Molecular pore-wall engineering of mesozeolitic conjugated polymers for photoredox hydrogen production with visible light ☆

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A B S T R A C T

A chemical protocol based on molecular engineering of polymeric matrix is developed for the chemical optimization of ordered mesoporous carbon nitride (OMCN) in this study to address the concerns on the serious nanostructure-induced semiconductive defects, in particular the remarkable hypsochromic shift of absorption threshold and the increased excition dissociation energy. Physical characterizations demonstrate that the successful incorporation of 3-aminothiophene-2-carbonitrile (ATCN) aromatic donor in OMCN matrix can efficiently extend the π-conjugated system, red-shift the optical absorption toward longer wavelengths and promote exciton splitting, thus well overcoming the serious semiconductive defects. In addition, the unique structural benefits of OMCN, such as the well-orientated nanoarchitectures with large specific surface area and uniform nanosized pore, have been well remained in ATCN-modified sample (OMCNA) via adjusting the ATCN/cyanamide molar ratio to minimize the unavoidable matrix disturbance. Hence, an obviously enhanced photocatalytic activity toward H_2 evolution and selective oxidation of alcohols are obtained on optimized OMCNA samples, greatly underlining the advantage of molecular engineering in supporting nanostructured photocatalysts.

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1. Introduction

Covalent carbon nitride polymeric frameworks with highly ordered nanoarchitecture are of great interest [1], because of their unique structure-dependent properties and many promising applications across the fields of absorbents [2], sensors [3], fuel cells [4], supporters [5,6], templates [7] and as well as catalysis [8–10]. Recently, OMCN has also functioned as a sustainable energy transducer to catalyze H_2 production from organic or Na_2S aqueous solution under visible light irradiation by taking advantage of the π-conjugated electronic features with proper band structure, further expanding its valuable applications to photocatalysis and photochemistry [11–13]. In such case, its unique structural merits, in particular the well-orientated nanoarchitecture with high specific surface area and uniform nanosized pore, can greatly increase the surface accessibility to reactants, as well as shorten the bulk diffusion length of charge carriers in the polymeric matrix [14]. Hence, OMCN always exhibits an enhanced H_2 evolution performance over the bulk counterpart, greatly underlining the advan-

tages of nanotechnology in photocatalysis field [11,12]. However, several considerable drawbacks are simultaneously generated by nanostructural engineering of carbon nitride polymers. For example, an undesirable hypsochromic/blue shift of absorption threshold from ca. 470 nm to ca. 430 nm is always observed on OMCN due to the rather strong quantum confinement effect, reducing the visible light harvesting ability, evidently [11,12]. In addition, the Coulomb interaction between light-excited electron–hole (e^-–h^+) pairs becomes much stronger with reduced particle size in nanoscale to largely overlap the wave functions of electron and hole, resulting in a high exciton binding energy [15]. Experimentally, all of these structure-induced semiconductive defects counteract the promotion of OMCN in photochemical applications seriously [14,16]. It is therefore highly desirable to address such drawbacks to make full use of the material and structure functions of OMCN for heterogeneous photocatalysis.

Considering about the aromatic π-conjugated features of OMCN, it is highly recommended to modulate the π electrons in a controllable fashion to solve such semiconductive demerits [14,17]. Furthermore, as supported by the density-functional-theory (DFT) calculation [18,19], the creation of surface dyadic heterostructures via grafting/fusing other aromatic motifs on carbon nitride solids by copolymerization, can efficiently extend the delocalization of π electrons to red-shift the optical absorption toward deeper visible light region [17,18], as well as to promote exciton splitting to
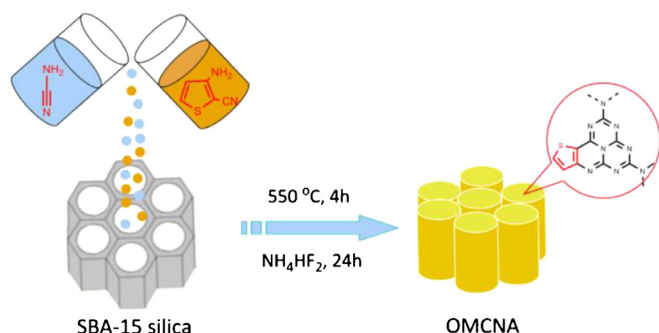
Scheme. 1. Illustration of the synthesis of OMCNA.

generate free charge [15]. This interesting finding affords us a feasible chemical pathway to adjust the electronic structure of OMCN with improved opto-related properties. Nevertheless, a new problem emerges at the same time. The incorporation of foreign groups in carbon nitride conjugated network is a semiconductor doping behavior, which alters the local packing of tri-s-triazine subunits greatly, and thus reduces the chemical ordering of polymeric matrix [19]. For material synthesis, such troublesome matrix disturbance indeed brings us lots of difficulties in maintaining the highly ordered nanoarchitecture of OMCN. Chemical engineering of OMCN frameworks with functional dopants while still keeping highly-ordered nanoarchitecture remains a big challenge in material science.

Herein, 3-aminothiophene-2-carbonitrile (ATCN) molecule with strong electron donor ability was chose as the suitable monomer to modify OMCN semiconductor by a bottom-up synthesis strategy, basing on several experimental results that it does less harmfulness to structural orderliness [17–19]. As illustrated in Scheme 1, the mixture of ATCN and cyanamide in a certain mass ratio is introduced in the nanochannels of SBA-15 silica by an optimized inclusion method [12]. Then, OMCNA can be easily produced via the thermal-induced copolymerization and the NH_4HF_2 etching step by step. According to the amount of ATCN in starting materials, the resultant samples are further labeled as OMCNA-*X*, where *X* (1, 2, 3, 4) refers to 15, 30, 90 and 150 mg ATCN, respectively. The obtained OMCNA-*X* samples were then carefully examined by physical analyses to study the influence of ATCN on their morphology, texture, and as well as optical and electronic properties. Their visible-light-driven photoredox performance toward hydrogen evolution and organic synthesis is also investigated in details to highlight the importance of molecular engineering of mesoporous polymeric frameworks in supporting nanostructured photocatalysts.

