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Full Length Article

Pyridinic-nitrogen-dominated nitrogen-doped graphene stabilized Cu for efficient selective oxidation of 5-hydroxymethfurfural

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ABSTRACT

In this work, pyridinic-nitrogen-dominated nitrogen doped graphene with Cu incorporation (Cu/NG) are prepared via a facile and effective process. In prepared nitrogen doped graphene (NG), high nitrogen content up to 13.5 wt% was achieved and pyridinic-nitrogen dopant enriched to 11.9 at.%. Cu nanoparticles can be highly stabilized by NG materials and the stabilized Cu loading is linearly correlated with the pyridinic nitrogen content in NG. With Cu/NG as the catalyst and 2,2,6,6-tetramethyl-piperidin-1-oxyl (TEMPO) as co-catalyst, 5-hydroxymethylfurfural (HMF) was oxidized to 2,5-diformylfuran (DFF) in the new developed catalytic system under relative mild conditions (70 °C, 8 h) with high HMF conversion (99.8%) and DFF yield (99.2%). By various characterization and experimental data, Cu-N-C nano-centers were speculated to be the actives sites in catalytic oxidation of HMF. Comparison of high-resolution XPS spectra of N 1s between NG and Cu/NG material indicates the existence of strong interaction between Cu nanoparticles and pyridinic N. The developed catalytic system showed high efficiency in HMF oxidation and Cu/NG can be recycled for eight times without any obvious Cu leaching and catalytic activity loss.

1. Introduction

In recent years, biomass has been developed as alternatives to traditional fossil resources in energy or chemicals. 5-hydroxymethfurfural (HMF), produced via the dehydration of C6 carbohydrates, has been listed as one of the top-12 value-added chemicals produced from sustainable bio-substances by the United States Department of Energy [1]. By various catalytic processes, a variety of high value chemicals derived from HMF or its derivatives can be obtained. With oxidation method, HMF can be transformed into a series of derivatives including 5-hydroxymethyl-2-furan-carboxylic acid (HMFCA), 2,5-diformylfuran (DFF), 5-formyl-2-furancarboxylic acid (FFCA), 2,5-furandicarboxylic (FDCA) [1], maleic anhydride (MA) [2] and succinic acid (SA) [3] (Scheme 1). Among these products, DFF is particularly attractive due to its potential applications. It is considered as a highly useful chemical for pharmaceuticals, fungicides, organic conductor, and macrocyclic ligands [4]. Thus, oxidation of HMF into DFF is tremendous attractive and also a challenge to achieve high yield from the HMF oxidation.

Traditionally, DFF has primarily been synthesized from the oxidation of HMF by using stoichiometric oxidants, including NaOCl [5], $BaMnO_4$ [6] and pyridinium chlorochromate [7] etc. To reduce the cost in DFF production and harm to the environment, in recent years, there is growing attention on the synthesis of DFF from the oxidation of HMF with molecular oxygen as terminal oxidant catalyzed by heterogeneous metal catalysts like Co/Ce/Ru [8], Ru [8–10], Cu [11,12], Cu/V [4], Mn [13], Mo/V [14], V [15,16]. The metal-containing catalysts usually give relative high DFF yield. However, the supported metal catalysts applied in oxidation are often easily sintering, leaching and difficult to remove from product. Besides, the leached metal component are often toxic to product and frequently obtained from limited natural resources [17]. Researchers also developed metal-free carbocatalyst such as graphene oxide [18], nitrogen-doped graphene [19] and modified active carbon [20] in oxidation of HMF, amines [21] or benzylic alcohols [22,23] etc. But, the catalytic reactivity of these metal-free catalysts are relative low in some reaction and results in high loading of the carbocatalyst, high reaction temperature or long reaction time to ensure satisfied product yield. If the drawbacks of metal-catalysts listed above can be overcomed, high catalytic reactivity in aerobic oxidation

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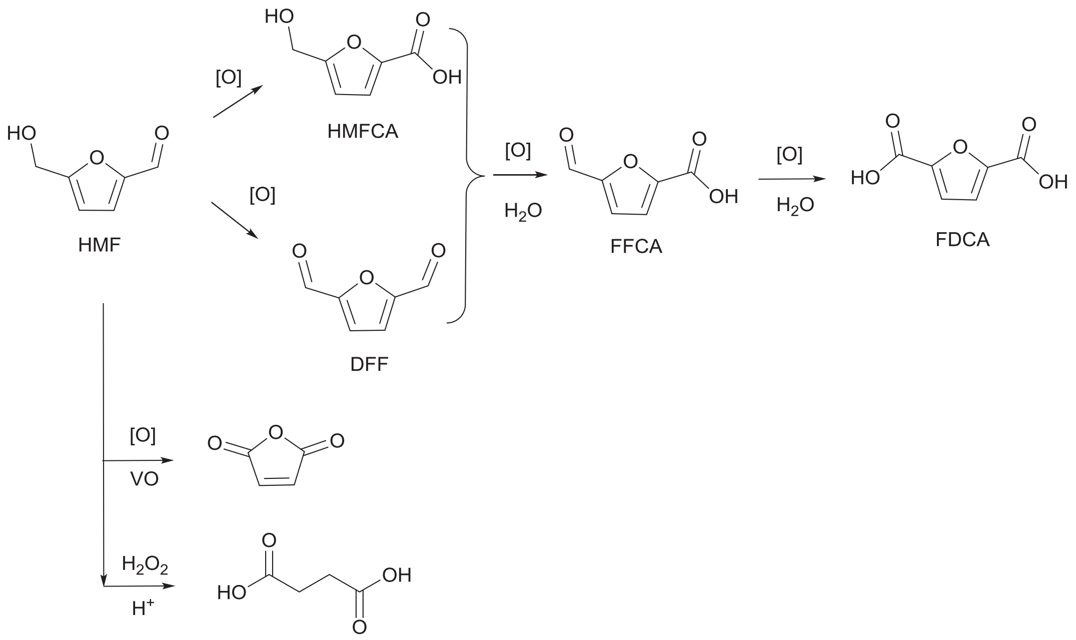

