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Flower-like porous hematite nanoarchitectures achieved by complexation–mediated oxidation–hydrolysis reaction

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ABSTRACT

Flower-like porous hematite (α-Fe_2O_3) nanoarchitectures composed of ultra-thin nanoflakes were prepared by annealing the iron oxide precursor formed via the oxidation-hydrolysis reaction between Fe(II) ions and Tris(hydroxymethyl)aminomethane (abbreviated as Tris). The microstructure of the prepared FeOOH and hematite samples were fully characterized by field-emission scanning electron microscopy, transmission electron microscopy, X-ray diffraction analysis, Fourier-transforming infrared spectra, thermogravimetric analysis, and nitrogen adsorption–desorption isotherm. Based on the influences of reactant concentrations, reaction time and reaction temperature on the morphologies of the resultant samples, a formation mechanism of etching was proposed, Fe(II)–Tris complexes were self-assembled via hydrogen bonds into brick-like building blocks, which then aggregated into rudimentary nanoparticles, and the synergistic effect between the crystallization of FeOOH and dissociation of Fe(II)–Tris complexes make the rudimentary nanoparticles evolve into the flower-like products. The as-prepared flower-like α-Fe_2O_3 nanostructures possessed a Brunauer–Emmett–Teller specific surface area of 191.63 $m^2\,g^{-1}$, hierarchical pore distribution ranging from micropores to macropores, and good crystallinity, and excellent visible photocatalysis in terms of removing chemical oxygen demand of dimethyl sulfoxide industrial wastewater. The current work provides a reliable approach for building functional hierarchical nanoarchitectures and the prepared iron oxide nanomaterials demonstrate an excellent ability to remove toxic pollutants in industrial wastewater.

1. Introduction

While natural processes routinely generate nanoscale structures of surprising complexity and delicacy, researchers continue to seek straightforward and inexpensive chemical methods for controllable production of functional nanostructures. Recent successes in the chemical production of hierarchical structures composed of nanoscaled building blocks, such as nanoflakes [1–5], nanowires [6–8], nanorods [9–12], nanobelts [13–15], nanotubes [16], have received much attention in the light of their high specific surface area and novel optical, electronic, optoelectronic, catalytic and absorption properties. Two main approaches are generally developed to fabricate these structures. One depends on templates of self-assembled organic media [11,17–19], while the other utilizes either the special properties of organic solvents which influence the nucleation and growth of nanostructures [3–5,20,21] or the anisotropic properties of crystal nucleation and growth [8,12,22,23]. Most approaches either encounter the inevitable complexity of removing the template or rely on organic compounds unfriendly to the environment. Moreover, the current synthetic avenues for production of 3-dimensional hierarchical nanostructures are bottom-up routes based on either Ostwald ripening or the self-assembly of many nanosized building blocks, ultimately shaping materials with overall size on micron scale. For example, on the basis of the coordination reaction between ethylene glycol and $FeCl_3$ mediated by urea, flower-like hematite nanostructures were synthesized through fast nucleation of amorphous primary particles and subsequent slow aggregation and crystallization [1]. Taking advantage of direct reaction between $FeSO_4$ and $NaClO_3$ under mild conditions, Zhu et al. synthesized flower-like hematite superstructures through an initial aggregation of primary nanoparticles and a succedent oriented attachment of nanorods in the absence of any organic additives [24]. Zeng et al. developed another solvothermal method to prepare porous hematite flower-like nanostructures based on an ethanol-mediated self-assembly process [25]. Recently, our group also synthesized flower-like hematite nanostructures by a simple approach consisting of a forced hydrolysis-oxidation of iron (II) salts in the presence of D-(+)-glucose as structure-directing agents and annealing process [26]. It is noted that the above mentioned flower-like hematite

