available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article

Enhanced photocatalytic performance of polymeric C₃N₄ doped with theobromine composed of an imidazole ring and a pyrimidine ring

Zehao Li ^a, Qian Yang ^a, Chengcheng Chen ^a, Zhengguo Zhang ^{a,b}, Xiaoming Fang ^{a,b,c,*}^a Key Laboratory of Enhanced Heat Transfer and Energy Conservation, The Ministry of Education, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, Guangdong, China^b Guangdong Engineering Technology Research Center of Efficient Heat Storage and Application, South China University of Technology, Guangzhou 510640, Guangdong, China^c Key Laboratory Fuel Cell Technology Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, Guangdong, China

ARTICLE INFO

Article history:

Received 13 November 2018

Accepted 26 February 2019

Published 5 June 2019

Keywords:

Polymeric carbon nitride

Molecular doping

Theobromine

Photocatalytic oxygen evolution

Dye degradation

ABSTRACT

Molecular doping has been proven to be an effective approach to adjusting the electronic structure of polymeric carbon nitride (PCN) and thus improving its optical properties and photocatalytic activity. Herein, theobromine, a compound composed of an imidazole ring and a pyrimidine ring, was first copolymerized with urea to prepared doped PCN. Experimental investigations and theoretical calculations indicate that, a narrowing in band gap and a positive shift in valence band position happened to the theobromine doped PCN, owing to the synergistic effect between the pyrimidine ring and the imidazole ring in the theobromine molecule. Moreover, it is shown that the doping with theobromine at a suitable mass fraction makes the obtained sample exhibit decreased photoluminescent emission, enhanced photocurrent density, and reduced charge-transport resistance. Consequently, an enhancement in the photocatalytic activity for water oxidation is found for the sample, which oxygen evolution rate is 4.43 times higher than that of the undoped PCN. This work sheds light on the choice of the molecular dopants for PCN to improve its photocatalytic performance.

© 2019, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Polymeric carbon nitride (PCN) is a potential polymeric semiconductor photocatalyst and has the advantages of abundant and inexpensive raw resources, good physical and chemical stability, and suitable band positions. These advantages make PCN show great potentials in photocatalytic water splitting to produce hydrogen and oxygen and degradation of dyes or antibiotics [1]. However, besides UV light, only a very narrow band of visible light with a wavelength shorter than 450

nm can be absorbed by pristine PCN because of its relatively wide bandgap [2]. Moreover, the symmetrical substitution of low-electronegativity carbon atoms by high-electronegativity N atoms leads to the easy anchoring of the photogenerated electrons, thereby increasing the difficulty for electrons transport in PCN and leading to recombination of the photogenerated carriers [3]. Consequently, pristine PCN just achieves a low quantum efficiency, thus limiting its practical applications.

Various explorations for enhancing the photocatalytic activity of PCN have been reported in recent years. These efforts

* Corresponding author. Tel: +86-20-87112997; Fax: +86-20-87113870; E-mail: cexmfang@scut.edu.cn

This work was supported by the National Natural Science Foundation of China (21276088, U1507201), Natural Science Foundation of Guangdong Province (2014A030312009), and China Postdoctoral Science Foundation (2018M640784).

DOI: S1872-2067(19)63337-1 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 40, No. 6, June 2019

mainly include construction of PCN-based composite photocatalysts [4–7], surface sensitization [8–10], nanostructured designing [11,12], and elemental [13–17] or molecular doping [18–23]. Among them, molecular doping is an effective and unique method for PCN to modify its molecular and electronic structures, by introducing other organic monomers into PCN via a copolymerization between a precursor and an organic monomer [18–22]. Thus far, various organic monomers have been used to change the framework of PCN; these monomers can be classified into three types: benzene and its derivatives [21,24,25], six-membered heterocyclic compounds [3,18,22,26–28], and five-membered heterocyclic compounds [20,29]. The six-membered heterocyclic compounds mainly include pyrimidines and pyridine compounds, while the five-membered heterocyclic compounds usually refer to thiophene compounds. Note that benzene and its derivatives as well as six-membered heterocyclic compounds are isoelectronic systems, while five-membered heterocyclic compounds are electron-rich systems. As a result, the electron cloud density of five-membered heterocyclic compounds is higher than that of benzene and its derivatives and six-membered heterocyclic compounds. As for the five-membered heterocyclic compounds, the presence of the heterocyclic atoms can correspond to the introduction of the activated groups, such as $-\text{NH}_2$, $-\text{OH}$, or $-\text{SH}$, which groups can induce the activation of the rings. It has been reported that the molecular doping with the thiophene compounds can extend the conjugate structure of PCN and thus improve its optical absorption property and photocatalytic activity [5,20]. Compared with those thiophene compounds, an imidazole ring contains two N atoms, making it possess higher electron density and stronger electronegativity. It can be expected that, the molecular doping with an organic compound containing an imidazole ring may play a more positive role in adjusting the electron structure of PCN and thus improving its optical property and photocatalytic performance. However, there have been no reports on the molecular doping of PCN with a compound containing an imidazole ring yet.

