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Metal organic frameworks/macroporous carbon composites with enhanced stability properties and good electrocatalytic ability for ascorbic acid and hemoglobin



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ABSTRACT

The thermal, water and electrochemical stability of Cu-based metal organic frameworks (Cu-MOFs) confined in macroporous carbon (MPC) hybrids has been investigated. Thermogravimetric analyses, X-Ray diffraction, scanning electron microscopy, and cyclic voltammetry were employed to confirm the stability of pure Cu-MOFs, MPC, and Cu-MOFs-MPC. As compared to pure Cu-MOFs, the porous composite materials of MPC and Cu-MOFs interact and seem to form new materials having homogenous structure and chemistry, which show structural stability in aqueous media and electrochemical stability in phosphate buffer solution (PBS pH 7.4). The detection of ascorbic acid and hemoglobin is performed as an electrochemical probe, indicating Cu-MOFs-MPC holds great promise for the design of electrochemical sensors.

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1. Introduction

Metal organic frameworks (MOFs) have many exciting characteristics including structural adaptivity and flexibility, ordered crystalline pores, and multiple coordination sites. There are an enormous number of MOFs that can be synthesized with various combinations of organic linkers and metal centers, providing an opportunity to tailor surface area, pore size, and surface functionality [1,2]. MOFs have become a leading class of porous materials for applications, such as gas storage or separation, drug delivery, optoelectronics, imaging, heterogeneous catalysis and even toxic gas removal [3–8]. In addition, the investigation of MOFs in electrochemical area is quite recent but expanding (e.g. electrode materials for batteries [9,10], electrocatalysts for oxygen reduction reaction [11], electrode materials for supercapacitors [12,13], and so on [14–17]). This is due to the redox behavior of metal cations inside MOFs which could provide a pathway for electrons. Alternatively, the tuning of the linker structure may lead to better charge transfer inside the framework. Importantly, the large majority of electrochemical reactions are occurring in aqueous phase. Yet, one of the major shortcomings of several classes of MOFs is their instability in the presence of moisture. This is because the entire framework of MOFs is supported by coordination bonds

and/or other weak cooperative interactions such as H-bonding, π - π stacking, and van der Waals interaction. Thus, structural flexibility is often occurring easily even under mild conditions. The poor water stability gives rise to the framework collapse of the MOFs, even leading to the electrochemical instability [18]. Although some water-stable MOFs have emerged recently [19–21], the other current issue with implementing many types of MOFs into practical electrochemical applications is their weak conductivity. Therefore, the single-phase MOFs are still limited in electrochemical performance because of their intrinsic weaker material properties such as electronic conductivity, water and electrochemical stability. Based on these considerations, heterogeneous nanostructured materials with multi-nanocomponents have attracted our attention. An efficient strategy is to mix MOFs with conductive phases (metal nanocrystals, carbon nanostructures, conductive polymers, etc.) [22–24]. This will provide electron conduction at a macroscopic level. Recently, our group has still studied the MOFs-carbon combination composites. In the previous study, we reported the easy preparation of novel Cu-based MOFs loaded on macroporous carbon (MPC) hybrids [25]. Through the analyses of the characterization and electrochemical experiments, we found that the nano-sized and nanocrystalline novel material has greatly improved electronic conductivity and enhanced electrocatalytic ability. In this communication, the thermal, water and electrochemical stability of the pure Cu-MOFs and Cu-MOFs-MPC composite was investigated and discussed in detail for the first time. More importantly, the Cu-MOFs-MPC exhibits significant catalytic activity for biomolecules

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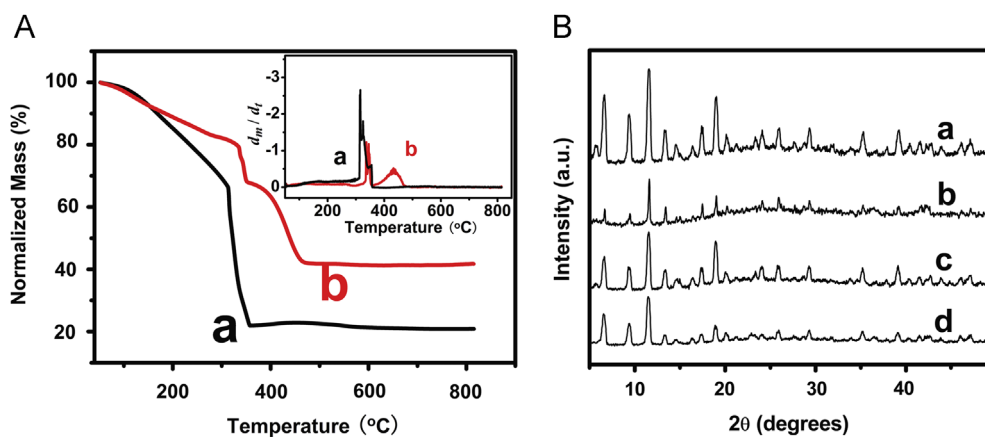


Fig. 1. (A) TGA and DTG (inset of Fig. 1A) curves of Cu-MOFs (a) and Cu-MOFs-MPC (b) at air atmosphere. (B) XRD patterns of Cu-MOFs before (a) and after (b), Cu-MOFs-MPC before (c) and after (d) immersion in water.

