Materials and Design 155 (2018) 346–351

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Flexible glassy grid structure for rapid degradation of azo dye

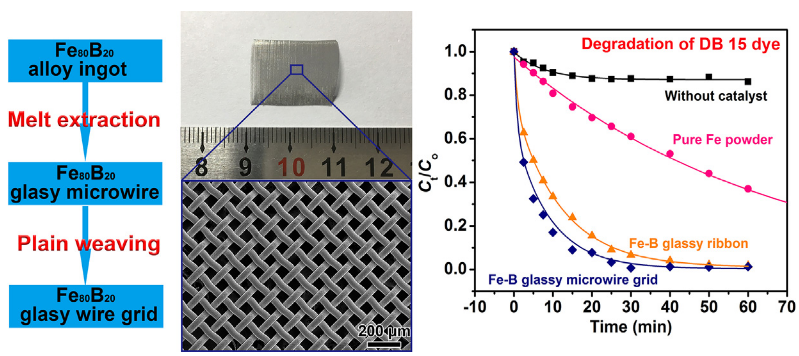
R. Li [a,b], X.J. Liu [a,*], H. Wang [a], Y. Wu [a], K.C. Chan [b,*], Z.P. Lu [a,*]

[a] State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Beijing 100083, PR China
[b] Advanced Manufacturing Technology Research Centre, Department of Industrial and Systems Engineering, The Hong Kong Polytechnic University, Hong Kong, PR China

HIGHLIGHTS

- Flexible $Fe_{80}B_{20}$ glassy wire-woven grid structure with tunable mesh size is newly designed and reported.
- The glassy wire grid is fabricated by melt-extraction and the subsequent plain weaving method.
- The grid structure exhibits higher degradation efficiency than that of bare ribbon and commercial Fe powders.
- High surface area and intrinsic activity of the glassy grid structure contribute to the enhanced degradation efficiency.
- The tunable meshes endow the grid structure with the capability of degrading and filtering wastewater simultaneously.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 February 2018
Received in revised form 11 June 2018
Accepted 11 June 2018
Available online 15 June 2018

Keywords:
Metallic glass
Grid structure
Wastewater treatment
Degradation

ABSTRACT

Degradation of organic contaminants in industrial wastewaters has become a worldwide conundrum and attracted extensive attention. In this paper, we report a flexible grid structure with uniform mesh fabricated by plain weaving melt-extracted $Fe_{80}B_{20}$ glassy micro-wires, and the produced wire grid with a dosage of 0.3 g/L can completely degrade 0.2 g/L DB 15 azo dyes for <30 min at room temperature. The calculated degradation efficiency of the sample is approximately 4.3 min, 2.1 times faster than that of the $Fe_{80}B_{20}$ glassy ribbons and 28 times for commercial pure Fe powders. The enhanced degradation performance is primarily attributed to the uniform grid structure with high internal surface area in addition to the intrinsic activity of metallic glasses. Our findings not only provide high-performance candidate for degrading and filtering wastewater with organic pollutant simultaneously, but also promote the practical applications of metallic glasses as functional materials.

1. Introduction

Due to the increasing demand of colorants and dyes in modern textile or other manufacturing industries, effective treatment of the organic wastewater has been becoming a worldwide conundrum [1–3]. Consequently, exploring new approaches to developing high-efficiency catalysts for the degradation of organic contaminants have become the focus of study in the wastewater treatment field. Over the years, considerable degradation approaches and catalysts have been reported, such as flocculation by catalysts, adsorption onto active materials and catalytic or photocatalytic degradation by nanostructured materials [4–11]. Current approaches to degrading or decolorizing the organic wastewater contaminants generally include the reduction reaction or Fenton oxidation process by zero-valence metals, especially zero valent iron powders, which have attracted increasing industrial interests due to their low cost, efficient degradation activity and nontoxicity

* Corresponding authors.
E-mail addresses: xjliu@ustb.edu.cn, (X.J. Liu), kc.chan@polyu.edu.hk, (K.C. Chan), luzp@ustb.edu.cn (Z.P. Lu).

https://doi.org/10.1016/j.matdes.2018.06.022

[12–17]. However, the high corrosion rate of crystalline elemental iron during degradation tends to result in rapid decay of the degradation efficiency [18, 19]. Meanwhile, agglomeration and difficult reclaim of pure micro/nano-scale Fe powders are also the handicap for their industrial applications. Consequently, developing novel materials with superior degradation efficiency have become a focus area in the field of dyeing wastewater treatment.

