



# Synthesis and characterization of nanometal-ordered mesoporous carbon composites as heterogeneous catalysts for electrooxidation of aniline



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## ABSTRACT

The Cu, Co and Ni nanometal embedded ordered mesoporous carbons (NM-OMCs) were fabricated by a soft-template method using phenol/formaldehyde as carbon source and triblock copolymer F127 as template agent. The morphology, structure, surface physicochemical properties and pore structure of the NM-OMCs were characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and nitrogen adsorption-desorption isotherms. Their potential application to the electrocatalytic degradation of aniline was investigated using electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and  $\cdot\text{OH}$  radicals generation test. Furthermore, the electrochemical oxidation process of aniline was also investigated in the presence of the OMC-based catalyst particles suspended in a  $\text{Na}_2\text{SO}_4$  solution using a  $\text{PbO}_2$  anode. Results revealed that the NM-OMCs inherited the ordered mesostructure of pristine OMC and the metal nanoparticles (Cu, Co or Ni) were embedded in the carbon framework. The Cu-OMC exhibited significantly higher catalytic activity than OMC and other NM-OMCs for the electrooxidation of aniline. In electrochemical oxidation process of aniline, nearly all of aniline could be degraded after 120 min of electrolysis with Cu-OMC particles as catalyst, while 89%, 92%, and 97% with OMC, Co-OMC and Ni-OMC catalysts, respectively, obviously higher than 76% of electrochemical oxidation without assistance of catalysts. After characterization of intermediates, a possible electrochemical degradation pathway of aniline was proposed.

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## 1. Introduction

Aniline and its derivatives are important raw materials for production of various synthetic compounds, including dye, pharmaceutical agents, pesticides, explosives, perfume, rubber, and so on [1], which have been found to be widely distributed in water environment due to their widespread use and inappropriate treatment [2]. However, the aniline is a typical toxic and persistent organic pollutant [3]. It has been found to be carcinogenic and also react easily in the blood to convert hemoglobin into methaemoglobin, thereby preventing oxygen uptake [2]. It is therefore important to find a suitable alternative methodology/technology to remediate aniline-containing effluents.

Electrochemical oxidation technology is one of the most effective methods for the treatment of wastewater containing toxic organic pollutants due to its strong oxidation performance, easy implementation, environmental compatibility and low cost [4], where organic pollutants can be completely mineralized into  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and inorganic compounds, or at least transformed into more biodegradable products [5]. The material of anode is crucial for the degradation efficiency of pollutants in electrochemical oxidation process [6]. Thus, various stable anodes with high electro-catalytic activity and long lifetime were studied by researchers [4,7,8]. However, the electrochemical systems with common two-dimension (2D) anodes have some weaknesses such as low current efficiency and high energy consumption due to their low surface areas [3]. Thus, three-dimension (3D) electrodes, such as granulated activated carbons (GAC) [9,10], granulated graphite [11] and carbon aerogel (CA) [12], emerged to improve the current efficiency of electrochemical oxidation. Their large specific surface

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area can provide more activity sites and accelerate the electro-generation of  $\cdot\text{OH}$  radicals. In addition, the catalysts were also introduced into the electrochemical oxidation systems to further improve the oxidation efficiency. Gu et al. [13] synthesized a novel catalyst of  $\text{CuO-Co}_2\text{O}_3\text{-PO}_4^{3-}$  modified kaolin for catalytic oxidation of anionic surfactants. Its COD removal efficiency reached up to 90% in 60 min, much higher than those without assistance of catalysts. Chen et al. [14] enhanced the electrochemical degradation of dinitrotoluene wastewater by Sn-Sb-Ag-modified ceramic particulates (SCP). The strong oxidizing agents were generated by SCP in the electrochemical system and contributed to the electrochemical degradation of dinitrotoluene wastewater. Our previous studies using Cu-rare earth/ $\text{Al}_2\text{O}_3$  as catalysts for electrochemical oxidation of *p*-nitrophenol have also reported that *p*-nitrophenol removal was significantly enhanced by the Cu-rare earth/ $\text{Al}_2\text{O}_3$  catalysts [15]. However, in these studies, the catalysts were all prepared using an impregnation method, and only small amount of metal oxides were loaded on the surface of supports, which probably limited the catalytic activity of particles.

Recently, as a kind of novel carbon nanomaterial, ordered mesoporous carbons (OMCs) have attracted much attention due to their high surface area (up to  $2500\text{ m}^2\text{ g}^{-1}$ ), large pore volume, uniform and adjustable pore size (2.0–5.0 nm), regularly aligned pore architecture, chemical inertness and good electrical conducting property [16–18]. More importantly, the regular pore channels of OMCs can provide a confined space for the growth of nanomaterials, which helps developing unique nano-reactor with notable performance [19]. These outstanding features make them be applied in versatile processes such as hydrogen storage, catalysis, and electrochemistry devices fabrication. Joo et al. [20] synthesized highly order, rigid arrays of nanoporous carbon using ordered mesoporous silica as templates. The resulted material supported a high dispersion of platinum nanoparticles, exceeding those of other common microporous carbon materials. Hydrogen adsorption on OMCs incorporated with Pd, Pt, Ni and Ru was enhanced by a factor 2.7–5.4 times over the pure carbon at hydrogen pressure of 800 Torr [21].

