculated based on particle size and surrounding media.

Key words: Ag-TiO₂ aerogels, photochromism, particle size, crystal structure, surrounding media

1. INTRODUCTION

Photochromism materials, which change their colors reversibly in response to light, can be applied to smart windows, displays and optical memories. Photochromism occurs in a wide variety of materials, including both inorganic and organic compounds. Silver halide is one of the representative material.^[1-3] Recently, multicolour photochromism of Ag-TiO₂ system thin film was reported by Ohko et al.^[4] and Okumu et al.^[5] Okumu et al. proposed the mechanism of multicolour photochromism behaviour caused by a particle-plasmon-assisted electron transfer from silver nanoparticles to TiO₂ and subsequent trapping by adsorbed molecular oxygen. The characteristic point of this multicolour photochromic material is semiconductor porous structure loaded with noble metal particle. To study the mechanism and furthermore to meet the requirement of applications for this multicolour material, such as rewritable or electronic paper, the following work was done. Sol-gel and supercritical drying methods were applied to synthesize Ag loaded TiO₂ aerogels for investigating the mechanism and developing new system materials. Because of the sizes, shapes of noble-metal particles and dielectric properties of the surrounding media have big affects on plasma resonance wavelength, the aim of this work is to investigate the effects of some parameters, such as: particle sizes of Ag and crystal structure of surrounding media (TiO₂), on the photochromic activity of Ag-TiO₂ system.^[6]

2. EXPERIMENTAL

Titania wetgel was prepared using four precursors: titanium tetra iso-propoxide (Ti(PrOH)₄), deionizer water (H₂O), nitric acid (HNO₃) and ethanol (EtOH). The optimum molar ratios of the precursors were consequently identified as about 1:20:2.5:0.08. Titania sol was obtained by mixing the precursors following some procedures. After TiO₂ sol turned to wetgel, the obtained wet gel was soaked into the AgNO₃ solution for one week for the complete absorption of Ag⁺ particles onto the gel networks in the sealed vessel. To remove residual nitric acid and water in wet gel, the metal particle soaked wet gel was rinsed in isopropanol solution in several times. Then the metal particle loaded wet gel was treated in supercritical drying process under 9.11 MPa and 100 °C for 2 hr for the formation of titania aerogel (AG).

In order to investigate the effects of some parameters, such as: particle sizes of Ag and crystal structure of surrounding media (TiO₂), on the photochromic activity of Ag-TiO₂ system, three typical samples were selected for characterization and discussion. Sample 1 was as-prepared aerogel, samples 2 and 3 were post-annealed aerogels at 400°C and 200°C for 4 hours, respectively.

The crystal structure of the prepared samples were identified by X-ray diffraction (XRD; RINT 2000, Rigaku), the surface morphology and particle shape were observed by atomic force microscope (AFM, JSPM-5200TM, JEOL), To observed photochromic behavior of the Ag-TiO₂ aerogels, the samples were irradiated by using commercial black-fluorescent-light (50

mW/cm², 300-400 nm), monochromic visible light using xenon lamp. The optical reflectance and transmittance of the irradiated films were measured immediately after irradiation by UV-VIS Spectrophotometer (JASCO-V570, spectral range 250-2000 nm)

3. RESULT and DISSCUSSION

3.1 Crystal structures

XRD patterns of as-prepared, post-annealed at 200 °C and 400 °C Ag-TiO₂ aerogels are shown in Fig. 1. Good anatase-TiO₂ phase can be detected after post-annealed at 400°C for 4 hrs in air. No any peak originated from Ag can be found probably due to the silver particles are existing as Ag⁺ lasting from raw materials (AgNO₃) at low temperature heat-treated condition (400°C). The sample heat-treated at 200 °C exhibits very weak anatase-TiO₂ peak because of the bad crystal quality. The as-prepared Ag-TiO₂ aerogels are identified as amorphous.

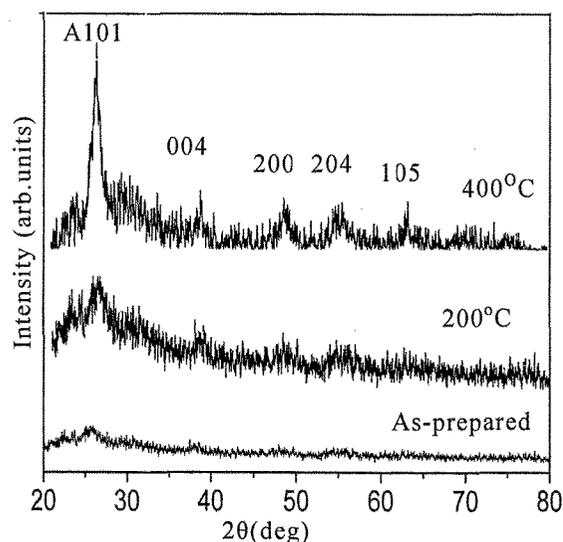
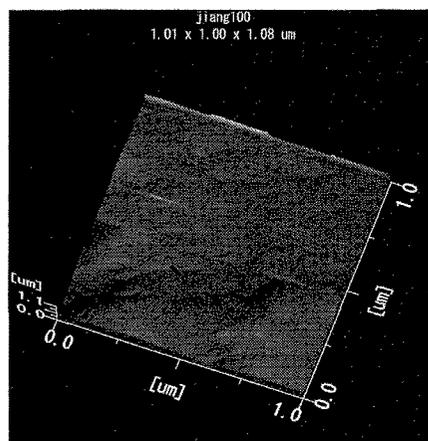