Metallic glasses (MGs), a novel class of metastable materials, have exhibited promising properties for catalytic applications due to their amorphous structure bearing no long-range order but abundant low-coordination sites at the surface [20–23]. Superior catalytic capability has been reported in degradation of azo dyes or removing of organic matters in wastewater using some MGs as catalysts, such as Fe-, Mg-, MgZn-, and Co-based MGs [24–30]. Currently, most researches on MG catalysts are either based on the form of ribbons or powders. However, for glassy ribbons, their low specific surface area limits the degradation efficiency, while for glassy micro/nano-scale powders, the potential problems as reported in crystalline powders (e.g., agglomeration, clogging and recycling) still remain to be solved. To further enhance degradation performance, lifetime and recyclability of MG catalysts, design of new material forms is needed.

In this paper, a wire-woven grid structure of Fe-based MGs with superior performance in degrading organic chemicals is newly designed and reported. Fabrication strategy of the glassy wire grids involves the melt-extraction method to prepare Fe-based MG micro-wires and the subsequent plain weaving of the glassy wires. By controlling the wire diameters, the mesh size of the wire-woven grid can be tuned conveniently. This novel Fe-B glassy microwire grid exhibits prominent degradation activity and reusability when compared with commercial pure Fe powders and glassy ribbons with the same composition. Our findings are expected to provide new opportunities of MGs for future applications in wastewater treatment and shed light on designing the grid-structured multicomponent metal catalysts with significantly enhanced performance.

2. Experimental

2.1. Materials

High-purity metal raw materials and 300 mesh Fe powders (purity >99.5 wt%) were purchased from Trillion Metals Co., Ltd. (Beijing, China). Direct blue 15 (DB 15, $C_{34}H_{27}N_6NaO_{16}S_4$) dye was bought from Sigma-Aldrich (America). Hydrogen peroxide (H_2O_2) solution (30%) was provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals were of analytical grade and used without further purification. Deionized water (18.2 MΩ cm) was generated by a Barnstead water system.

2.2. Preparation of $Fe_{80}B_{20}$ glassy wire woven structure

$Fe_{80}B_{20}$ (at.%) ingot was prepared by arc-melting high purity elements (Fe: 99.99 wt%, B: 99.9 wt%) under a Ti-gettered argon atmosphere. The pre-alloy ingots with a weight of ~2 g was re-melted in a ceramic crucible by high frequency induction heating, and then the $Fe_{80}B_{20}$ glassy wire with a continuous length of over 10 m was obtained by melt-extraction using a copper wheel with a steep edge. By controlling the linear speed of the copper wheel at 30, 40 and 50 m/s, $Fe_{80}B_{20}$ glassy wires with different diameters of 97, 66 and 45 μm were produced, respectively. The $Fe_{80}B_{20}$ glassy wires were then manufactured into grid structure by plain weaving method: each $Fe_{80}B_{20}$ glassy wire was woven alternately over and under the warp glassy wires through the cloth at 90-degree angle. The mesh sizes of the $Fe_{80}B_{20}$ glassy wire grids were controlled in the range of 68 to 134 μm by using the glassy wires with different diameters.

