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Carbazole-decorated covalent triazine frameworks: Novel nonmetal catalysts for carbon dioxide fixation and oxygen reduction reaction

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ABSTRACT

Task-specific carbazole-based covalent triazine frameworks (CTF-CSUs) have been designed and prepared. The obtained materials could serve as excellent catalysts for both CO_2 chemical fixation and oxygen reduction reaction (ORR). Results shown that using CTF-CSUs as catalysts, the cycloaddition reactions between CO_2 and epoxides were readily achieved with extremely high yields (99%) under mild conditions (0.1 MPa, 25 °C). The catalysts could be reused for five times without any obvious loss of catalytic activity. In addition, the as-made carbazole-containing CTFs catalysts delivered attractive ORR activity, superior durability and methanol tolerance relative to commercially available Pt/C reference electrocatalyst (E-TEK). Rich N contents (15.33 wt%) and large surface areas (982 $m^2\ g^{-1}$) combining abundant mesopores favor a combination of two-electron and four-electron reduction pathway under alkaline condition. All these attracting characteristics were attributed to their unique structures and strong synergistic effect between carbazole and triazine moieties.

1. Introduction

Porous organic frameworks, i.e. covalent organic frameworks (COFs) and metal organic frameworks (MOFs), which can atomically allow precise integration of building blocks into crystalline framework networks, are emerged as new platforms for designing high performance materials during the past decade [1–3]. Recently, covalent triazine frameworks (CTFs), which were first developed by Antonietti and Thomas et al. [4], are arisen as a special kind of crystalline, porous, extended solids starting from commercially available nitriles. Compared to its analogs, CTFs contain higher thermal and chemical stabilities. Owing to their high specific surface area, nitrogen-rich skeleton structure, adjustable pore size, modifiable surface properties and so on [5,6], CTFs have been proved very promising for tremendous application such as gas separation [7], gas storage [8], energy devices [9–11] and heterogeneous catalysis [12–14].

More recently, porous organic polymers (POPs), which represent as one of the fastest developing type of porous materials, have been widely employed as catalysts for CO_2 chemical fixation and oxygen reduction reaction (ORR). Notably, some metal coordinated POPs (e.g. Al, Cr, Co salen-coordinated MOPs [15], PAzo-POP-Ag [16] and Zn@SBMMP [17]) have been approved very promising for CO_2 capture and chemical fixation. On the other hand, the metal-incorporated C-COP material has been successfully used as a novel ORR catalyst for fuel cells, which shows the effective electrocatalytic activity of 4e oxygen reduction with excellent stability in alkaline and acidic media [18]. However, the development of metalized polymer materials generally requires specific *pre*-modification or *post*-impregnation processes, which demand cumbersome and time-consuming steps to successfully dope a targeted amount of metal [19–21]. In addition, such metal-polymer hybrid catalysts often suffer the loss of metal active sites during the recycling process, which result in the rapid deactivation of catalysts [22]. Moreover, the use of precious metals as catalysts for ORR [23–25] and the requirement of high pressure for CO_2 chemical fixation severely limit their popularity in scale-up applications [26]. Hence, it is significant to develop nonmetal catalysts for CO_2 chemical fixation and oxygen reduction reaction under mild conditions.

The introduction of electron-accepted N atoms into the carbon framework is critical to the ORR because the N atom can increase the positive charge density for its adjacent carbon atoms and weaken the O—O bond [27,28]. Therefore, the electrocatalytic activity for ORR could be enhanced by introducing N atoms as active sites. Moreover, N-doped polymer materials have been reported as active catalysts for the CO_2 cycloaddition reaction, in which N atoms can serve as CO_2-philic sites and catalytic active sites and play crucial roles in the catalytic cycle [29].

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In this article, a new class of CTFs with abundant N atoms, more specifically, carbazole-based CTFs (Simplified as CTF-CSUs), which combine the advantages of carbazole and triazine units, was synthesized and investigated as nonmetal catalysts for CO_2 cycloaddition and oxygen reduction reaction. The resultant CTF-CSUs were utilized as efficient and reusable heterogeneous catalysts to convert captured CO_2 into cyclic carbonates and exhibited high catalytic activity and good recycle stability under mild conditions. Moreover, the as-prepared frameworks showed attractive electrocatalytic activities, high stability and strong methanol tolerance toward oxygen reduction reaction in alkaline media, opening up new avenues to nanostructured polymers for fuel cell, and batteries applications.

2. Experiment section

2.1. Synthesis of CTF-CSUs

CTF-CSU1 was synthesized by heating the 3,6-dicyano-9H-carbazole (0.3 g, 1.4 mmol) and $ZnCl_2$ (0.184 g, 1.4 mmol) in a quartz tube. The quartz tube was sealed under vacuum, heated and maintained at a terminal temperature of 400 °C for 48 h. After cooled to room temperature, the resultant mixture was milled, and then sufficiently washed through water, and further stirred in 1 M HCl solution for 12 h to remove the residual metal catalyst. The as-made black powder was filtered and washed successively with water and methanol, then subjected to a further purification including an overnight soxhlet extraction with acetone, methanol and hexane as elution solvent, and finally vacuum-dried at 150 °C. Yield: 93%.

Synthesis procedure of CTF-CSU19 was fundamentally same with CTF-CSU1, and a black powder was obtained when substrate was 3,6-dicyano-9-methylcarbazole. Yield: 91%.

