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Dual-functional catalytic materials: Magnetically hollow porous Ni-manganese oxides microspheres/cotton cellulose fiber

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ABSTRACT

An eco-friendly magnetically hollow porous $NiMn_2O_4$ microspheres (HPS-$NiMn_2O_4$)/cotton cellulose fiber (CCF) composite (HPS-$NiMn_2O_4$/CCF) was designed by using regenerated cotton as the potential cotton cellulose fibers (CCF) source. Magnetically HPS-$NiMn_2O_4$ microspheres were in-situ grown on the CCF surface uniformly by using hydrothermal method with subsequent calcination for removing the cellulose matrix to obtain magnetic HPS-$NiMn_2O_4$/CCF. HPS-$NiMn_2O_4$/CCF exhibited dual-functional catalytic properties on reduction of 4-nitrophenol and photodegradation of dye pollutants compared with $NiMn_2O_4$ nanoparticles (NPs-$NiMn_2O_4$) and HPS-$NiMn_2O_4$. The mechanisms for the dual-functional catalytic reactions over HPS-$NiMn_2O_4$/CCF were inferred. The special morphology of HPS-$NiMn_2O_4$, the presence of $NiMn_2O_4$ with 'd^8' (Ni element) and 'd^5' (Mn element) electronic configurations and the introduction of CCF facilitated positively the catalytic reaction and efficient electron–hole separation. Because of its green and magnetic separability, HPS-$NiMn_2O_4$/CCF can be potentially applied in catalysis, water purification and green chemistry.

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1. Introduction

Nowadays, dual-functional metal oxides catalysts designed from renewable and eco-friendly resource have aroused much attention because it provided the promising sustainable development technologies. Due to their chemically and thermally stable magnetic properties [1–3], spinel type metal oxides (AB_2O_4; A, B=Co, Ni, Zn, Mn, Fe) [4], combination of two simple low-cost transition metal oxides, were used for many applications, such as drug delivery, electronic devices, magnetic resonance imaging, and information storage [5–8]. Also, because of prominent electrochemical performance and easier to large-scale synthesis, they are emerging in electrode materials for both electrochemical capacitors and lithium ion batteries [9,10]. More applications of AB_2O_4 materials include adsorbents for removing toxic substances [11,12], treatment of heavy metal waste [13] and chemical sensors [14]. It is worth noting that spinel type AB_2O_4 containing 3d metal ion is developing prospects to be the most hopeful economical catalysts [15,16]. For example, Ali [17] studied the catalytic activity of $NiFe_2O_4$ for hydroxylation of benzene into phenol. Mathew [18] synthesized orthoalkyl phenols by using $Cu_{0.5}Co_{0.5}Fe_2O_4$ as the catalyst. Moreover, because of a narrow band gap, AB_2O_4 also has excellent photocatalytic performance [19,20]. AB_2O_4 may be used alone, or together with other photocatalysts as photocatalysts [21,22]. When used as composite photocatalysts, AB_2O_4 exhibited enhanced degradation efficiency [23,24]. As an important spinel binary metal oxide, $NiMn_2O_4$ has significant applications because of its magnetic and catalytic properties [2,25], such as magnetism [26], catalysis [27], super capacitor [28], sensors [29], etc.

Along with the particle size decreasing and the increase of the surface energy for the catalyst, the interparticle aggregation will deteriorate and hinder seriously the catalytic activity. It is regarded a beneficial approach anchoring metal oxide particles on the substrates to prevent the interparticle aggregation and improve the catalytic efficiency. Recently, carbon-based materials, such as graphite [30], carbon black [31], carbon nanotubes [32,33], mesoporous carbon [34], graphene [35,36], and carbon spherules [37] have drawn increasing attention as catalyst carrier materials. Compared with these carbon-based materials, reproducible cotton as the potential cotton cellulose fibers (CCF) matrix are low cost, abundant, pollution-free, and renewable, also possess desired fibrous structure. Meanwhile, cotton cellulose fibers can endow the bare particles with more high active sites and offer a favorable platform to anchor the particles. The cotton cellulose fibers made of reproducible cotton has a great interest toward sustainable future and controlling the white pollution.