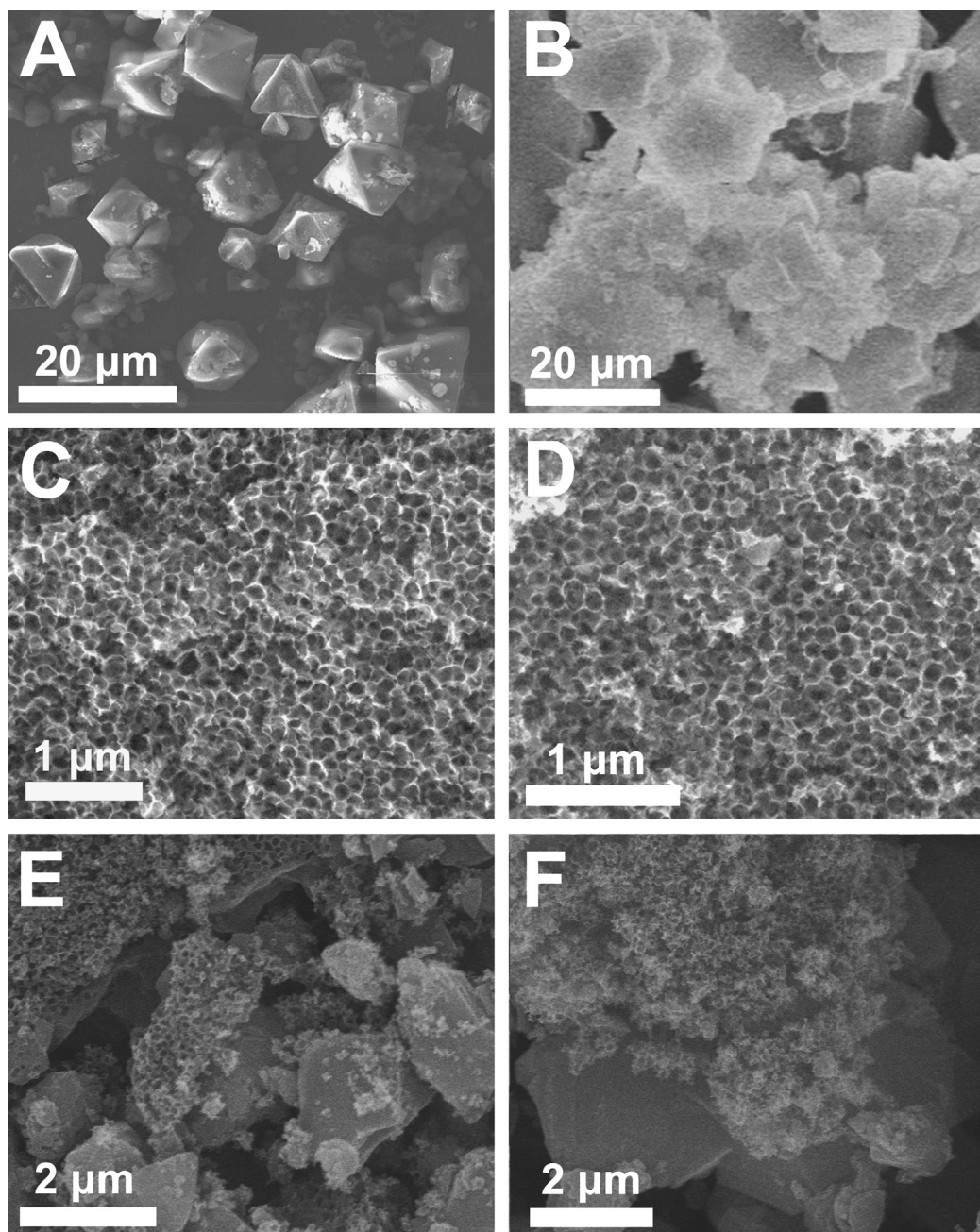


Fig. 2. SEM images of pure Cu-MOFs (A and B), MPC (C and D), and Cu-MOFs-MPC (E and F). (A), (C), and (E) are before and (B), (D), and (F) are after being exposed to water.

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