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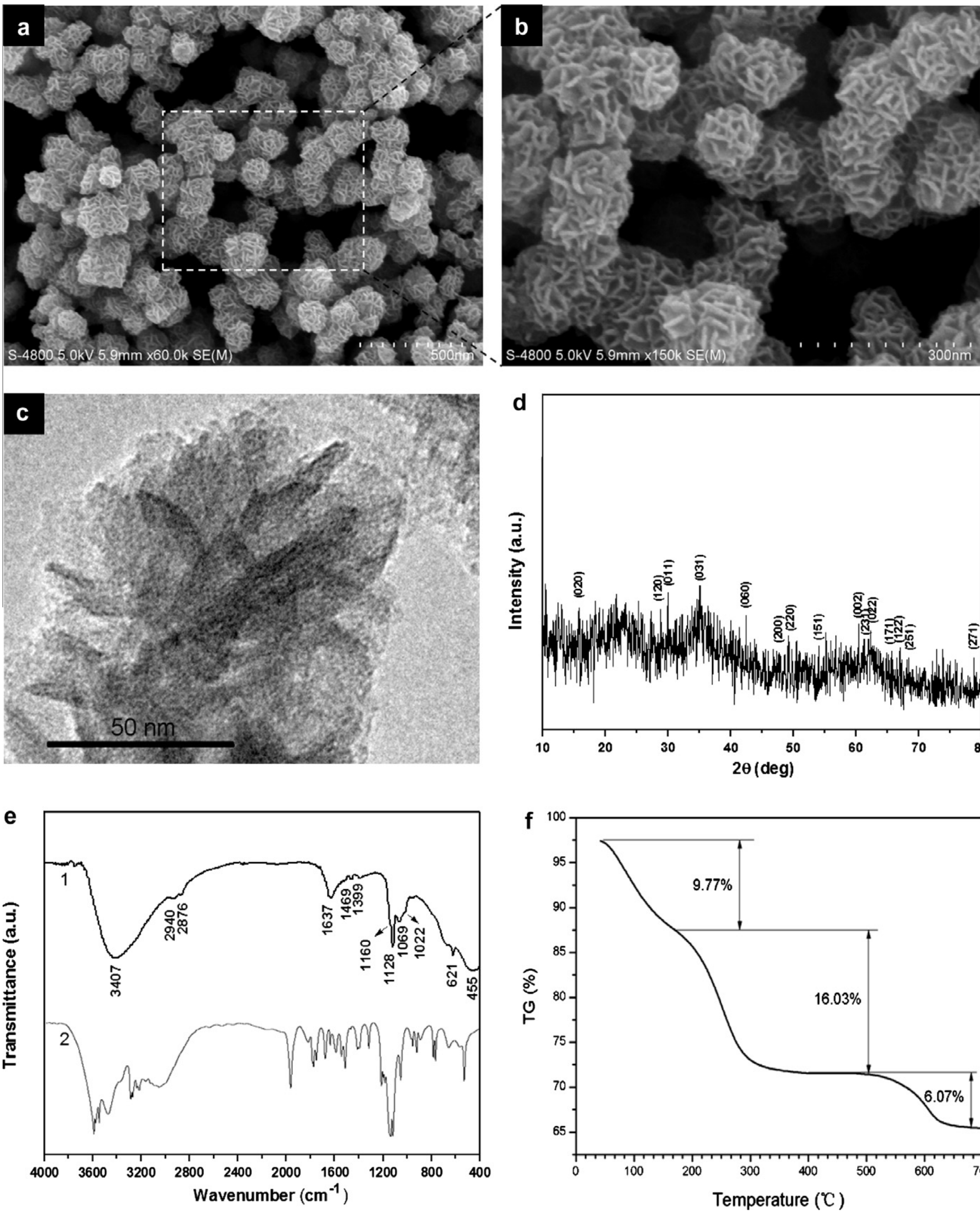

Fig. 1. (a and b) SEM images, (c) TEM image, (d) XRD pattern of the as-prepared flower-like FeOOH nanostructures, (e) FTIR spectra of the as-prepared flower-like FeOOH nanostructures (1) and Tris (2), and (f) TG curve of the as-prepared flower-like FeOOH nanostructures.

nanostructures generally show the overall size on the micrometer scale and the building blocks tend to aggregate and debase the BET surface area. As a result, most of them do not exhibit BET surface area big enough to endow with excellent photocatalytic efficiency, although hematite is a promising photocatalytic material under the irradiation of visible light. Thus, it is necessary to develop syn-