Preparation of silver-modified TiO_2 nanotube for removing liquid dyes and gaseous elemental mercury

Cheng-Yen Tsai,[a] **Chen-Wuing Liu,**[a,]* **Kuen-Song Lin,**[b] **Yi-Wen Lin,**[a] **Li-Chi Lai,**[a] **Hsing-Cheng Hsi**[c]

[a]*Department of Bioenvironmental Systems Engineering, National Taiwan University, Taipei, 106, Taiwan*
[b]*Department of Chemical Engineering and Materials Science, Yuan Ze University, Taoyuan, 320, Taiwan*
[c]*Graduate Institute of Environmental Engineering, National Taiwan University, Taipei, 106, Taiwan*
**Corresponding author: +886-2-23639557, cwliu@ntu.edu.tw*

Abstract: The TiO_2 nanotubes (TNT) modified with two different Ag compounds were fabricated via hydrothermal process. The TNT samples had a higher Brunauer-Emmett-Teller surface area since the resulted TNT was free of calcination, which is different from the traditional synthesized method. The photocatalytic activity of synthesized samples was assessed through the removal of elemental mercury (Hg^0), carcinogenic malachite green (MG), crystal violet (CV), and mixture of both dyes photodegradation under ultraviolet irradiation. The Ag-modified TNT sample showed to have higher removal efficiencies than that of non-modified TNT sample for Hg^0, carcinogenic MG, CV and mixtures of dyes.

Keywords: Photocatalysis, calcination-free, carcinogenic dye.

1. Introduction

Water and air pollutions are both serious global problems. Different types of organic dyes are utilized in the textile and handloom industries to dye the threads to make the clothes with various colors. After the dying processes, the discharged dye wastewater may cause the pollution of surface water and groundwater that can further harm to the aquatic animals and human beings. Additionally, exhaust of mercury (Hg) through anthropogenic sources is another global issue due to the stability, bioaccumulation in ecosystems, and severe neurotoxic impacts of Hg to human health. Numbers of techniques including adsorption, chemical oxidation, and degradation have been developed to remove chemical dyes from water medium and Hg^0 from gas phase, among the aforementioned methods, photodegradation is considered to be a highly efficient technique. In the present study, we synthesized Ag-modified TNT composites. This is the first study to use P-25 and silver compounds as direct precursors for synthesis of Ag-modified TNT without calcination or reduction step for removing gas-phase Hg^0, MG, CV and both dyes in a mixture.

2. Experimental

This study fabricated the Ag-modified TNT through an alkaline hydrothermal method by using commercial Degussa P-25 TiO_2, with Ag_2O and $AgNO_3$ as the precursors. Non-modified TNT was fabricated by mixing 5 g of Degussa P-25 TiO_2 and a 200 mL of 10 M NaOH aqueous solution in a Teflon-lined autoclave at 130 °C. Subsequently, the resulting product was washed alternatively with 0.5 N HCl solution and distilled water several times. Ag-modified TNT was synthesized by the resembling process. By changing the added amount of silver compounds to synthesize the Ag-modified TNT with 10 and 20 wt.% Ag_2O (or $AgNO_3$) loading, the resulting products were designated as Ag_2O (10)-TNT, Ag_2O (20)-TNT, $AgNO_3$ (10)-TNT, and $AgNO_3$ (20)-TNT, respectively, while non-modified TiO_2 nanotube was labeled as TNT. The resulting Ag-modified TiO_2 nanotubes were characterized by X-ray diffraction (XRD), N_2 adsorption isotherm, and transmission electron microscopy (TEM). The photodegradation and adsorption efficiencies of the resulting samples were examined for the degradation of carcinogenic MG, CV and a mixture of both dyes. Moreover, the resulting samples were also investigated for removal of gas-phase Hg^0.