In the current work, theobromine, a compound composed of an imidazole ring and a pyrimidine ring, was chosen as a molecular dopant to copolymerize with urea. On one hand, the presence of the pyrimidine ring can make the theobromine molecules easier to be condensed with the heptazine rings in PCN, thereby introducing the imidazole ring. On the other hand, the synergistic effect between the pyrimidine ring and the imidazole ring makes the theobromine molecules possess stronger electronegativity, which may result in a greater impact on the electron structure of PCN. Specifically, different amounts of theobromine were copolymerized with urea to prepare a series of doped PCN. The morphology, optical properties, band structure, photoelectrochemical characteristics, and photocatalytic performance of the theobromine-doped PCN samples were investigated thoroughly. DFT calculations were employed to predict the difference in electronic structure between the doped PCN and the pristine one. It is found that, the theobromine doped PCN exhibits a positive shift in the valence band position, thus increasing the oxidation ability of its photo-generated holes. Moreover, a narrowed band gap, reduced

charge recombination, facilitated charge transport, along with the positively shifted valence band position, make the optimized theobromine-doped PCN sample show enhanced photocatalytic activity in both oxygen evolution and dye degradation. This work sheds light on the organic molecules for use to dope PCN for improving its photocatalytic activity.

2. Experimental

2.1. Preparation of theobromine doped PCN

A series of doped PCN samples were prepared by the thermal polymerization process, in which the mass ratios of theobromine to urea were set at 0.0032, 0.0036, 0.0040, 0.0044, and 0.0048, respectively. Namely, 10 g of urea and 40 mg of theobromine were mixed in 40 mL of distilled water, afterward stirring at 30 °C overnight. Then the obtained solution was heated to 80 °C for removing water, and the obtained solid is further dried at 60 °C for 8 h in a vacuum oven to obtain a precursor. Finally, the precursor was calcined at 600 °C for 2 h in air at a heating rate of 10 °C/min to obtain a doped PCN sample. According to the addition amounts of theobromine, all the obtained samples were named CN x ($x = 32, 36, 40, 44$, and 48). For comparison purpose, a pristine PCN sample was prepared in the same method without theobromine, which was denoted as CN.

2.2. Characterization

To investigate the crystal structure of the samples, X-ray diffraction (XRD) patterns were collected with a Bruker D8 Advance diffractometer equipped with a Cu K_α radiation source. The Fourier transform infrared (FT-IR) spectra were recorded using a Bruker Vector 33 FT-IR spectrophotometer. The data for Brunauer-Emmett-Teller (BET) analysis were collected with a Micromeritics ASAP 2020 apparatus. The morphologies and microstructures of the samples were characterized by scanning electron microscopy (SEM, Hitachi SU8220) and transmission electron microscopy (TEM, JEM-1400 plus), respectively. The surface composition and chemical bonds were investigated by X-ray photoelectron spectroscopy (XPS) on an instrument (Kratos Axis Ultra DLD) equipped with a Mg K_α source. The C and N elemental analyses (EAs) were performed with an Elementar Varia EL cube. Thermogravimetric analysis (TGA) was conducted on a Netzsch STA449 F3 from room temperature to 800 °C at a ramp rate of 10 °C/min under an N_2 atmosphere. UV-vis diffuse reflectance spectroscopy and photoluminescence (PL) spectroscopy were carried out with a Shimadzu UV-3600 UV-vis spectrophotometer and a Hitachi F-4600 FL spectrophotometer, respectively. The time-resolved fluorescence decay spectra were collected with an Edinburgh PLS980 spectrometer at room temperature. Electron paramagnetic resonance (EPR) signals were recorded with an electron paramagnetic resonance spectrometer (Bruker model A300) at room temperature. The spin-trapping electron spin resonance/DMPO technique (ESR) was investigated using a Bruker model A300 EPR spectrometer equipped with a 300 W

Xe lamp ($\lambda > 420$ nm).

