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Fabrication of superhydrophobic Pt_3Fe/Fe surface for its application

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ABSTRACT

Well-defined Pt_3Fe/Fe superhydrophobic materials on iron sheet with special properties, such as corrosion resistance, superhydrophobicity and superoleophilicity, was fabricated. The fabrication process involved etching in hydrochloric acid aqueous solution and simple replacement deposition process without using any seed and organic solvent, and then annealing. The electrochemical measurements show that the resultant surface in 3.5% sodium chloride solution displays good corrosion resistance. Also, it is proved that the obtained surface has better mechanical abrasion resistance via scratch test. The superoleophilicity and low water adhesion force of the obtained surface endow it high oil/water separation capacity. The as-prepared nanocomposites display enhanced catalytic activity and kinetics toward degradation of methyl orange. In particular, it possesses the most efficient degradation capacity (95%) towards methyl orange at a high concentration (17.5 mg/L) in 80 min. The improved stability and excellent catalytic activity of the Pt_3Fe/Fe nanocomposites promise new opportunities for the development of waste water treatment.

1. Introduction

The tendency of metals to absorb water dramatically shortens their service life and results in a deleterious waste of resources. Iron that serves as an engineering material is widely applied in many areas, including mechanical equipment, building construction, and automobile manufacturing. Unfortunately, iron materials can be easily corroded in humid environment, causing significant performance degradation and even economic loss [1]. One promising method for improving water resistance is the use of superhydrophobic coatings, because these coatings can minimize such damage resulting from the interaction between metals and water. By convention, artificial superhydrophobic surfaces (SHSs) with an extremely high water contact angle (WCA) more than 150° and low contact angle hysteresis (CAH) or sliding angle (SA), are firstly reported by Ollivier a century ago [2]. Water-repellent surfaces with liquids inspired by nature, for instance, the water striders that walk on water without wetting their legs and self-cleaning properties of lotus leaves [3], are closely connected to industrial production and daily life of mankind. Therefore some physical and chemical methods have been developed to prepare SHSs. Physical methods cover, such as the following: plasma treatment [4], phase separation [5], lithography [6] and spin-coating [7]. Several such chemical methods generally include chemical vapor deposition [8], sol–gel processes [9], electrochemical methods [10], layer-by-layer assembly [11] and self-assembly [12]. In work of Li et al. [13] the antireflective (maximum transmittance: 94% at 550 nm) superhydrophobic coatings were successfully assembled by layer-by-layer assembly method. An interesting proposal was presented by Hu et al. [14] who obtained micro-nano hierarchical structured superhydrophobic nickel films with a WCA of 154° by a simple and low cost electrodepositing method. To summary, most methods applied for the preparation of SHSs require a tedious and time-consuming process. Hence, it is necessary to find an efficient, versatile approach to fabricate SHSs. The electroless galvanic deposition is an environmentally friendly, fast, and low-cost method for preparation of SHSs. Based on this, this paper is prone to deposit a second metal on iron, without modifying by low surface energy material.

Environmental problems induced by hardly-degradable and toxic organic pollutants (containing dyes, dioxins, pesticides, halides, etc.) have posed a grave menace to human well-being and development in the 21st century. The organic pollutant such as dyes in the effluents is hard to degrade due to their complex aromatic structures and stability. Among the available strategies, photocatalytic degradation of organic pollutant is considered to the low cost and effective method to purify waste water. To the best of our knowledge, nanomaterials of noble metals (such as Pt, .Au, Ag and Pd) have been successfully adopted as photocatalyst to remove the refractory pollutants because of their inherently robust physical and chemical properties. For instance, Wang et al. effectively prepared Au coated ZnO nanorods and it exhibited complete photocatalytic degradation of rhodamine B [15].

