



Fabrication of functional silver loaded montmorillonite/polycarbonate with superhydrophobicity



Li Tian ^{a,*}, Zhang Yuanyuan ^b, Mai Yingying ^a, Huang Ran ^a

^a School of Chemistry and Chemical Engineering, Guangdong Pharmaceutical University, Zhongshan 528458, China

^b Department of Food, Guangdong Light Industry Technical College, Guangzhou 510300, China

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ABSTRACT

The polycarbonate (PC) solution was mixed with silver loaded modified montmorillonite (Ag-Mt) and then treated with 1,4-dimethylbenzene to obtain functional Ag-Mt/PC with superhydrophobicity. The Ag-Mt/PC with the Ag-Mt content of 1.5 wt.% showed a high water CA (152.5°) and excellent durability, the water CA decreased only 10% during a week's continuously water flow at the rate of 0.2 mL/s. The scanning electron microscopy (SEM) and surface area measurement results proved that the crystallization situation was more complicated on the interface of PC and Ag-Mt interlayer, resulted in different phase separation rate, provided more opportunity for the formation of pores with appropriate size diffusion, and finally fabricated a micro-nano-scaled surface with superhydrophobicity. Otherwise the Ag-Mt/PC performed high catalytic activity on the degradation reaction of methylene blue (the nearly complete degradation took only 25 min), slow release property and antibacterial activity on both *Staphylococcus aureus* ATCC6535 and *Escherichia coli* ATCC8739 (the mean diameter of inhibition zone was almost 50% larger than PC), which indicated that this simple and inexpensive approach could be more broadly applied to fabricate large-area functionalized surface via engineering materials with superhydrophobicity and utilize potential practical applications in the future.

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1. Introduction

In nature, many creatures possessed surfaces with special wettability after billions of years of lengthy evolution. Nowadays, more and more attention was paid to the structure of these surfaces because of their unique properties such as the anisotropic de-wetting behavior and self-cleaning effect. The established theoretical models as well as many experimental results proved that all the special wettability of biological organisms in nature and the unique micro-nano-sized protrusions on their surfaces are intimately connected, although they were made of various different chemical composition (Zhang et al., 2012). Researchers tried to obtain materials with such special micro-nano-structure by building blocks in both micrometer and nanometer scales, as the high surface free energies and huge specific surface areas could show great advantage in anti-wetting or self-cleaning applications. For example, Liang et al. (2015) found that the discharge speed of the gas bubbles could be mainly accelerated by the accessorial gas channels with superhydrophobicity, which would enhance the property of methanol fuel cell very effectively. In order to explore the hypotaxis of materials with micro-nano-structures between structure and function, numerous efforts were devoted at present. Several different ways like sol-gel processing, plasma technique, electrochemical and layer-by-layer methods

etc. were explored to fabricate rough surfaces on inorganic or organic materials that would lead to superhydrophobicity (Zhang et al., 2007; Zhang et al., 2014). Hurst et al. (2012) extended the Teflon sanding method via inclusive modification of surface chemistry and terrain. The time for plasma treatment to achieve surface roughness in dual level can be significantly decreased when combining sanding with O₂ plasma. Hosono et al. (2005) reported a water CA of 178° on the cobalt hydroxide brucite-type crystalline nano-pins coated with dodecanoic acid, which was one of the highest water CAs that has ever been achieved so far.

However, most of these preparation routes suffered from finite substrates, exorbitant vacuum apparatuses or chemical modifiers, lengthy fabrication steps and harsh preparation requirements such as the precise control of water relative humidity or temperature, which may seriously limit them being created for large area uniform coatings in practical application (Zhang et al., 2008). Besides these manufacturing difficulties, there was another primary barrier that prevented the superhydrophobic surfaces being used in extensive fields, as many products had to endure very rough using ambient over long term while the so obtained surfaces were always easily worn or impured during normal use. There should be quantitative and qualitative feasibility studies on the respective raw materials, only in this way can we obtain durable superhydrophobic surface rapidly and cheap, which can be processed the potential industrial applications requires (Cho et al., 2013). Researchers focused on polycarbonate (PC), polymethyl

* Corresponding author.

E-mail address: phdlitian@163.com (Z. Yuanyuan).

Table 1
Various compositions of Ag-Mt/PC.

Sample code	PC content	Ag-Mt content
Ag-Mt/PC-0.5	99.5	0.5
Ag-Mt/PC-1	99.0	1.0
Ag-Mt/PC-1.5	98.5	1.5
Ag-Mt/PC-2	98.0	2.0
Ag-Mt/PC-2.5	97.5	2.5
Ag-Mt/PC-3	97.0	3.0

methacrylate (PMMA) etc. as appropriate materials because of their high impact resistance and working temperature, good biocompatibility, low moisture absorption and relatively low cost (Xie et al., 2004; Xiao and Chaudhuri, 2012). Palumbo et al. (2011) obtained PC by chemical tailoring and nano-textured plasma treatment, but he also confirmed that this was not a suitable process for producing polymeric surface with stable hydrophilicity. However, the substrates were cheap and easy to get; these superhydrophobic surfaces still lack of functional use.