2.3. Photoelectrochemical measurement

Electrochemical measurements were performed on an electrochemical workstation (Chenhua CHI660E, Shanghai) via a conventional three-electrode system with Pt sheet (counter electrode, 10×10 mm²) and a Hg/Hg₂Cl₂ electrode (reference electrode). The working electrode was prepared by the following method. First, the FTO glass was ultrasonically washed with acetone and ethanol, followed by drying with nitrogen. 0.1 g of photocatalyst and 0.01 g of ethylene cellulose were added to ethanol, followed by grounding into slurry. Finally, the obtained slurry was dip-coated onto a piece of FTO glass (10×10 mm²); the obtained working electrode was heated at 150 °C for 2 h. In the testing process, the working electrode was immersed in 70 mL Na₂SO₄ aqueous solution (0.5 M); a 300 W Xe lamp with a UV-cutoff filter ($\lambda > 420$ nm) was used as a visible-light radiation source.

2.4. Evaluation of photocatalytic oxygen evolution

The photocatalytic O₂ evolution was investigated with a multipass light catalytic reaction system (Perfectlight PCX50B Discover). Briefly, 30 mg of each sample was well dispersed into 40 mL of AgNO₃ aqueous solution (0.01 M) containing 50 μ L of a Co(NO₃)₂ solution (75 mg/mL, as a cocatalyst) and La₂O₃ (0.08 g, as a pH buffer agent). Nine LED white lights (5 W, 7.70 mW/cm²) were used for irradiation in conjunction with a timing switch to ensure that every reaction bottle was subjected to the same reaction conditions. Before irradiation, each reaction bottle was sealed to form a closed system; the system was evacuated and supplied with high-purity Ar three times to replace the air with Ar. The obtained gases were detected with the thermal conductivity detector of a gas chromatograph (GC7600, Tian Mei); high-purity Ar was used as the carrier gas.

2.5. Evaluation of photocatalytic degradation performance

Rhodamine B (RhB) was selected as a model contaminant for evaluating the photocatalytic degradation activity under 5-W LED white light (7.70 mW/cm²) with a multipass light

catalytic reaction system (Perfectlight PCX50B Discover). Specifically, 30 mg of each sample was well dispersed into 50 mL of RhB solution (10 mg/L), and the resultant mixture was stirred in the dark for 40 min to reach a balance of adsorption and desorption between the catalyst and the RhB solution. During the irradiation, three milliliters of this mixture was collected and centrifuged every 5 min, followed by filtration through a 0.45 μ m Millipore filter to remove the catalyst powder. The concentration of RhB in the solution was detected using a UV-vis spectrophotometer at 554 nm. To determine the active ingredients in the photodegradation reaction, several trapping agents, including isopropanol (IPA), ammonium oxalate (AO), and *p*-benzoquinone (BQ), were added to the mixture of CN40 and the RhB solution to trap hydroxyl radicals ($\cdot$ OH), holes (h^+), and superoxide radicals ($\cdot$ O₂⁻), respectively. Additionally, N₂ and O₂ were pumped into the reaction systems in separate experiments.

2.6. DFT calculations

The electron distribution and band structures of the undoped and doped PCN samples were evaluated using Gaussian 09 DFT calculations with B3LYP functionals and the 6-31G(d,p) basis set for all atoms [30]. The trimer of the PCN was used as the calculation model to calculate the energy levels (highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO)) of the undoped and doped PCN samples.

3. Results and discussion

3.1. Structure, morphology, and formation mechanism

The XRD patterns of the samples are shown in Fig. 1(a). CN and CN_x have the same diffraction peaks at 12.75° (100) and 27.53° (002), which correspond to the periodic array of the intraplanar tri-s-triazine motif stacking of 0.68 nm and to the interlayer structure aromatic packing of 0.33 nm, respectively [31,32]. These results suggest that the addition of theobromine did not change the crystalline structure of PCN. Furthermore, in Fig. 1(b), the FT-IR spectra of CN and CN_x are similar due to the low content of theobromine in CN_x along with the overlapping

Fig. 1. XRD patterns (a) and FT-IR spectra (b) of CN_x.

Table 1

Physicochemical properties and apparent rate constant of the as-prepared samples for degrading RhB.