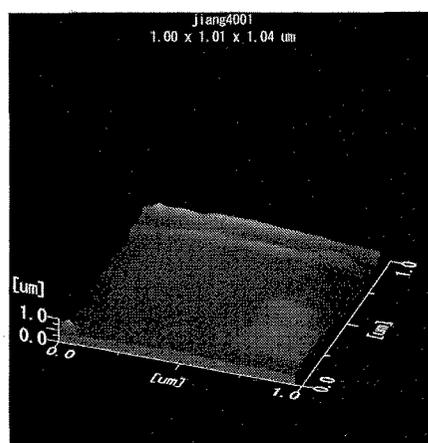
Fig. 1 XRD patterns of as-prepared Ag-TiO₂ aerogels, heat-treated at 200 °C and 400 °C for 4h, respectively.

3.2 Surface morphologies

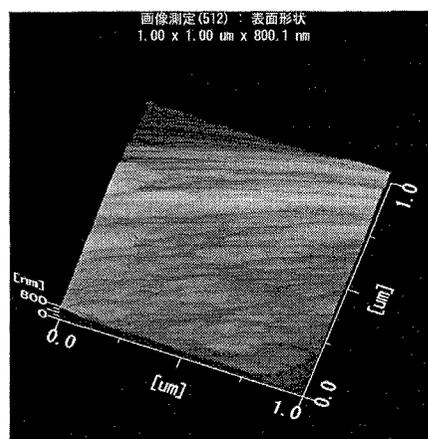
To observe the particle sizes of Ag depending on the post-annealed temperature, AFM analysis were employed for the powders spread on glass substrate. Figure 2 (a), (b) and (c) give the AFM images for the as-prepared, post-annealed at 200 °C and 400 °C aerogels, respectively. Probably due to the affection of amorphous aerogels, no obvious shape of particles are found for as-prepared and post-annealed at 200 °C, respectively as shown in Fig. 2 (a) and (b). While for the sample consisted of crystal anatase-TiO₂ due to post-annealed at 400 °C, rod-like particles with several hundreds nanometer can be observed in Fig. 2 (c). Possibility, because of no photo- or electro-reduction of Ag⁺ to crystal Ag particles, it is difficult to discern Ag with TiO₂ in Fig. 2 (c).



(a)



(b)



(c)

Fig. 2 AFM images of Ag-TiO₂ aerogels: (a) as-prepared (b) post-annealed at 200 °C (c) post-annealed at 400 °C.

3.3 Optical properties

Fig. 3 (a), (b) and (c) show the sample's images of post-annealed at 400 °C Ag-TiO₂ aerogels powders sandwiched by glass slides. The colorless sample changed

to dark brown after the UV irradiation (Fig. 3 (b)), and returned to the first state after the white light irradiation (Fig.3 (c)). The color change originated by monochromatic light irradiation is too obvious to be observed by digital camera, while the absorption spectrum can provide a proof for those of change.

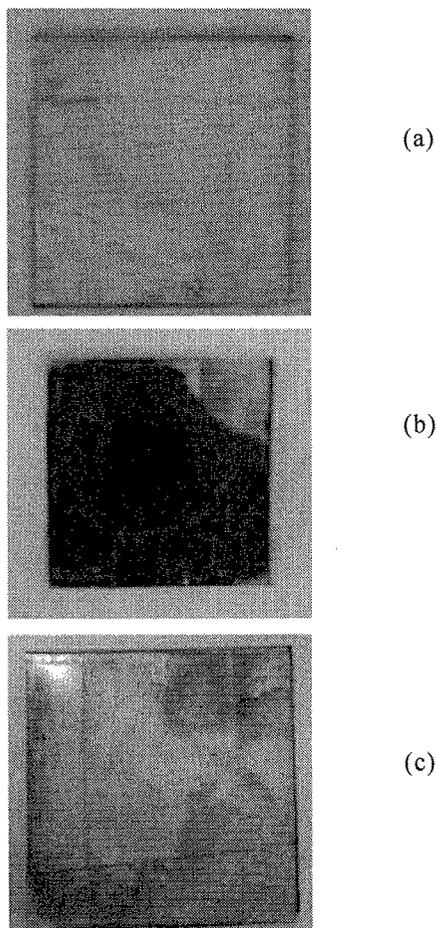


Fig.3 Digital camera photos of Ag-TiO₂ aerogels post-annealed at 400 °C Ag-TiO₂ aerogels powders sandwiched by glass slides. (a) Before the irradiation (b) after the UV irradiation, and (c) after the white light irradiation.