2. Experimental

2.1. Synthesis of catalyst

Pluronic P123 (*M*w = 5800), tetraethylorthosilicate (TEOS, 98%), HCl (37%), cyanamide (99%), triethanolamine (99%), $H_2PtCl_6 \cdot 6H_2O$ (≥37.5% Pt basis), NH_4HF_2 (95%), α,α,α-trifluorotoluene (99%), benzyl alcohol (99.8%), benzaldehyde (99.5%) were purchased from Sigma-Aldrich. 3-aminothiophene-2-carbonitrile (ATCN) was prepared according to previous report [19]. All chemicals were used as received, without further purification.

Synthesis of SBA-15 silica: In a typical preparation, TEOS (5.58 g) was mixed with P123 (3.46 g) in 1.6 M HCl solution (38 mL) and stirred at 35 °C for 24 h. The mixture was heated at 150 °C for 24 h under static condition in a Teflon-lined autoclave. After the reaction, the resulting white precipitate was filtered, dried at 80 °C overnight. It was further calcined at 550 °C in air for 4 h with heating rate of 1 °C/min to get SBA-15 silica as templates.

Synthesis of OMCN: First, the as-prepared SBA-15 silica was acidized by 1 M HCl solution (1.0 g silica/20.0 mL HCl) at 80 °C for 24 h, followed by drying at 80 °C for 12 h. Then, 1.0 g HCl-treated SBA-15 silica and 8 g liquid cyanamide were kept sonication and vacuum at 55 °C for 4 h. Third, 15.0 mL water was then added to the mixture, followed by centrifugation, drying and calcination at 550 °C for 4 h. The resulting powder was treated with 4 M NH_4HF_2 solution (40 mL) for 24 h to remove the silica template, followed by filtration, washing with water and ethanol several times, and finally drying at 80 °C to produce OMCN.

Synthesis of OMCNA: First, 8 g cyanamide was mixed with a certain amount of ATCN at 55 °C for 24 h under N_2 protection. Then 1.0 g HCl-treated SBA-15 silica was added to this liquid mixture, kept sonication and vacuum at 55 °C for 4 h. Third, 15.0 mL water was added to the mixture, followed by centrifugation, drying and calcination at 550 °C for 4 h. The resulting powder was treated with 4 M NH_4HF_2 solution (40 mL) for 24 h to remove the silica template, followed by filtration, washing with water and ethanol several times, and finally drying at 80 °C. The resultant samples were further labeled as OMCNA-*X*, where *X* (1, 2, 3, 4) refers to the amount of ATCN as 15, 30, 90 and 150 mg, respectively.

2.2. Characterization of catalyst

X-ray photoelectron spectroscopy (XPS) data were measured in powder form using a Thermo ESCALAB250 instrument with a monochromatized Al K_α line source (200 W) at 3.0×10^{-10} mbar. UV–Vis diffuse reflectance spectra (UV–Vis DRS) were performed on Varian Cary 500 Scan UV–visible system. Sample picture was taken by Nikon D 3100. Electron paramagnetic resonance (EPR) measurements were recorded using a Bruker model A300 spectrometer with a 300 W Xe lamp equipped with an IR-cutoff filter ($\lambda < 800$ nm) and an UV-cutoff filter ($\lambda > 420$ nm) as visible light source. X-ray diffraction patterns (XRD) measurements were performed on Bruker D8 Advance diffractometer with Cu $K_{\alpha 1}$ radiation ($\lambda = 1.5406$ Å). Thermogravimetric analysis (TGA) was performed on STA 449 F3 (NETZSCH Co.). Scanning electron microscopy (SEM) and transmission electron microscopies (TEM) were operated by Nova Nano 230 microscope and Zeis 912 microscope, respectively. Small-angle X-ray scattering (SAXS) measurements were carried out using a Nonius rotating anode (Cu K_α radiation, $\lambda = 1.5406$ Å) with pinhole collimation and a MAR CCD area detector (sample-detector distance of 740 mm). Nitrogen adsorption-desorption isotherms were collected at 77 K using Micromeritics ASAP 2020 Surface Area and Porosity Analyzer.

2.3. Activity test

Photocatalytic activity for water splitting: Reactions were carried in a Pyrex top-irradiation reaction vessel connected to a glass closed gas system. H_2 production was performed by dispersing 20 mg of catalyst in an aqueous solution (100 mL), using triethanolamine (10 vol%) and 3 wt% Pt as electron donor and cocatalyst, respectively. The reaction solution was evacuated several times to remove air completely prior to irradiation under a 300 W Xenon-lamp. The wavelength of the incident light for H_2 evolution was controlled by applying appropriate long-pass cut-off filters. The temperature of the reaction solution was maintained at 12 °C by a flow of cooling water during the reaction. The evolved gases were analyzed by gas chromatography equipped with a thermal conductive detector (TCD) and a 5 Å molecular sieve column, using argon as the carrier gas.

Photocatalytic activity for organic synthesis: The reaction was carried out at 1 bar pressure of oxygen, in a 10 mL Pyrex glass reactor fitted with a reflux condenser, oil bath, thermocouple, and