2.2. Characterizations

FT-IR spectra were collected on a VARIAN 1000 FT-IR (scimitar series) spectrometer. Samples were prepared by dispersing the complexes in KBr and compressing the mixtures to form disks. The crystal structure of each sample was investigated by X-ray diffraction (XRD, D/Max2250, Rigaku Corporation, Japan) with nickel-filtered Cu Ka radiation ($\lambda = 1.5406$ Å), by depositing powder on silicon wafer substrate, from $2\theta = 1.5^\circ$ up to 35° with 0.02° increment. The morphologies and microstructures were probed utilizing Scanning electron microscope (SEM, Nova NanoSEM 230) and transmission electron microscope (TEM, FEI TECNAI G2 F20). Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis decided quantitatively metal content of the samples on an IRIS Advantage 1000 instrument. CHN analysis was performed on a Vario ELIII CHNOS Elementaranalysator from Elementar Analysensysteme GmbH. The adsorption and desorption isotherms using N_2 and CO_2 were recorded on an Autosorb-iQ (Quantachrome) analyzer under selected conditions. Low pressure N_2 adsorption and desorption isotherms for BET measurements were measured at 77 K. NL-DFT pore size distributions were determined using the carbon/slit-cylindrical pore model of the Quadrawin software. CO_2 adsorption isotherms were investigated at two different temperatures of 273 and 298 K from 0 to 1.0 bar. The surface compositions of the materials were studied by X-ray photoelectron spectroscopy (XPS, K-Alpha 1063, Thermo Fisher Scientific) spectrometer, where the shifts in energy (charging) were calibrated using the C1s peak at 284.6 eV as a reference peak. A PERKIN ELMER TGA7 was utilized to investigate the stability, and the TGA traces were performed at a heating rate of 10 K min^{-1} under nitrogen atmosphere. The Solid-state ^{13}C CP/MAS (cross-polarization with magic angle spinning) spectra of our samples were obtained through a Bruker Avance III 400 NMR spectrum. The signals were probed at 100.61 MHz at an MASrate of 5.0 kHz using zirconia rotors 4 mm in diameter using a contact time of 3.0 ms and a relaxation delay of 2.0 s.

2.3. Cycloaddition reaction

CTF-CSUs catalyst (10 mg), TBAB (1 mmol) and the corresponding epoxide (10 mmol) were added to a 25 mL stainless steel reactor equipped with a magnetic stirring bar and pressure controller. The vessel was pressurized with CO_2 (0.1 MPa). After stirring for 48 h at 25 °C, the reaction mixture was filtered off and washed with CH_2Cl_2 to ensure complete removal of the product and any unreacted starting materials from the pores of the CTF-CSUs organocatalyst. The filtrate was concentrated and the crude samples were analyzed by ^1H NMR spectroscopy. To measure the recyclability, the separated powder catalyst was continuously recovered by centrifugation, washing with dichloromethane, desiccation. Finally, the catalyst was used again for the subsequent cycle operation with fresh reactants under the same reaction conditions.

2.4. Electrochemical measurements

Electrochemical tests (including CV, chronoamperometry and LSV) were recorded on a Zahner electrochemical analyzer with a rotating disk electrode (RDE). All electrochemical ORR measurements were performed on a normal three-electrode system and Ag/AgCl/3 M KCl electrode as a reference electrode. All the potential of this work had been transformed into a reversible hydrogen electrode RHE (see supporting information). 0.1 M KOH solution was used as electrolyte in the process of electrochemical measurements, which deaerated by high purity O_2 (99.99% pure) according to the concrete conditions. Cyclic voltammetry (CV) experiments were recorded from 0 to 1.2 V (*vs.* RHE), and the scan rate was 50 mV s^{-1}. Linear sweep voltammetry (LSV) experiments were performed from 0 to 1.2 V (*vs.* RHE) at 5 mV s^{-1} under rotating speeds varying from 400 to 1600 rpm. The current densities were obtained without background current subtracted. The ORR onset potential E_{onset} is defined as the potential at the intersection of the tangent lines before and after the disk current rise in the RDELSV curve. The ORR stability performance was tested by the current–time (*i-t*) chronoamperometric responses at 1.67 V (*vs.* RHE) for 12,000 s. Methanol crossover was performed by adding 3 M methanol at 300 s in response to *i-t* at 0.67 V (*vs.* RHE). Koutechy-Levich (K-L) Eqs. (1–3) is used to calculate the current density and the number of transferred electrons (n):

$$\frac{1}{J} = \frac{1}{J_K} + \frac{1}{B\omega^{1/2}} \tag{1}$$

$$B = 0.2nFD_0^{2/3}\upsilon^{-1/6}C_0 \tag{2}$$

$$J_K = nFkC_0 \tag{3}$$

J_k and J are the kinetic current density and the measured current density, respectively. D_0 is the diffusion coefficient of O_2 ($1.9 * 10^{-5}$ $cm^2\ s^{-1}$), C_0 is the concentration of O_2 ($1.2 * 10^{-6}$ mol cm^{-3}), υ is the kinetic viscosity (0.01 $cm^2\ s^{-1}$), F is the Faraday constant (96,485 C mol^{-1}) and ω is the electrode rotation speed.