Study of Nano SiO$_2$/TiO$_2$ Superhydrophobic Self-Cleaning Surface Produced by Sol-Gel

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Abstract: Self-cleaning coatings can be used in many different industrial areas to improve the usability and functionality of varied materials. In this paper, SiO$_2$ and TiO$_2$ nanoparticles are first synthesized by sol-gel methods. Then, SiO$_2$/TiO$_2$ superhydrophobic self-cleaning layers are fabricated on glass. The samples were characterized by x-ray diffraction (XRD) and transmission electron microscopy (TEM) analysis after heat treatments. The XRD results show the sharp picks of the samples after annealing. The SEM results show that the size of nanoparticles is in the size range of 5-10 nm in diameter. Finally the photography of the samples with self-cleaning coatings revealed that the round water droplet roll down the surface, mop up the dirt particles on the way and drip off.

Key words: self-cleaning coating, superhydrophobic, nano SiO$_2$/TiO$_2$, sol-gel

INTRODUCTION

Self-cleaning surface is potentially a very useful addition for many commercial products due to economic, aesthetic, and environmental reasons. Super-hydrophobic self-cleaning, also called Lotus effect, utilizes right combination of surface chemistry and roughness to force water droplets to form high contact angle on a surface, easily roll off a surface and pick up dirt particles on its way. Self-cleaning materials that can be cleaned by simply being rinsed with water can be potentially applied in many areas. As exterior surfaces, such materials will be cleaned just with regular rain significantly reducing maintenance costs, due to less labor required and no need for detergents, with minimal impact on the environment (Parkin, I.P. and R.G. Palgrave, 2005; Sun, T., 2005; Milanesi, F., 2010). Therefore, self-cleaning surfaces are intensively studied and commercialized for such applications as windows (Gould, P., 2003) paints (Li, X.M., 2007) solar energy panels (Ma, M., R.M. Hill, 2006) and automotive windshields (Ma, M., 2008). Incorporating the self-cleaning functions in building materials such as tiles, concrete, paints and glasses by which air pollution or pollution of the surface itself can be controlled and diminished.

A photocatalyst can facilitate the breakdown and removal of a variety of environmental pollutants at room temperature by oxidation, using either sunlight or artificial light as an energy source. In the photo-oxidative removal of potentially toxic organic or inorganic compounds present in the environment, primary attention has been devoted to the role of titanium dioxide (TiO$_2$) on the SiO$_2$ over compounds such as ZnO, CdS. This attention is due to its high photocatalytic activity, biological and chemical inertness and stability, resistance to photocorrosion, low cost, nontoxicity, and favorable band-gap energy (Ma, M., 2008). The photocatalytic activity of titania is strongly affected by physicochemical features of the particles, with respect to both structural and morphological characteristics. From a structural point of view, TiO$_2$ can crystallize in three different polymorphic forms: anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic). The anatase polymorph is generally reported to show the highest photoactivity compared to either brookite or rutile polymorphs because of the low recombination rate of its photogenerated electrons and holes. When TiO$_2$ catalysts are subjected to irradiation with photons of energy equal to or higher than their band gap, the generated electron–hole pairs can induce the formation of reactive oxygen species, such as hydroxyl radical and superoxide radical that are directly involved in the oxidation processes leading to the degradation of both contaminants and microorganisms (Xue, C.H., 2010; Stamate, M. and G. Lazar, 2007; Lee, H.J. and S. Michielsen, 2006; Rossbach, V., 2003; Feng, X.J. and L. Jiang, 2006).

The superhydrophobic surfaces have a very high water contact angle (>150°) and a very low roll-off angle allowing water droplet to roll at a very low tilt angle of a surface (Wong, M., 2006). In contrast to a sliding motion, rolling droplets easily pick up dust particles and remove them from a surface, realizing the self-cleaning effect (Adams, L.K., 2006). In addition to being self-cleaning, such surfaces have stain resistance properties, due to the high contact angle and limited contact area of contaminated water droplets (Li, X.M., 2007). However the development of new fabrication techniques, which allow manipulating of surface morphology on the micro and nano levels, has significantly increased scientific interest to this problem in recent years (Kwon, S., 2008; Armelao, L., 2007; Daoud, W.A. and J.H. Xin, 2004). Artificial superhydrophobic surfaces can be produced in many ways, including template synthesis, phase separation, crystallization control, etching, sol-gel processing, layer by layer deposition, and electrospinning (Ma, M., R.M. Hill, 2006; Gogniat, G., 2006).
In this article, the SiO$_2$ and TiO$_2$ nanoparticles are first synthesized by sol-gel method under given conditions with sodium silicate (Na$_2$SiO$_3$) and Titanium (IV) isopropoxide Ti[OCH(CH$_3$)$_2$]$_4$. Then, the self-cleaning SiO$_2$/TiO$_2$ superhydrophobic layers are fabricated on glass. The characterization of the samples is studied by TEM and XRD analyses after annealing.