Fig. 4 (a), (b) and (c) give the absorbance spectra of three Ag-TiO₂ AG samples: as-prepared, post-annealed at 200 °C and 400 °C, before and after irradiation respectively from 300-800 nm in wavelength. After the UV irradiation, the absorbance increased about 40%, 15% and 15% from 400nm to 800 nm comparing with those of initial absorbance spectra for the as-prepared and two post-annealed samples as shown in Fig. 4 (b) and (c), respectively. Both the two annealed samples returned to initial state after irradiation by visible white lights as identified by absorbance spectra in Fig.4. For the no post-annealed sample, it also shows the similar tendency with those of two post-annealed samples. It is worthwhile to note that the absorption spectra exhibit a little red shift

after the UV irradiation. Part of Ag⁺ from source material AgNO₃ was photo-reduced to metal Ag by UV irradiation. Consequently, the red shift of the absorption spectra after UV irradiation may attribute to the appearance of metal Ag particles in TiO₂ matrix.

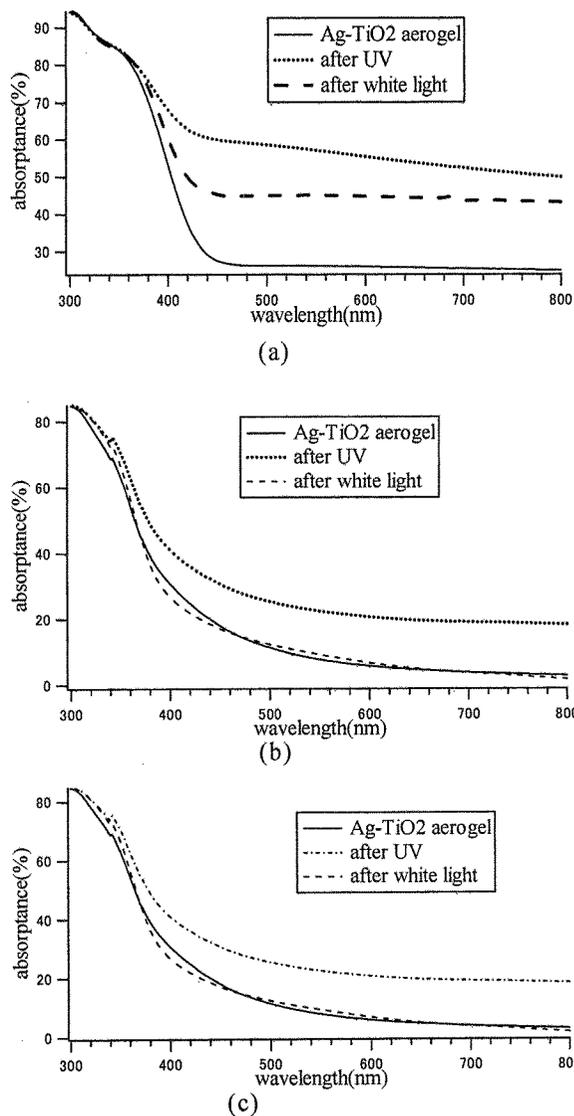


Fig.4 Absorbance spectra of samples before and after the irradiation (a) as-prepared (b) post-annealed at 200 °C (c) post-annealed at 400 °C

No broaden behavior of absorbance spectra depending on the size of Ag particles can be observed which may relates with the low post-annealed temperatures and the chemical states of Ag. Possibly, Ag⁺ particles from raw AgNO₃ material are not so easy to aggregate as that of metal Ag particles at 400 °C. Furthermore, the crystal structure of the surrounding TiO₂ media around Ag particles does not show any effect on the shapes and edges of absorption spectra for all of three samples. Two reasons are considered for explaining to this result, firstly, the amount of loaded Ag particles is not enough to exhibit metal behavior because the absorption curves are closer to TiO₂ and hardly any effect from Ag; secondly, although

anatase phase is obtained after post-annealed at 400°C, due to the poor crystal quality, no big difference would be arise for the refractive indices for the three synthesized host AG.

4. CONCLUSIONS

Ag loaded TiO₂ aerogels were synthesized by sol-gel and supercritical drying methods. Anatase-TiO₂ phase was obtained after post-annealed at 400°C for 4 hrs in air. AFM image revealed that post-annealed sample at 400°C consisted by the rod-like particles with several hundreds nanometer. The colorless sample changed to dark brown after the UV irradiation, and returned to the initial state after the white light irradiation. The absorption spectra exhibited a little red shift after the UV irradiation, which may attribute to the appearance of metal Ag particles in TiO₂ matrix. Due to the poor crystal quality and no aggregation for Ag⁺ during post-annealed process, no big wavelength tuning had happened as speculated based on particle size and surrounding media.

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