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Research paper

Durable and fluorine-free superhydrophobic coatings from palygorskite-rich spent bleaching earth

Penglin Zhang[a], Shuantao Dong[a,b], Bucheng Li[b], Xudong Wei[c], Junping Zhang[b,*]

[a] College of Material Science and Engineering, Lanzhou University of Technology, Lanzhou 730050, PR China
[b] Key Laboratory of Clay Mineral Applied Research of Gansu Province, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China
[c] Department of Otolaryngology-Head and Neck Surgery, Gansu Provincial Hospital, Lanzhou 730000, PR China

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ABSTRACT

With the increasing consumption of vegetable oils, value-added recycling of spent bleaching earth (SBE) is of wide concern. Here, we report a simple and sustainable method for converting SBE containing palygorskite (PAL) to hybrid carbon materials (PAL/C) with a nanorod-like structure, which can then be used as building blocks for the preparation of durable and fluorine-free superhydrophobic coatings. The PAL/C composites were prepared by calcination of the SBE containing PAL in air. Then, the homogeneous suspensions in ethanol were prepared by hydrolytic condensation of *n*-hexadecyltrimethoxysilane onto the PAL/C nanorods. Superhydrophobic coatings can be readily prepared by spray-coating the suspensions onto substrates. The PAL/C composites and the superhydrophobic coatings were characterized using a variety of analytical techniques including scanning electron microscopy, transmission electron microscopy and X-ray photoelectron spectroscopy. Superhydrophobicity of the coatings depends upon their surface topography, which can be precisely regulated by the calcination temperature of SBE and the concentration of the PAL/C composites in the suspensions. The superhydrophobic coatings show high water contact angle and extremely low sliding angle of 1.2°. The superhydrophobic coatings also feature high mechanical, thermal and chemical durability. This is because the PAL/C nanorods are closely linked and encapsulated together by polysiloxane (POS) among them, forming a highly crosslinked network. We believe that this study will shed light on the value-added recycling of SBE and cost-effective preparation of bioinspired antiwetting coatings.

1. Introduction

With the development of the economy and society, more and more waste is produced every day in the whole world, which threatens ecosystems and human health. Therefore, it is in high demand to develop efficient methods for the collection and reuse of different kinds of waste, such as discarded electronics, metal, plastic and spent bleaching earth (SBE), etc.

Crude vegetable oils usually contain some coloring matters and hazardous compounds. It is necessary to remove these components and improve the oil quality by using activated clay minerals including montmorillonite and attapulgite (Tang et al., 2015). PAL is widely used for adsorption (Tian et al., 2015; Tang et al., 2016; Carazo et al., 2017; Yang et al., 2018) and decolorization (Tian et al., 2014; Xavier et al., 2016; Tian et al., 2017) because of its natural micro-/nanopores and low cost. Consequently, more than 0.6 million tons of SBE containing 20%–40% of oil is formed annually, which contains phospholipids, natural pigments, fatty acids, vitamins and grease, etc. More than 50% of SBE is currently directly discarded as garbage or burned for the purpose of quick waste disposal (Foo and Hameed, 2012). Obviously, these methods are not the rational way to solve the issue, and will cause secondary pollution to soil and water. Therefore, it is highly necessary to develop novel and cost-effective approaches to promote the value-added recycling of SBE.

Carbon materials are attracting increasing attention because of their unique structures and excellent properties, and thus have potential applications in many fields such as energy storage (Che et al., 1998), nano-devices (Collins et al., 1997), catalysis (Konwar et al., 2014), adsorption (Carrott and Carrott, 2007) and separation technology (Shiflett and Foley, 1999), etc. Therefore, various methods have been developed for the preparation of carbon materials, e.g., carbonization (Yang et al., 2012), arc discharge synthesis (Volotskova et al., 2010), chemical vapor deposition (Li et al., 2009) and hydrothermal reaction (Yoshioka et al., 2003), etc. Also, different precursors including graphite (Wicklein et al., 2015), cellulose (Li et al., 2017) and other organic compounds (Li et al., 2013b; Hu et al., 2017) have been used for

* Corresponding author.
E-mail address: jpzhang@licp.cas.cn (J. Zhang).

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the preparation of carbon materials. Carbonization of SBE should be an interesting approach for the preparation of hybrid carbon materials. This approach could not only generate new hybrid carbon materials, but also solve the problem of pollution of SBE to soil and water. In addition, the PAL nanorods in SBE could act as support for the as-formed carbon materials.

In the past two decades, bioinspired superhydrophobic surfaces with water contact angles (CA) higher than 150° have drawn widespread attention and have potential applications in many fields including self-cleaning (Bhushan et al., 2009; Long et al., 2017), fluid transportation (Yuan et al., 2016), oil/water separation (Zhang et al., 2017) and anti-icing (Cao et al., 2009; Emelyanenko et al., 2017). For the successful preparation of superhydrophobic surfaces, the hierarchical structures and materials of low surface energy are essential. Numerous methods have been developed for construction of the hierarchical structures, which are mainly the physical and chemical approaches, such as lithography (Li et al., 2012), templating (Wang et al., 2014), chemical vapor deposition (Gallyamov et al., 2007) and layer-by-layer assembly (Peng et al., 2016), etc. Thus, most of the methods are complicated, expensive and low efficient, and may cause environmental problems. Preparation of superhydrophobic surfaces from natural materials is receiving rapidly growing attention (Webb et al., 2014; Chen et al., 2016; Han et al., 2017). We report the first PAL-based superhydrophobic coating, which is durable and cost-effective (Li et al., 2013a). In addition, the low mechanical stability of most of superhydrophobic coatings is the bottleneck hindering their real-world applications (Kulinich et al., 2010; Jin et al., 2013; Kulinich et al., 2015). Although some mechanically durable superhydrophobic coatings have been invented (Li et al., 2015; Li and Zhang, 2016), fluorinated chemicals are frequently used because of their very low surface energy. However, fluorinated chemicals including perfluoroalkylsilanes and fluoroacrylic copolymers have potential dangers to the environment and human health (Martin et al., 2003; Wang et al., 2015). Thus, fluorine-free superhydrophobic coatings are of great interest (Martin et al., 2004; Sawada et al., 2008).

