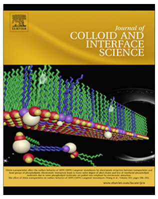
Journal of Colloid and Interface Science 522 (2018) 283–290

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

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



MOG-derived porous FeCo/C nanocomposites as a potential platform for enhanced catalytic activity and lithium-ion batteries performance

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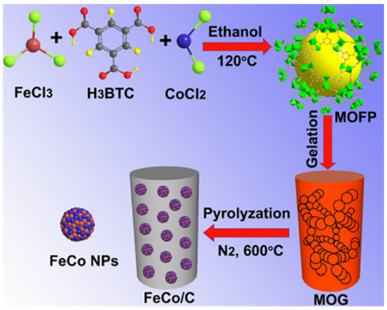
GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 December 2017
Revised 17 March 2018
Accepted 24 March 2018
Available online 26 March 2018

Keywords:
Metal-organic frameworks
Nanoalloys
Porous carbon nanocomposites
Heterogeneous catalysis
Lithium-ion batteries

ABSTRACT

The transition metal alloy nanoparticles (NPs) have received significant attention because of their unique physicochemical properties as well as low cost. Herein, we report a facile and clean synthetic route to prepare porous FeCo/C bimetallic alloy nanocomposites by using metal-organic gels (MOGs) as precursors. The bimetallic MOGs based on iron and cobalt bridged by tri-carboxylate organic ligands were first synthesized by a general and fast solvothermal method. The desired FeCo/C nanocomposites were then obtained by a one-step annealing process in which MOGs served as both the precursor and the self-sacrificing template. Significantly, the as-synthesized FeCo/C nanocomposites exhibit excellent catalytic activity and lithium-ion batteries performance. This fast and clean synthetic strategy is extended to synthesis diversity and range of potential applications of porous carbon-coated transition-metal alloy nanocomposites.

1. Introduction

The first-row transition metal (FRTM) nanoparticles (NPs) have attracted remarkable research interest, not only for their relatively low costs but also for many attractive applications in cancer therapy, environmental remediation, energy conversion and storage, and catalysis [1–3]. However, these monometallic FRTM NPs are easily etched by acidic or alkaline reaction conditions, which is one of the key limitations for their practical applications [4]. When FRTM NPs are alloyed with other metal NPs, their stabilities under harsh reaction conditions can be much improved, which depends on the nanoalloy composition, degree of alloying, and the alloy NPs size [5,6]. Though great effort has already been invested, the naked small FRTM NPs have high surface energy and readily aggregate to larger NPs during usage, deteriorating their initial performance greatly. Another great concern of FRTM-based NPs

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https://doi.org/10.1016/j.jcis.2018.03.081

is the easy oxidation. Hence, developing suitable surface engineering methods to stabilize these FRTM NPs is highly desired [7]. As we all know that supporting NPs with porous carbon material is an effective method to stabilize the growth of monometallic or alloy NPs [8]. Porous carbon is an interesting and unique supporting material for NPs due to its light weight, chemical and mechanical stability, and easy modification [9]. Therefore, a simple and repeatable strategy to synthesize FRTM-based bimetallic NPs loaded on porous carbon with a good dispersion and stability is necessary.

As a newly developed crystalline nanoporous materials, metal-organic frameworks (MOFs) have been rapid development and widely exploited in recent years because of their fascinating architectures as well as their diverse potential uses in many fields [10,11]. A special structural feature in MOFs is the tunable porosity and the large internal surface area, which makes them exhibit outstanding performance in catalysis [12], drug delivery [13], gas storage and separation [14], and water treatment [15]. MOFs are built from transition metal ions/clusters as nodes and organic ligands as struts, and they have been used as promising precursors or sacrificial templates to construct novel porous carbons and metal/metal oxide nanostructures, which have application in heterogeneous catalysis, supercapacitors, lithium-ion batteries, and energy storage [16–18]. The thermal transformation of MOFs into carbon nanomaterials can not only effectively preserve the large surface area and porosity of MOFs, but also can be easily obtained the porous carbons modified with uniform metallic species [19]. To date, there have been several important works on the usage of MOFs as templates in the synthesis of highly porous FRTM-based metal/metal oxide/C nanocomposites [9,20,21], but report on stabilizing FRTM-based bimetallic alloy NPs on carbon materials using MOFs as the sacrificial templates remain limited thus far [22,23].