Sample	A_{BET} (m^2/g)	Pore volume (cm^3/g)	Band-gap (eV)	Rate constant (min^{-1})
CN	103.3	0.1791	2.99	0.02966
CN32	110.0	0.1621	2.92	0.1309
CN36	111.3	0.1719	2.89	0.1409
CN40	110.4	0.1655	2.85	0.1506
CN44	116.6	0.1780	2.80	0.1317
CN48	125.2	0.1889	2.77	0.07468

between the characteristic peaks of theobromine and PCN. Specifically, the broad band in the region from 2800 to 3600 cm^{-1} corresponds to the N–H stretching vibration and the O–H band of water molecules. This indicates the existence of the uncondensed amine groups. The peaks located at 1100–1800 cm^{-1} are mainly ascribed to the vibration of skeletal C–N heterocycles in the C_6N_7 ring [33]. The peak at 809 cm^{-1} is due to the stretching vibration of triazine cycles [34].

The N_2 adsorption-desorption isotherms of CN and CN x have been recorded, and the corresponding BET surface areas and pore volumes of CN and CN x are listed in Table 1. As shown in Fig. S1, the adsorption-desorption curves of all the samples are type IV [35]. The BET surface area of CN x is slightly higher than that of CN and exhibits a gradual enlarging as the theobromine amount is increased from 40 to 48 mg. The reason for this is probably because excess theobromine is not involved in the thermal polycondensation reaction [22]. Moreover, SEM and TEM have been used to observe the morphologies and microstructure of the samples. All of the samples show similar morphologies that consist of numerous porous sheets (as shown in Figs. S2 and S3).

The compositions and chemical states of CN and CN40 have been characterized by XPS. C, N, and O are detected in all of the samples, as displayed in their XPS survey spectra (Fig. S4). Both CN and CN40 exhibit similar typical characteristic peaks in their high-resolution XPS C 1s and N 1s spectra (Fig. 2(a) and (b)). Specifically, the peaks at 285.1 and 288.2 eV in the typical high-resolution XPS C 1s spectra correspond to C–C and C–N, respectively. The typical high-resolution XPS N 1s spectra of CN and CN40 present three characteristic peaks. The peaks at 399.2, 398.5, and 400.6 eV are attributed to the bridging N atoms in N–(C) $_3$, the sp^2 -bonded N atoms in triazine rings (C–N=C), and C–N–H, respectively. Moreover, the area percentages of these peaks for C 1s and N 1s have been calculated separately and are listed in Table S1. Compared with the percentage of the C–C peak for CN, that for CN40 is substantially smaller. This decrease should be attributed to the incorporation of theobromine into the PCN-conjugated network because of its high N content. Moreover, the intensity of the N–(C) $_3$ peak for CN40 is reduced, further verifying the introduction of theobromine. In addition, both the XPS and EAs results indicate that the C/N mole ratios of CN x first decrease and then increase with the increase in the amounts of theobromine (Table S1). This phenomenon may be due to excessive theobromine undergoing carbonization rather than participating in the reaction.

Furthermore, the TGA curves of urea, theobromine, the precursor, CN, and CN40 have been recorded for elucidating the formation mechanism of the doped PCN. As shown in Fig. 2(c), for CN and CN40, no weight losses occur before 600 $^{\circ}\text{C}$, suggesting that they are polymers; in the temperature range between 600 and 750 $^{\circ}\text{C}$, PCN rapidly loses almost 100% of its mass because it has sublimed. The onset decomposition temperature of CN40 is higher than that of CN, which implies that

Fig. 2. XPS of CN and CN40: C 1s (a); N 1s (b), together with TG curves of urea, theobromine, precursor, CN, and CN40 (c); solid-state ^{13}C NMR spectra of CN, CN40, and theobromine (d).

