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Full Length Article

Magnetic porous Fe_3O_4/carbon octahedra derived from iron-based metal-organic framework as heterogeneous Fenton-like catalyst

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ABSTRACT

The synthesis of effective and recyclable Fenton-like catalyst is still a key factor for advanced oxidation processes. Herein, magnetic porous Fe_3O_4/carbon octahedra were constructed by a two-step controlled calcination of iron-based metal organic framework. The porous octahedra were assembled by interpenetrated Fe_3O_4 nanoparticles coated with graphitic carbon layer, offering abundant mesoporous channels for the solid-liquid contact. Moreover, the oxygen-containing functional groups on the surface of graphitic carbon endow the catalysts with hydrophilic nature and well-dispersion into water. The porous Fe_3O_4/carbon octahedra show efficiently heterogeneous Fenton-like reactions for decomposing the organic dye methylene blue (MB) with the help of H_2O_2, and nearly 100% removal efficiency within 60 min. Furthermore, the magnetic catalyst retains the activity after ten cycles and can be easily separated by external magnetic field, indicating the long-term catalytic durability and recyclability. The good Fenton-like catalytic performance of the as-synthesized Fe_3O_4/carbon octahedra is ascribed to the unique mesoporous structure derived from MOF-framework, as well as the sacrificial role and stabilizing effect of graphitic carbon layer. This work provides a facile strategy for the controllable synthesis of integrated porous octahedral structure with graphitic carbon layer, and thereby the catalyst holds significant potential for wastewater treatment.

1. Introduction

Organic wastewater emitted from dye, pharmaceutical, sanitary and catering has become a major threat to human and ecology due to the toxicity and non-biodegradability [1–3]. Recently, advanced oxidation process (AOPs) have been the useful treatments for organic wastewater [4,5]. Among them, Fenton reaction ($Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH$) is a well-studied and effective AOP, which is based on the generated hydroxyl radicals (•OH) with a high oxidation potential [$E^0({}^{\bullet}OH/H_2O) = +2.8\ V_{NHE}$] and nonselectivity for mineralization of organic pollutants [6]. However, the conventional homogeneous Fenton process consisted of ferrous salts and hydrogen peroxide generates iron sludge along with the reaction, resulting in secondary pollution and non-recyclability of the catalyst.

Significantly, to deal with the negative effect, heterogeneous Fenton-like reactions have been developed through using solid catalysts and hydrogen peroxide to generate hydroxyl radicals for the degradation of organic pollutants [7–9]. Currently, iron-based solid catalysts, such as zero-valent iron [10], iron-containing materials [11], iron oxides and modified iron oxides [12], were widely used for Fenton-like reactions. Among these catalysts, magnetite (Fe_3O_4) is considered to be a suitable Fenton-like catalyst, owing to the unique physicochemical properties with good electric, catalytic and magnetic performance. Importantly, the magnetite has inverse spinel structure and Fe(II) Fe(III) in the octahedral sites with fast electron-transfer, resulting in reversibly oxidation-reduction of iron species and nondestruction of the crystal structure [13]. Moreover, the magnetic property of magnetite allows it to be easily separated from wastewater by external magnetic field. However, the reported Fe_3O_4 nanoparticles suffered from poor Fenton-like catalytic performance and easy agglomeration during the reaction, leading to a reduced catalytic activity [14,15]. Continuous efforts were made to improve the situation through introducing organic or inorganic supports to form iron oxide-based Fenton-like composite catalysts, such as Fe_3O_4@β-CD [16], Fe_3O_4@SiO_2 [17], Fe_3O_4-MWCNTs [18] or Fe_3O_4/rGO [19] to prevent agglomeration of the Fe_3O_4 nanoparticles for slowing down deactivation and improving recyclability of the catalysts. Among them, carbon-based supports are ideal candidates, due to their stabilizing effect and

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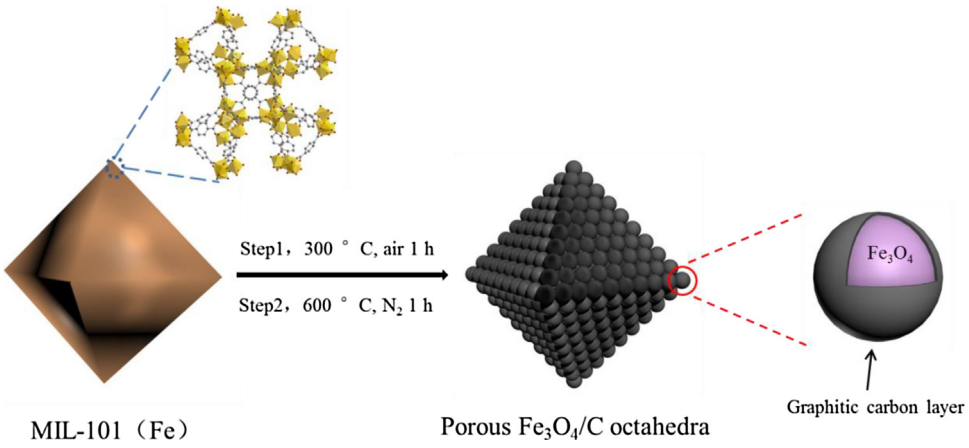

Fig. 1. Schematic illustration of the preparation process of MOF-derived magnetic porous Fe_3O_4/carbon octahedra.

catalytic performance with electron donor-acceptor surface properties for hydrogen peroxide decomposition into radical species. In addition, structure-controlling to form porous structure is an effective way to improve the catalytic performance for increasing solid-liquid contact area and exposure active sites. However, it is still a challenge for the rational design of integrated porous structure with carbon coated magnetite for good Fenton-like catalytic performance.