Scheme 1. Representative oxidation products of HMF.

of HMF under mild reaction conditions may be achieved. Graphene is a two-dimensional network of sp^2-bonded carbon atoms, and the delocalized electrons in graphene can move freely in the network with a low resistance [24]. Due to the inherent acidity and redox ability, graphene oxide has been widely used as a metal-free acid catalyst [25] or redox catalyst [26]. Using GO as a building block, researchers also developed various graphene-based nanocomposites and applied as a basic catalyst [27], photo-catalyst [28–30] or redox-catalysts [31–33] etc. In addition, the unique electronic properties of graphene suggest its great potential as a new carbon support for modifying the structure and chemistry of metal nanoparticles [24,34–36]. Recent studies have demonstrated that the two-dimensional structure of graphene facilitates the hybridization between graphene sp^2 states and the dsp states of metal nanoparticles, favoring the electron feedback between the graphene sheet and metal sites. Such an electron feedback is demonstrated to promote the averaged d-band center of the metal particle shifting toward its Fermi level [36]. The incorporation of nitrogen (N) atom into the graphitic basal plane creates positive charges on the adjacent carbon atoms, thus facilitating molecular oxygen adsorption and reduction reaction. The doped pyridinic N shows high capability in stabilizing transition metal, metal carbides, metal oxides, metal nitrides and metal-N_4 carbides into graphene matrix, and the obtained hybrid metal-graphene materials can give improved electrocatalytic activities in ORR reaction [37].

Inspired by the thermal stability of nitrogen-doped carbon materials and its excellent capability in stabilization of metal nanoparticles, subnano clusters [38,39] or even single-atom-catalysts [40–43], we prepared pyridinic-nitrogen-dominated, high content nitrogen doped graphene material (NG) and it was utilized to stabilize highly dispersed non-noble metal Cu nanoparticles via a facile and effective process. The statistic results revealed that the average particle size of Cu confined in NG matrix is ca. 3 nm and is much smaller than those supported on graphene oxide. With 2,2,6,6-tetramethyl-piperidin-1-oxyl (TEMPO) as the co-catalyst, high DFF yield ($>$ 99.2 mol.%) under mild reaction conditions (70 °C, 8 h) was achieved. Furthermore, the NG confined Cu nanoparticles shows high stability in catalytic cycle test in HMF oxidation.

2. Results and discussion

2.1. Characterization of prepared materials

Detailed procedure for preparation and characterization of graphene-based materials and supported Cu catalysts on different graphene materials were provided in Supporting information. The exfoliated GO material has a BET surface area 560.1 m^2/g with an average pore diameter 17.3 nm. After chemical reduced with ammonia, hydrazine hydrate or thermal annealed under high temperature H_2 or NH_3 atmosphere, and incorporated with Cu, the obtained Cu/GO, Cu/G-900H and Cu/NG_4 samples does not show obvious difference in the BET surface area and average pore diameter compared with starting GO sample (Supporting information, Table S1). ICP test was conducted to check the loading of Cu on different supports, as listed in Table S1. A high Cu loading of 3.52 wt% was detected on Cu/GO, however, relative low Cu loading of 0.72 wt% was observed on Cu/G-1000H, and 2.11 wt % Cu loading was observed on Cu/NG_4. It was speculated that the functional groups or heteroatoms in graphene played a crucial role in Cu stabilization. As displayed in Table S2, high oxygen content of ca. 46.8 wt% in GO was detected by elemental analysis and much lower oxygen content in G-900H of 4.5 wt% was detected, combined with the detected Cu loading on GO and G-900H, it implied that the oxygen content in graphene oxide was important in Cu nanoparticles stabilization on graphene surface, which can be attributed to the electrostatic interaction of the positive charged Cu^{2+} in $Cu(NO)_3$ with the negatively charged O atom on GO surfaces. With successive reduction and nitridation with ammonia, hydrazine hydrate and high temperature NH_3, the oxygen content in NG_4 decreased to 2.3 wt% and similar to reported literature [44], a relative high N content, up to 13.5 wt% in NG_4 was obtained (Table S2) and results in a moderate Cu loading in Cu/NG_4.

The detailed procedure for catalyst preparation, characterization, catalysts reactivity tests and analysis of reaction products were provided in Supporting information. Additional characterization of prepared materials and experimental results are also provided in supporting information. Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.apsusc.2018.07.067.

To get a better and straight-forward observation of supported Cu nanoparticles on different graphene surface, the morphological