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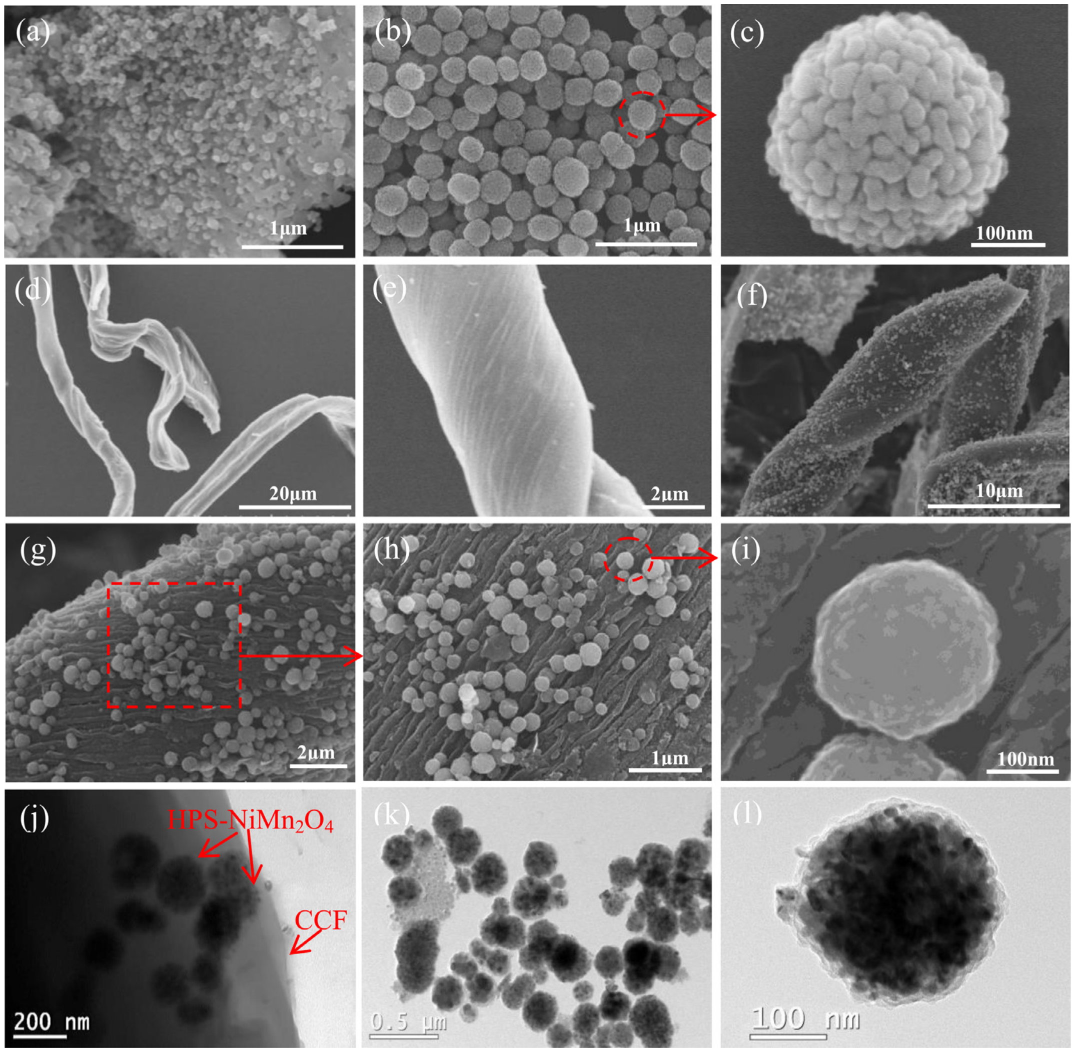
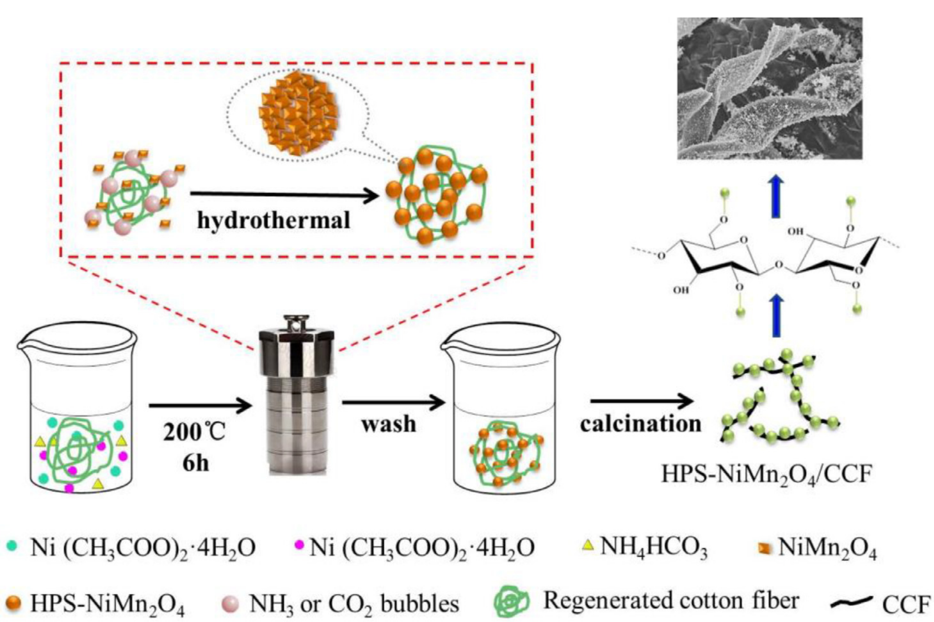


Fig. 1. SEM images of (a) NPs-$NiMn_2O_4$, (b and c) HPS-$NiMn_2O_4$ microspheres, (d and e) CCF, (f–i) HPS-$NiMn_2O_4$/CCF, TEM images (j and k) of HPS-$NiMn_2O_4$/CCF, (l) mono-spheres HPS-$NiMn_2O_4$/CCF with more details.



Scheme 1. Schematic illustration of the formation of HPS-$NiMn_2O_4$/CCF.

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