Researchers tried other efficient way to fabricate functional superhydrophobic surface via polymer composites because of their cheap price and high mechanical strength combined with low density. While a second layer was added, the superhydrophobicity of these bulks can be remarkably increased, which was already implemented in various ways including: assembling particles in different size to produce papillary structure like bilberries, sputtering and heating gold on top of the substrate to constitute golded nano-clusters, which can give high CA of 160° (Roach et al., 2008). Lau et al. (Lau et al., 2003) modified the vertically aligned CNT exterior with polytetrafluoroethylene (PTFE) coating and fabricated a very stable superhydrophobic surface. Jung and Bhushan (Jung and Bhushan, 2009) reported the preparation of superhydrophobic CNT/epoxy composite with low CA hysteresis surface via a spray method. The results of waterfall test and conflict studies indicated excellent mechanical properties and abrasion resistance, thanks to the uniform distribution and strong bonding of CNT on the surface of resin. Zhang et al. (Zhang et al., 2005) prepared CaCO₃-loaded hydrogel spheres and adhered them sparsely onto a facade, which may serve as a mouldboard for adsorption and nest of polystyrene or silica globes hereafter. The so formed surfaces can display an obviously different hydrophilicity when compared to the bald substrate and consequently give rise to superhydrophobicity after a gold-coated and thiol-functionalized process.

As so far it was known that the more random arrays of particles, the higher contact angles can be triggered when creating superhydrophobic surfaces. Montmorillonite (Mt) that pertained to the universal family of 2:1 layered silicates, can be an extremely suitable material to prepare functional polymer composite with superhydrophobicity owing to its

huge surface area (Carretero, 2002; Dimitris and Dadachov, 2003; Kasirga et al., 2012). Moreover, Mt contained either Mg²⁺, Al³⁺ or Fe²⁺ as ordinary ions in the interlayer, and A³⁺ often permuted some of the Si⁴⁺, which may give rise to high ion exchange capability and functional activity. Mt/polymer nanocomposites captured substantial attention for diverse engineering utilizations in virtue of their enhanced thermal stability, mechanical properties and functional properties (Paul et al., 2003; Rhim et al., 2006; Valera-Zaragoza et al., 2006; Xu et al., 2006; Lavorgna et al., 2010; Li et al., 2014b). Hence promising functional superhydrophobic materials can be obtained by combining functional Mt with polymer and then etching to provide dual-scale roughness.

In this study, PC was soluted in dichloromethane (DCM) and mixed with silver loaded montmorillonite (Ag-Mt), a piece of glass was used as the substrate that dipped into the solution and undergone a very fast evaporation of the solvent afterwards. The as formed Ag-Mt/PC film was treated by a short 1,4-dimethylbenzene bath, where the liquid-liquid demixing and rapid crystallization of PC occurred, resulting in diverse nanostructures and superhydrophobic surface. The whole process used in this paper to obtain such a surface was a very facile and quick physical treatment and involved no chemical reaction. It was merely the combination of inorganic mineral and engineering polymer material that allowed the common plastic material to be superhydrophobic and functional. When compared with the natural superhydrophobic like rice leaves, the so obtained artificial superhydrophobic surface was more robust and stable, as only the surface was modified by the treatment while the matrix of the PC composite retained its outstanding mechanical properties. The coatings' surface was investigated via a scanning electron microscope (SEM) and specific surface measurement. Their superhydrophobic durability and applications were also discussed.

2. Experimental

2.1. Materials

Na⁺-montmorillonite (Mt) K10 (surface area = 240 m²/g) was purchased from Johnson Matthey Company (USA). L-Cystine (AR) was purchased from Shanghai Ziyi Reagent Company. Silver nitrate (AR), 1,4-dimethylbenzene (AR) and dichloromethane (AR) were all obtained from Shanghai Aobo Biologic Technology Company. Polycarbonate (PC, 1200 kg/m³, MI = 1 g/min) was supplied from Bayer Co.

2.2. Preparation of Ag-Mt/PC

2.2.1. Preparation of modified Mt

About 5 g K10 was scattered in 100 mL deionized (DI) water at 60 °C, then 100 mL of L-cystine solution (pH = 1.8) was added and stirred for 1 h vigorously. The modified Mt was segregated by a centrifuge and

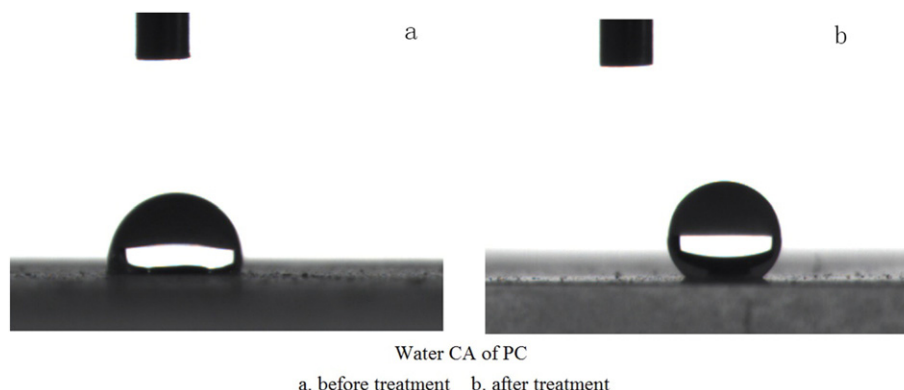


Fig. 1. Water CA of PC.

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