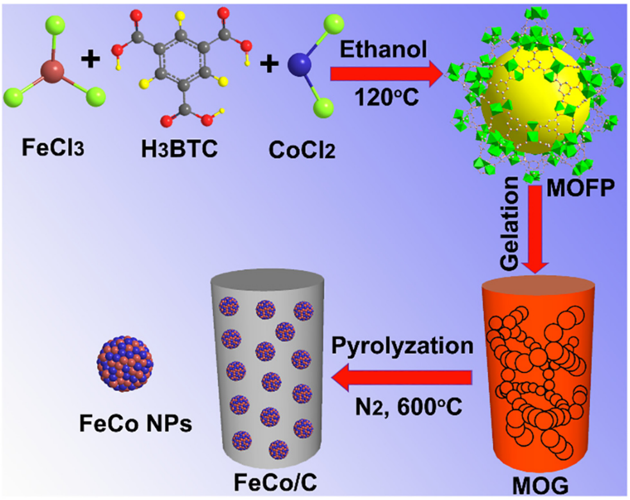
On the other hand, as a recently developed class of extended MOF porous materials, metal-organic gels (MOGs) experienced widespread research interest in recent years [24]. MOGs are constructed through the principle of coordination chemistry, and self-assembled to form three-dimensional (3D) frameworks by the supramolecular interactions, including π-π stacking, hydrogen bonding, and van der Waals attraction [25]. Compared to MOFs, the most important advantage of MOGs is the easy preparation, such as low reaction temperature, short reaction time, neutral condition, and clean ethanol solvent [26]. Therefore, these porous MOGs based materials are more suitable to be used in industry on a large scale. However, the use of MOGs as the FRTM-based bimetallic alloy NPs precursor has never been reported.

Herein, we report a fast and clean strategy to obtain porous carbon-coated FeCo bimetallic NPs with a regular morphology and good particle dispersion using a bimetallic MOG (Fe/Co-MIL-100) as both the precursor and the self-sacrificing template (Scheme 1). The synthesis process is easy, tunable, and cost-effective, and therefore it is highly promising for large scale production. The application of the resulting porous materials, i.e. FeCo/C nanocomposites, in heterogeneous catalysis and lithium-ion batteries, was also explored.

2. Experimental section

2.1. Materials and methods

Benzene-1,3,5-tricarboxylic acid (H_3BTC) was purchased from Sigma-Aldrich. Ferric trichloride hexahydrate ($FeCl_3{\cdot}6H_2O$), Cobalt chloride hexahydrate ($CoCl_2{\cdot}6H_2O$), Sodium borohydride ($NaBH_4$), and 4-nitrophenol (4-NP) were purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd.



Scheme 1. Schematic illustration for the preparation process of porous FeCo/C alloy nanocomposites derived from bimetallic MOGs.

The powder X-ray diffraction (PXRD) patterns were recorded by an X-ray diffractometer at 36 kV and 25 mA, using Cu target from 10 to 70°. Transmission electron microscopy (TEM) images were characterized by a JEM-2100F transmission electron microscope at 200 kV. Nitrogen adsorption-desorption isotherms were carried out with a Micromeritics TriStar II 3020 adsorption analyzer at 77 K. The magnetization measurement was measured under a varying magnetic field from -30000 to 30,000 Oe on a BHV-55 vibrationg sample magnetometer (VSM) at room temperature. TGA were carried out between 25 and 800 °C under nitrogen atmosphere, using a TGA/DSC1. UV–vis absorption spectra were carried out with a Shimadzu UV-1800 spectrophotometer. X-ray photoelectron spectra (XPS) experiments were carried out using an Mg Kα radiation (1253.6 eV) at the Photoemission End station of National Synchrotron Radiation Laboratory (NSRL), University of Science and Technology of China (USTC).

2.2. Synthesis of Fe-MIL-100 gels

The monometallic MOGs Fe-MIL-100 was prepared according to our recently published work with some modifications [27]. Typically, H_3BTC (0.52 g, 2.48 mmol) was dissolved in 9 mL ethanol under stirring to form a clear solution. Then another 9 mL of ethanol containing $FeCl_3{\cdot}6H_2O$ (1.0055 g, 3.72 mmol) were added under stirring for 10 min at room temperature. After dissolved thoroughly, the mixture solution was transferred into a 50 mL autoclave and heated up to 120 °C for 1 h. After cooling, the xerogels were obtained by drying the wet gels under air at 80 °C.

2.3. Synthesis of Fe/Co-MIL-100 gels

Bimetallic MOGs of Fe/Co-MIL-100 with different molar ratio of Fe and Co were prepared by using variable concentrations of metal ions (Fe:Co = 8:1, 4:1, 2:1, 1:1) while total amount of metal was kept as a constant of 3.72 mmol. Typically, for preparation of Fe/Co(2:1)-MIL-100 gel, $FeCl_3{\cdot}6H_2O$ (0.6703 g, 2.48 mmol) and $CoCl_2{\cdot}6H_2O$ (0.2951 g, 1.24 mmol) were firstly dissolved in 9 mL ethanol at room temperature. After dissolved thoroughly, another 9 mL of ethanol containing H_3BTC (0.52 g, 2.48 mmol) were added under stirring for 10 min. Then the mixture solution was transferred into a 50 mL autoclave and heated up to 120 °C for 1 h. After cooling, the xerogels were obtained by drying the wet gels under air at 80 °C.