Hence, the aim of the present work is to in situ synthesize metal nanoparticles (Cu, Co and Ni) embedded ordered mesoporous carbons (denoted NM-OMCs) using a soft-template method for enhancing electro-catalytic oxidation removal of aniline. Their structure, composition, morphology, and textural properties were characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and nitrogen adsorption-desorption isotherms. Their electrochemical performances were also investigated using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Furthermore, their catalytic activity for degradation of aniline was also studied. The primary intermediate products of aniline were identified by high performance liquid chromatography (HPLC) and the main degradation pathways were elucidated.

## 2. Experimental

### 2.1. Materials

Triblock copolymer F127 ( $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$ ,  $M_{\text{av}} = 13,338\text{ g mol}^{-1}$ ) was purchased from Sigma Aldrich. All other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd, China. All the chemicals were of analytical grade and were used as received without any further purification. All solutions were prepared using ultrapure water.

### 2.2. NM-OMC preparation

OMC and NM-OMCs were prepared according to the reported methods with some modification [22,23].

Firstly, 6.1 g of phenol was melted at  $42\text{ }^\circ\text{C}$  in water bath, and then 1.3 g of NaOH solution (20 wt%) was added and stirred for 10 min. After that, 10.5 g of formaldehyde (37 wt%) was slowly added into the above solution and the solution was stirred at  $72\text{ }^\circ\text{C}$  for 60 min. After natural cooling, the pH value of solution was adjusted to 7.0 using  $6\text{ mol dm}^{-3}$  HCl and then dried to a constant weight at  $45\text{ }^\circ\text{C}$  in a vacuum drying oven to form resol. The resulting resol was dissolved in ethanol to get resol ethanolic solution (20 wt%).

Then, NM-OMC composite materials were prepared by co-assembly of F127, resol precursor, and Cu, Co, Ni species through evaporation induced self-assembly strategy. The fabrication process of NM-OMCs is schematically described in Fig. 1. In a detail procedure, 1 g of F127 was firstly dissolved in 14 ml of ethanol at  $40\text{ }^\circ\text{C}$  to form solution A.  $0.25\text{ mM Cu}(\text{NO}_3)_2$ ,  $\text{Co}(\text{NO}_3)_2$  or  $\text{Ni}(\text{NO}_3)_2$  was dissolved in 6 ml of ethanol to form solution B. Then solution B was slowly added into solution A, and the mixed solution was vigorously stirred for 30 min. Then, 5 g of resol ethanolic solution (20 wt%) was added dropwise into the above mixture. After further stirring for 1 h, the homogenous solution was obtained and transferred into dishes to evaporate the solvents at room temperature for 12 h. Then, the dishes were transferred into an oven and heated up to  $100\text{ }^\circ\text{C}$  for 24 h in order to thermopolymerize the precursors. The formed soft films collected from dishes were placed into a temperature-programmed vacuum furnace for heat treatment in nitrogen atmosphere with a heating rate of  $1\text{ }^\circ\text{C min}^{-1}$  and were kept at  $350\text{ }^\circ\text{C}$  and  $720\text{ }^\circ\text{C}$  for 3 h and 2 h, respectively. During calcinations, the triblock copolymer template F127 was removed and NM-OMC composites (Cu-OMC, Co-OMC and Ni-OMC) were obtained. For comparison, the pristine OMC was also obtained through above steps without adding nitrates.

### 2.3. Characterization

XRD patterns of samples were acquired on a Rigaku D-max/3C diffractometer using  $\text{Cu K}\alpha$  radiation, operated at 45 kV and 30 mA.

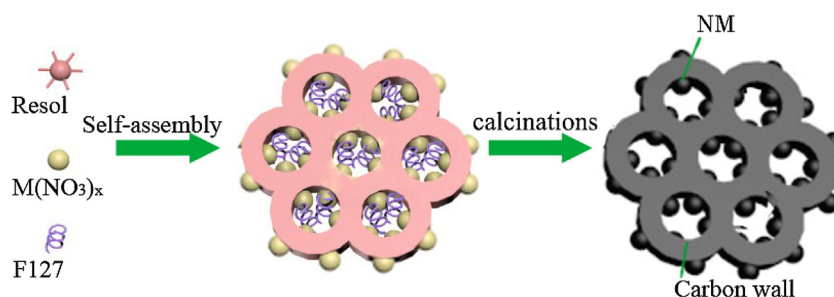


Fig. 1. Schematic view of the procedure for preparing NM-OMC materials.

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