Metal-organic frameworks (MOFs), a novel class of hybrid porous crystalline composed of metal center/clusters bridged by functional organic ligands, have attracted extensive research interest [20]. Due to the unique properties with large surface area and tunable porosities, MOFs have been demonstrated great potential application in gas adsorption, drug delivery, catalysis and sensor [21–23]. Most recently, MOFs exhibit promise for use as effective self-sacrificial templates or precursors to construct porous carbon-based metal oxide composites. For instance, porous ZnO/$ZnFe_2O_4$/C octahedra were fabricated using Fe^{III}-modified MOF-5 as precursors and shown excellent performance in high-rate lithium-ion batteries [24]. Hybrid Co_3O_4-carbon porous nanowire arrays were prepared by carbonization of the metal-organic framework and achieved ultrahigh oxygen evolution activity and strong durability [25]. Through the direct annealing of a Cu-based MOF in N_2, Cu/CuO_x/C nanocomposites were obtained and shown good catalytic performance for CO oxidation [26]. These great successes may attribute to the unique properties of MOFs with selectable

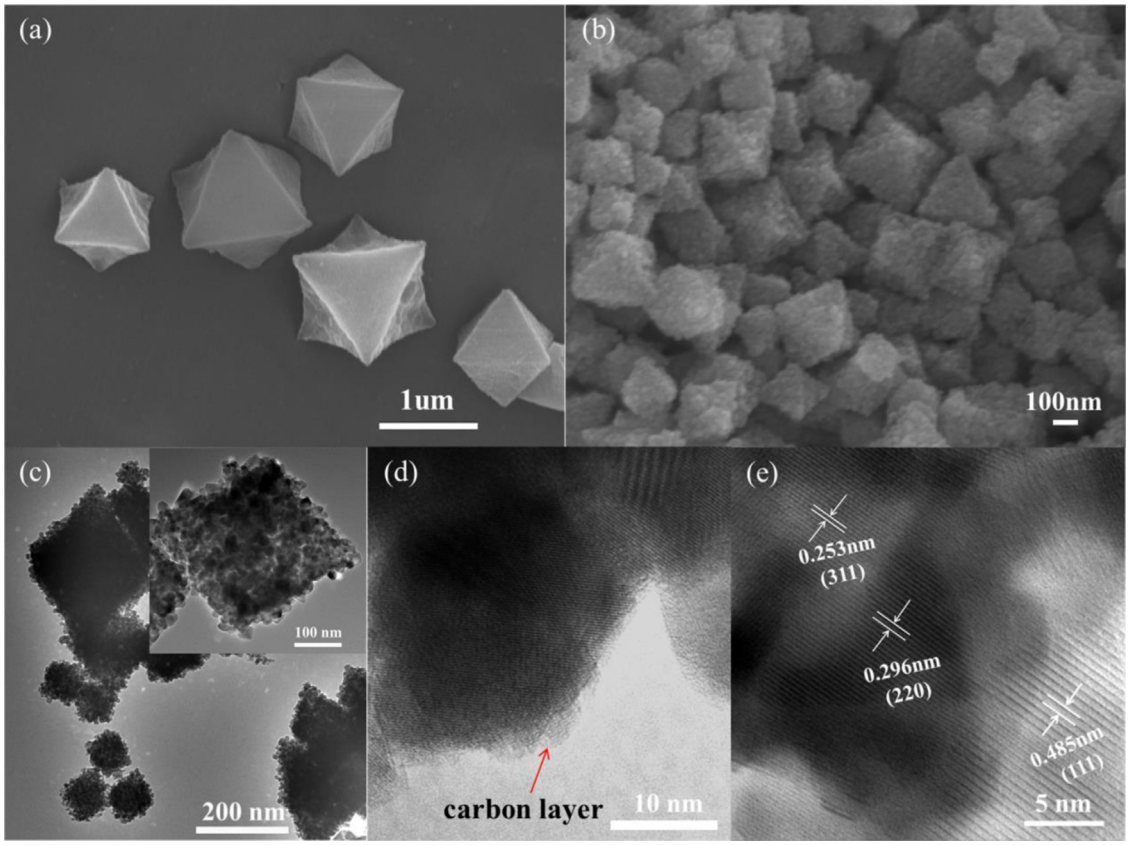

Fig. 2. (a) SEM image of MIL-101(Fe) precursors; (b, c) SEM and TEM (inset is the enlarged TEM image) and (d, e) HRTEM images of the as-synthesized porous Fe_3O_4/carbon octahedra.