Visible light induced superhydrophilicity on the WO_3/ITO/$CaFe_2O_4$ heterojunction thin film

Zhifu Liu, Masahiro Miyauchi*

Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

E-mail: m-miyauchi@aist.go.jp; Tel/Fax: +81-29-861-6299

1. Preparation of the heterojunction films

The $CaFe_2O_4$ (CFO), WO_3, WO_3/CFO, and WO_3/ITO/CFO films were prepared on quartz substrates by spin-coating and sputtering methods. Quartz glass substrates were cleaned by neutralized cleaning solution, pure water, and ethanol sequentially with ultrasonic, and then blow-dried by compressed air.

1-1. **CFO film**: $(CH_3COO)_2Ca. H_2O$ and $Fe (NO_3)_3. 9H_2O$ (Wako Pure Chemicals, Co.) precursors were dissolved in pure water (18.2 Ω) with Ca/Fe = 1/2 to form a 0.05 M (CFO) solution. Proper amount of PEG (Wm = 350W) was added to the solution for obtaining uniform films. Films were spin-coated on quartz glass substrates at 500 rpm for 10 s and 2000 rpm for 20 s. and then, the films were heated at 150 ^{o}C for 10 min. This process was repeated for two more times. Finally, the films were annealed at 450 ^{o}C for 2 h and 950 ^{o}C for 10 h.

1-2. **WO_3 film**: the WO_3 films were prepared according to the reported method. Briefly, the H_2WO_4 (Wako Chemicals Inc.) was dissolved in NH_3 solution to form 5 % H_2WO_4 precursor solution. Then films were spin-coated on quartz glass substrates at 500 rpm for 10 s and 2000 rpm for 20 s. and then, the films were heated at 150 ^{o}C for 10 min. This process was repeated for three times. WO_3 films were obtained by annealing the spin-coated films at 500 °C for 1h. The WO_3/CFO film was prepared by coating the WO_3 film on CFO film obtained in 1.1.

1-3. **WO_3/ITO/CFO film**: the ITO film was deposited on the substrate coated with CFO film by sputtering. The sintered ITO target (10% SnO_2) was used and ITO film with about 15 nm was deposited in 1 min at 0.5 Pa (filled with 97% Ar and 3% O_2) at room temperature with an out-power set at 200W. Then, the WO_3 film was coated on the top of ITO/CFO film following the same process as 1.2.

2. Optical absorption measurements

The ultraviolet-visible absorption spectra of the thin films were measured on a spectrophotometer (UV-2100, Shimadzu Co., Ltd). The absorption (A%) was obtained by measuring the transmittance (T%) and reflectance (R%) of the thin films, where $A = 100 – (T + R)$.

3. Contact angle measurements

The contact angle measurements were performed at room temperature (298K) using a commercial contact angle meter (DM 500, Kyowa Interface Science, Co. Ltd), with an experimental error of ±1 degree by the sessile drop method. This contact angle meter was equipped with a light source a light source to capture the water droplet images using CCD camera. The contact angle was determined by numerically drawing a tangent close to the edge of the droplet. All measurements were performed with high-purity water and the volume of the water droplet is 2 μl. The contact angle of the films was measured after stored in a light proof box for 2 days. In addition, oleic acid was coated on the surface of the films as contaminant and the change in the water contact angles were measured under visible light irradiation. For oleic acid coating, oleic acid was dissolved in ethanol with a concentration of 1 wt%, and this solution was coated on the films by spin coating at a speed of 2000 rpm. Then, the films were heated at 60 ^{o}C for 30 min to evaporate the solvents. A high power Xenon light source (XEF-501S, SAN-EI Electric MFG. Co., Ltd) was used to illuminate the samples with light intensity fixed at 100 mW/cm^2 by adjust the distance between samples and the light source and the output power of the light source. The light intensity was measured using a USR-45 spectro-adiometer (USHIO Inc.). Optical filters of Y-43 and C-50S (Asahi Technoglass) were used to eliminate the ultraviolet and infrared radiation.

4. Photocatalytic reduction of Ag^+

The photocatalytic reduction of these films was evaluated by measuring the amount of Ag deposited on the surface in an aqueous silver nitrate under light irradiation. We did not use visible light for irradiation but used UV light (black light bulb), since visible light irradiation causes the self-destruction of silver particles by surface plasmon absorption (c. f. Ohko et al. *Nat. Mater.* 2, 29, 2002). For this experiment, the films were immersed in proper amount of 0.05 M $AgNO_3$ (Wako Pure Chemicals, Co.) aqueous solution. Then the samples were irradiated under 2 mW/cm^2 UV light (black light bulb) for 30 min. After the light irradiation, the samples were washed thoroughly with pure water and blow-dried with compressed clean air. The amount of Ag deposited on the film surface was measured by X-ray photoelectron spectroscopy (XPS) using a Quantum 2000 scanning ESCA microprobe system (Physical Electronics, Inc.).