Many studies have focused on the development and applications of water-repellent surfaces for self-cleaning [16,17], special wettability

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[18], anti-fogging [19], anti-corrosio [20–23], oil–water separation [24,25], drag reduction [26], and catalytic properties. Our group has reported the superhydrophobic materials as catalyst for the reduction of p-nitrophenol, display vigorous catalytic property [27]. However, only a few studies have reported such research in this area until now. The exploring is not comprehensive. Therefore, we attempt to fabricate SHSs with excellent catalytic property.

In this direction, a method to fabricate a platinum SHS on iron foil was investigated. HCl and $PtCl_4$ solution were used to etch the iron surface and form microstructures, and the annealing treatment was adopted to generate SHS. The fabrication, characterization and evaluation of properties of the obtained surface were given. Corrosion resistance, mechanical abrasion resistance, superhydrophobicity, superoleophilicity and photoactivity of the obtained surface have been studied. Methyl orange was served as model dye and photocatalytic tests were investigated under UV light at different experimental conditions. The present study, hopefully, could help to provide a new strategy to design a newly structured SHS and favor the potential development of waste water treatment.

2. Experimental

2.1. Reagents and methods

Platinum tetrachloride powder ($PtCl_4$, 57.8%), acetone (C_3H_6O, 99.5%), hydrochloric acid (HCl, 36–38%), trichlormethane ($CHCl_3$, 99.0%), dodecane ($C_{12}H_{26}$, 99.3%), methyl orange ($C_{14}H_{14}N_3NaO_3S$, 85.0%) and ethanol (C_2H_5OH, 99.7%) were of analytical grade and ordered from China Beijing Fine Chemical Co. Ltd in this study. Aqueous solutions were formulated with a certain amount of distilled water and stored in the volumetric flask. Iron specimens were received from Beijing Cuibolin Non-Ferrous Technology Developing. All chemical solvents were used directly without further treatment. Distilled water was employed throughout the preparation process.

A typical experiment procedure was as follows: Initially, iron substrates with an average size of $1.0\times1.0\ cm^2$ and a thickness of 1.0 mm were completely washed with ethanol and acetone for approximately 10 min in turn in an ultrasonic machine to remove possible impurities. Afterward, the iron substrates were placed in a sealed beaker containing ethanol. Subsequently, the as-obtained iron specimens were took out and cleaned with filter paper, then were directly etched in diluted hydrochloric acid (2 M) for 6 min to form a rough surface, rinsing with excess deionized water extensively to dispose of the unreacted acid. The etched iron foils were put perpendicularly into a transparent and small centrifuge tube without a bottom, immediately they were immersed in 4 mmol L^{-1} $PtCl_4$ aqueous solution for 20 min at an ambient temperature. Eventually, the samples were putted on petri dish in an oven at 170 °C for 60 min. As evidenced in the field emission scanning electron microscopy (FESEM) measurement in Fig. 3(g), Pt_3Fe spherical nanoparticles with an average diameter 4.0 nm homogeneously covered the iron foil as a result of the annealing. Thus, the products with superhydrophobic property were fabricated. The reasons behind the selection of this specific annealing temperature and concentration of $PtCl_4$ solution will be emphatically discussed in later sections.

2.2. Sample characterization

The morphological characterization of the surfaces was performed by the field emission scanning electron microscopy (FESEM) (S-4800, Hitachi, Japan) under an electron beam. Prior to SEM observation, the conductivity of the specimens was improved by sputtering a thin layer of gold film on all samples using a sputtering coater (E-1045, Hitachi, Japan). The static WCA and dynamic SA or oil contact angles were checked by a contact angle meter (FTÅ 200, Data physics Inc, USA) using 8 μL water droplets as the indicator. Digital camera was used to observe photograph of water droplets. Averaging the values obtained at 5–6 different spots on each sample surface was used as the reported CA. The measuring error of the CA value was ±1°, as depicted by the error bar in the graph. SA was determined by gently tilting the sample stage until 8 μL water droplet began to move. The chemical composition of samples was observed using energy-dispersive X-ray spectra (EDX) (INCA Energy, Oxford CO, Japan). The chemical state of Fe and Pt in unannealed and annealed samples was investigated by X-ray photoelectron spectroscopy (XPS, Model PHI 5300, Physical Electronics, USA) equipped with Mg Kα (λ = 0.9891 nm) line as the monochromatic X-ray source with the reference of carbon binding energy. The structure and phase of the samples were confirmed using X-ray powder diffractometer (XRD) (D8 ADVANCE, Bruker, Germany) analysis equipped with Cu Kα radiation at X′Celerator's scanning rate of 5° min^{-1}. And the catalytic properties of the sample surfaces were tested by the HITACHI U-3310 UV–vis spectrophotometer in the wavelength range of 200–800 nm. Fig. 1 outlines the synthesis process of the superhydrophobic iron film.