Here, we report a simple and sustainable method for the preparation of durable and fluorine-free superhydrophobic coatings from SBE. First, the PAL/carbon (PAL/C) composites were prepared by calcination of the SBE containing PAL at the chosen temperature in air. Then, the homogeneous suspensions in ethanol were fabricated by modification of the PAL/C composites with *n*-hexadecyltrimethoxysilane (HDTMS) with ammonia as the catalyst. Hydrolytic condensation of HDTMS formed a layer of polysiloxane (POS) on the PAL/C nanorods. Superhydrophobic coatings can be readily prepared by spray-coating the suspensions onto substrates. The superhydrophobic coatings show high water contact angle (CA) and extremely low sliding angle (SA), and high mechanical and chemical durability. This work not only explored a cost-effective approach to convert SBE into functional PAL/C composites with a nanorod-like structure but also found a new application of the PAL/C composites as building blocks for the preparation of durable superhydrophobic coatings.

2. Materials and methods

2.1. Materials

SBE was supplied by Guosheng Minerals Co. Ltd. Jiangsu, China. HDTMS was bought from Gelest. Anhydrous ethanol and aqueous ammonia (25–28 wt%) were bought from China National Medicines Co. Ltd. Glass slides (24 × 50 mm) were supplied by Menzel, Braunschweig, Germany.

2.2. Preparation of PAL/C composites

SBE was calcined at 300, 400, 500 or 600 °C for 2 h in a ceramic fiber muffle furnace (TM-0612, Beijing Ying'an Meicheng Science Instrument Co., Ltd., China) to form the PAL/C composites. The as-prepared PAL/C composites were crushed and filtered by passing through a 180-mesh sieve.

2.3. Preparation of superhydrophobic PAL/C@POS coatings

First, the homogeneous suspensions in ethanol were prepared by hydrolytic condensation of HDTMS onto the PAL/C composites. An amount of the PAL/C composite (0–1000 mg) was dispersed in a solution containing 44 mL of anhydrous ethanol and 6 mL of ammonia aqueous solution. After sonicated for 0.5 h in an ultrasonic cleaner, 620 μL of HDTMS was injected quickly into the suspension under vigorous stirring at 600 rpm. After reacting at room conditions for 2 h, the homogeneous PAL/C@POS suspensions were formed.

The PAL/C@POS superhydrophobic coatings were prepared by spray-coating 4 mL of the suspensions onto the surface of glass slides with an airbrush (INFINITY 2 in 1, Harder & Steenbeck, Germany) with 200 kPa N_2. The glass slides were attached on a hot plate at 150 °C. The influences of calcination temperature ($T_{\text{calcination}}$) and PAL/C concentration in the suspensions ($C_{\text{PAL/C}}$) on wettability and microstructure of the coatings were systematically investigated. The POS coating was prepared via the same procedure, but without the addition of the PAL/C composite.

2.4. Durability tests

Water jetting and tape peeling tests were employed to evaluate mechanical stability of the coatings. The 45° tilted coatings were jetted by water at certain pressure from 20 cm high for some time. For the tape peeling test, the coatings were brought in contact with the surface of the 3 M adhesive tape (Scotch 600) and applied a load of 4.2 or 6.8 kPa, and then the adhesive tape was peeled off from the coatings. This process was repeated several times. In each cycle, a new piece of adhesive tape was used. The thermal stability of the coatings was tested in an oven. The chemical stability was studied by immersing the coatings in 1 M $HCl_{(aq)}$, saturated $NaOH_{(aq)}$, saturated $NaCl_{(aq)}$, toluene and ethanol for 24 h. The changes in the water CA and SA were recorded to evaluate the stability of the coatings.

2.5. Characterization

The water CAs and SAs of the coatings were measured using a Contact Angle System OCA20 (Dataphysics, Germany) at room temperature. The reported data was the average of six readings at different locations on the samples. The microstructure of the samples was observed using a field emission scanning electron microscope (SEM, JSM-6701F, JEOL) and a field emission transmission electron microscope (TEM, JEM-1200EX, FEI). The Fourier transform infrared (FTIR) spectra of samples were collected on a Thermo Nicolet NEXUS TM spectrophotometer (Thermo, Madison, USA) in the range of 4000–400 cm^{-1} using KBr pellets. The X-ray photoelectron spectra (XPS) of samples were recorded with a VG ESCALAB 250 Xi spectrometer. The thermal gravimetric analysis (TGA) was carried out using a STA 6000 simultaneous thermal analyzer (PerkinElmer Instrument Co., Ltd. USA) in the range 25–800 °C at a rate of 10 °C min^{-1} under O_2 atmosphere.

3. Results and discussion

3.1. Preparation of PAL/C@POS coatings

PAL is used every day for the efficient decoloring of crude vegetable oils, but a large amount of SBE is formed. Based on the concept of value-added recycling of SBE, herein SBE is used to prepare the PAL/C composites and the superhydrophobic coatings. The concept and process of preparation of the PAL/C composites and the superhydrophobic coatings from SBE are illustrated in Fig. 1. SBE was calcined at 400 °C in