**Experiment Details:**

The synthesis of SiO$_2$ and TiO$_2$ nanoparticles was carried out by chemical method. The sol-gel process of silica nanoparticles is as follow: sodium silicate (Na$_2$SiO$_3$) was slowly added into the butanol solution, and the mixture was stirred at 65°C. Then, 0.5 mol/L sulfuric acid solution was added gradually into the suspension in order to initiate the hydrolysiscondensation reaction at pH = 4. The resulting gel mixture was aged at 65°C for 8 hours. Nanosilica was calcinated at 550°C for 2 hours in atmospheric condition to remove the surfactant. Finally, the product was dissolved in the surfactant in order to colloid of SiO$_2$. Similarly, TiO$_2$ sol was prepared by hydrolysis and condensation of metal alkoxide. Titanium (IV) isopropoxide Ti[OCH(CH$_3$)$_2$]$_4$ was used as a precursor. It was slowly added to the ethanol as a solvent, with distilled water added for hydrolysis reaction. Finally, a small amount of hydrochloric acid (HCl) was slowly added to the solution with stirring. After condensation reaction and crystallization, transparent suspended TiO$_2$ sol was obtained. The product was then heated at 200° for 5 hours. The resulting powder was washed with distilled water until pH=7 and then dried at 75°C for 24 hours. The dried samples were calcinated at 550°C for 2 h. The morphology and structure of the prepared nanoparticles were characterized by TEM and XRD. The specification of the size and shape of the nanoparticles were examined by TEM analysis using a Philips EM 208. To determine the nanoparticles’ structure, the XRD measurement was performed using a Seifert with Cu-K$_\alpha$ radiation (wavelength = 1.54 Å).

**RESULTS AND DISCUSSION**

Figures 1 shows the XRD pattern of TiO$_2$ nanoparticles on SnO$_2$ annealed at 550°C for 2 hours. As you can see the sharp picks reveal the crystalline nanoparticles after heat treatment.

![Fig. 1: X-ray diffraction (λ = 1.54 Å, Cu-Kα radiation) pattern of the nanoparticles.](image)

Figure 2 show the TEM images of the SiO$_2$ and TiO$_2$ nanoparticles. As you can see from fig. 2(a) the SiO$_2$ nanoparticles are in the size range of 4-10 nm in diameter while from fig. 2(b) the size of TiO$_2$ nanoparticles is about 7 nm.

![Fig. 2: TEM images of the (a) SiO$_2$ and (b) TiO$_2$ nanoparticles.](image)
Figure 3 shows the photography of the samples without and with SiO$_2$/TiO$_2$ self-cleaning coatings. By self-cleaning coatings the round water droplets roll down the surface mop up the dirt particles on the way and drip off. This cleans up the surface without leaving any water behind. Due to the unavailability of water on such surface, the growth of bacteria, fungus is significantly reduced. Figure 3(a) shows the glass with droplet water before self-cleaning coating and fig. 3(b) shows the glass after self-cleaning SiO$_2$/TiO$_2$ superhydrophobic layers. As you can see from the pictures, the round water droplets roll down and the dust drip off on the surface.

Fig. 3: Photography of the samples (a) with and (b) without SiO$_2$/TiO$_2$ coatings.

Conclusion:
In conclusion, the self-cleaning SiO$_2$/TiO$_2$ superhydrophobic layers were fabricated on glass. The XRD pattern of annealed TiO$_2$ nanoparticles on SnO$_2$ shows the sharp picks that reveals the crystalline nanoparticles. TEM images of the SiO$_2$ and TiO$_2$ show the uniform nanoparticles to use for the self-cleaning processing. Finally, photography of the samples with SiO$_2$/TiO$_2$ self-cleaning coatings indicates that the round water droplets roll down and the dust drip off on the surface.

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REFERENCES