2.3. Microstructure characterization

Structural features of the $Fe_{80}B_{20}$ glassy microwire grids were characterized by X-ray diffraction (XRD, Rigaku DMAX-RB-12KW, Cu-Kα), scanning electron microscopy (SEM, Zeiss Supra 55) equipped with an energy dispersive X-ray spectrometer (EDS) and transmission electron microscope (TEM, Tecnai G2 F30). A Brunauer-Emmett-Teller (BET) test was also carried out to measure the internal surface area of the samples by N_2 absorption/desorption analysis conducted at 77 K.

2.4. Azo dye degradation measurement

The aqueous solution of DB 15 dye with the concentration of 0.2 g/L was used to evaluate the degradation performance of the samples. H_2O_2 with a concentration of 5 mM was added into the azo dye solution for oxidative degradation based on the Fenton-like reaction [31]. $Fe_{80}B_{20}$ glassy grids with a dosage of 0.3 g/L were used for degradation. Commercial pure Fe power (300 mesh) and $Fe_{80}B_{20}$ glassy ribbons (2–3 mm in width and 25–30 μm in thickness) with the same dosage were also tested for comparison. All experiments were conducted in 250 mL bottles, which were placed in a temperature-controlled water-bath trough. During each reaction, the solutions were rod-stirred at a constant speed. After degradation, 3 mL of filtered dye solution was pipetted out and subjected to UV–vis spectrum scanning at the wavelengths ranging from 200 to 1000 nm by using a UV spectrophotometer (UV-2800, Unico).

3. Results and discussion

Fig. 1a shows a partial configuration of the flexible wire grid specimen (20 × 20 mm^2) fabricated by plain weaving the melt extracted $Fe_{80}B_{20}$ wires with an average diameter of ~45 μm. It is seen that the $Fe_{80}B_{20}$ wires retain a high degree of mechanical flexibility after weaving. The high bending ability of the wires is mediated by dense shear bands around the bending region, as shown in Fig. 1b. The corresponding SEM image of surface profile of the glassy wire grid is shown in Fig. 1c. As can be seen, the $Fe_{80}B_{20}$ grid exhibits a uniform network structure and the mesh size was estimated to be ~68 μm. The XRD pattern shown in the inset of Fig. 1c displays a characteristic broad halo around 45°, demonstrating the amorphous structure of the $Fe_{80}B_{20}$ wire grid. The amorphous nature of the $Fe_{80}B_{20}$ microwire is further confirmed by high resolution TEM image (Fig. 1d) and corresponding selected area electron diffraction (SAED) pattern (the inset in Fig. 1d), in which neither crystalline lattice fringes nor crystalline diffraction spots were observed. The formation of amorphous structure of the wires is due to the large atomic size difference and negative heat of mixing (~23 kJ/mol) between Fe and B elements [32].Under the high cooling rate, the nucleation and growth of crystals were inhibited, and the liquid structure of the $Fe_{80}B_{20}$ was frozen-in to form the glassy structure. By the BET test at 77 K, the special surface area of the produced $Fe_{80}B_{20}$ glassy wire grid was measured to be 0.518 m^2/g, much higher than that of the $Fe_{80}B_{20}$ glassy ribbons (0.0236 m^2/g). Obviously, the high BET surface area is mainly benefited from the grid structure.

Fig. 2a shows a typical UV–vis spectra of the DB 15 aqueous solution treated by the $Fe_{80}B_{20}$ glassy wire grid for different reaction periods at room temperature. It is seen that the original DB 15 solution has a strong absorption peak at around 580 nm, and the absorption peak diminishes quickly with the prolonged treatment time, indicating the continuously rapid degradation of the DB 15 dye. The solution gradually becomes light red and then fully transparent after being degraded by the $Fe_{80}B_{20}$ glassy wire grid for <30 min (the inset in Fig. 2a). According to the experimental result of UV–vis spectra, 99.3% of DB 15 dye was degraded during the degradation process. These results demonstrate that the $Fe_{80}B_{20}$ glassy grid has excellent decoloration performance for the DB 15 dye aqueous solution. To further evaluate the efficiency of the glassy wire grid in degrading the DB 15 aqueous solution,