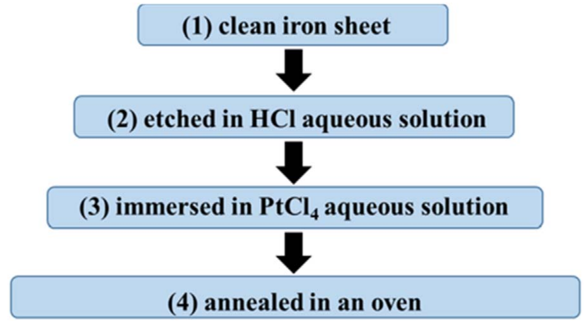

Fig. 1. The synthesis process flow chart of the superhydrophobic iron film.

3. Results and discussions

3.1. Surface morphology, composition, structure and wetting

Fig. 2 shows XRD and XPS spectra of samples. The samples with different preparation processing of etch, immersion and anneal were marked as sample 1, 2 and 3 respectively. The crystal structures of the sample 1, 2 and 3 were recorded by using XRD analysis in the scanning angle of 2θ range from 30 to 90°, as exhibited in Fig. 2a, respectively. It is clearly seen that three evident peaks at 44.6, 65.0 and 82.3° in curve 1 for sample 1 are assigned to diffraction from the (111), (200) and (211) crystal planes of the cubic structure of pure Fe (JCPDS Card No. 06–0696) with lattice constants of a = b = c = 2.866 Å, α = β = γ = 90°. Three new representative diffraction peaks at 39.8, 46.3 and 67.6°, can be indexed to the (111), (200) and (220) crystal planes of face centered cubic (fcc) Pt (JCPDS Card No. 65–2868) with lattice constants of a = b = c = 3.923 Å, α = β = γ = 90°, are detected in the XRD pattern for sample 2 (curve 2), suggesting that the coating layer is consisted of Pt nanoparticles. As shown in curve 3 of Fig. 2a, new peaks are generated for sample 3. The peaks at 2θ = 40.4, 47.0 and 68.7° are in accordance with the characteristic peaks of Pt_3Fe (JCPDS Card No. 29–0716) (111), Pt_3Fe (200) and Pt_3Fe (220) with lattice constants of a = b = c = 3.866 Å, α = β = γ = 90°, respectively, certifying that Pt_3Fe alloy is successfully coated on the iron substrate after annealing. In order to clearly detect the chemical state of the sample 2 and 3, XPS are performed for the elements emission on the spectrum interval of 0–1000 eV. As seen in Fig. 2b, it shows four photoemission peaks for Pt 4f, C 1s, O 1s and Fe 2p in full XPS patterns. Magnified Fe 2p peaks, composed of two peaks 708.6 and 722.4 eV are assigned to the spin–orbit splitting of 2p3/2 and 2p1/2 as shown in Fig. 2c, indicating dominant of Fe(0) [28]. The slight left shifting of Fe 2p peaks after annealing may be due to the synergistic effects between Fe and Pt in Pt_3Fe alloy. The XPS of Pt is exhibited in Fig. 2d, in the region of E_b =