3. Results and discussion

The XRD powder patterns of the TNT and Ag-modified TNT samples are illustrated in Fig. 1. The XRD results indicated that Ag-modified TNT contained a small amount of Ag and AgCl coexisting with anatase phase. The XRD data of resulting TNT showed that the compose of rutile phase in crude P-25 TiO_2 was destroyed after hydrothermal process and acid washing treatment. It is important that most studies reported the crystal phase of sample exhibited amorphous after hydrothermal process. Fig. 2 presents the morphology of the resulting samples through TEM analysis. The TEM images illustrated that TNT sample possessed openings on both sides, with a length of 100–200 nm and a diameter of approximately 5 nm. The tubular pattern of non-modified TNT sample was clearer than that of Ag-modified TNT sample, whereas Ag and AgCl crumbs were not observed. After adding silver compounds as the precursor, the TEM images displayed some polygonal shape objects and certain tubular shapes. According to the XRD results, these polygonal shape objects could be Ag and AgCl. The N_2 adsorption/desorption and pore size distribution for the as-prepared TNT and Ag-modified TNT samples were determined, as shown in Fig. 3. The physical characterization changes when silver compounds were added as the precursors were also observed by the N_2 adsorption/desorption (Fig. 3a). Adsorption hysteresis for all samples was observed in the region as relative pressure P/P_0 was > 0.5, indicating a type IV isotherm pattern according to the IUPAC classifications.[1] The tubular shape was formed by rolling-up of a nanosheet, which implied that the plate-like or sheet-like aggregates resulted in slit-shaped pores, thereby leading to the hysteresis.[2] The pore size distribution and pore volume are presented in Fig. 3b. The pore volume in the case of the 2.2 nm mode of TNT sample was 1.2 $cm^3\ g^{-1}\ nm^{-1}$; the volume decreased to 1.0 $cm^3\ g^{-1}\ nm^{-1}$ (at 1.8 nm) when added 20 wt.% $AgNO_3$ as a precursor. Overall, the Ag-modified TNT heterostructures illustrated enhanced dye and Hg^0 removal efficiency in comparison with the non-modified TNT sample.

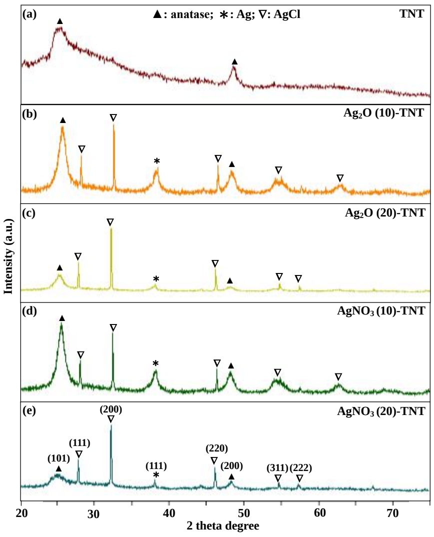

Figure 1. XRD spectra of TNT samples.

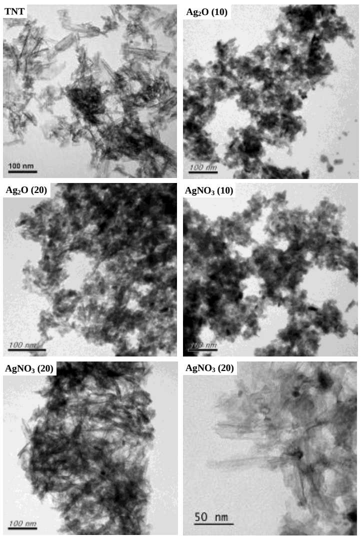

Figure 2. TEM images of samples.

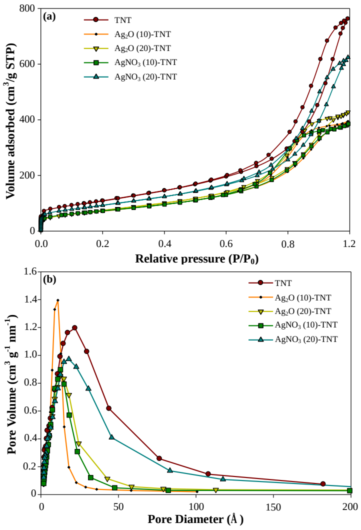

Figure 3. N_2 adsorption/desorption.

4. Conclusions

We successfully synthesized Ag-modified TNT by applying hydrothermal process in a single step without additional calcination. Anatase phase, cubic AgCl and Ag coexisted in the Ag-modified TNT sample. Except for $AgNO_3$ (20)-TNT sample, the tubular shapes of other three Ag-modified TNT samples were not observed clearly from the TEM images. The photocatalytic activities of the obtained samples were investigated by evaluating the photodegradation and removal efficiency for MG, CV, and elemental mercury under UV irradiation, respectively. The e^-/h^+ pairs separation efficiency increased because of the presence of AgCl and Ag species on the surface of Ag-modified TNT.

References

1. S.J. Gregg, K.S.W. Sing, (Eds.), Adsorption, Surface Area and Porosity, 2nd ed., Academic Press, London, 1982.
2. T. Kubo, A. Nakahira, J. Phys. Chem. C 112 (2008) 1658.