the incorporation of theobromine increases the thermal stability of the obtained sample. For the raw materials, theobromine exhibits a single weight-loss step, and its onset decomposition temperature is approximately 250 °C, higher than that of urea. More significantly, some differences are observed between the TGA curves of urea and the precursor. First, the first weight-loss step of urea occurs between 150 and 230 °C, and its ratio is 67.2%; by contrast, the temperatures of the first weight-loss step for the precursor range from 150 to 243 °C, and the corresponding ratio is 48.3%. Second, the curve of urea exhibits an inflection point at 230 °C, which is absent in the curve of the precursor. These results imply that the addition of theobromine changes the reaction paths. Third, the transformation temperature of urea is 350 °C, whereas that of precursor is delayed to 400 °C. This result means that, with the addition of theobromine into melem, a higher temperature is needed for generating PCN. Urea completed its weight loss at approximately 420 °C, whereas the weight loss of the precursor was not complete until the temperature exceeded 600 °C because of the incorporation of theobromine. In addition, from the solid-state ^{13}C NMR spectra, as shown in Fig. 2(d), three new peaks are clearly observed for CN40, while three sharp peaks at the same positions are found for theobromine. These results suggest the successful incorporation of theobromine into the PCN conjugated network of CN40.

Based on the above investigations, a possible reaction mechanism for generating the doped PCN from the precursor consisting of urea and theobromine can be speculated [36]. As illustrated in Fig. 3, first, urea decomposes and produces a large amount of NH_3 to generate isocyanic acid at temperatures under 230 °C [37]. With further heating, the generated isocyanic acid combines with urea to form biuret. Theobromine then combines with the biuret to form a heterocyclic compound and finally generate the theobromine-doped PCN.

3.2. Optical absorption and band structure

The UV-vis diffuse reflectance spectra of the samples are shown in Fig. 4(a), and their photographs are inserted in this figure. Compared with CN, CNx presents a red shift in its intrinsic absorption edge. Correspondingly, the color of the samples also changes from light-yellow to brown. All the CNx samples

Fig. 3. The co-polymerization of urea and theobromine into a graphitic carbon nitride network.

exhibit an additional absorption peak in the wavelength range from 450 to 550 nm, which is due to the intrinsic $n \rightarrow \pi^*$ electronic transitions, induced by the incorporation of theobromine into PCN [38,39]. Furthermore, the bandgaps of the samples have been estimated from Fig. 4(b) and are listed in Table 1. Compared with CN, CNx presents a gradual decrease in bandgap with increasing addition amounts of theobromine. This decrease in band gap is associated with the fact that theobromine is composed of an imidazole ring and a pyrimidine ring with strong electron affinity, thereby leading to a change in electron structure of PCN. Specifically, the bandgaps of CN and CN40 are 2.99 and 2.85 eV, respectively. The narrowed band gap and the additional visible light absorption make the doped PCN samples absorb more photons, and more photo-induced charge carriers can be thus generated.

To elucidate the differences in band structure between CN and CN40 more clearly, their VB-XPS spectra (Fig. 4(c)) and constructed Mott-Schottky (MS) plots (Fig. 4(d)) have been collected for estimating the relative positions of their conduction band (CB) and VB. Before using the MS plot to evaluate the flat band potential, electrochemical impedance spectroscopy (EIS) has been employed to confirm the prerequisite for MS analysis [40,41], as shown in Fig. S5. The real surface areas of CN and CN40 electrodes have been observed by using AFM, as shown in Fig. S6. In addition, MS plots for CN and CN40 have been also measured and analyzed in 0.5 M Na_2SO_4 (pH = 6.8) at 3 kHz and 5 kHz (Fig. S7). The negative slope in Fig. 4(d) indicates typical n-type semiconductor behavior for CN and CN40. Consequently, the flat band potentials of CN and CN40 can be determined to be -0.70 and -0.66 V vs. SCE (-0.48 and -0.44 V vs. NHE, respectively). Because the flat band potential varies little under different pH values, the value of the flat band potential is considered to be approximately equal to the Fermi level [42]. Moreover, the VB-XPS spectrum shows the energy gap between the VB and the Fermi level. Thus, the VB positions of CN and CN40 are 1.73 and 1.84 eV, respectively. Based on the bandgaps of CN and CN40, their CB positions are calculated to be -1.26 and -1.01 eV, respectively. Consequently, the energy bands of CN and CN40 can be illustrated in Fig. 4(e). The results reveal that the integration of theobromine into PCN led to a remarkable positive shift in the CB along with a slight positive shift in the valence position, thereby resulting in the narrowed bandgap of CN40. Consequently, the reducing capacity of the photogenerated electrons and the oxidizing ability of the holes have been changed in CN40. The positive shift in the valence position favors the photocatalytic oxidation reactions that are associated with the photogenerated holes.

Furthermore, the electron distribution and band structures of CN and CN40 have been evaluated by DFT calculations. As illustrated in Fig. 5, the HOMO of the CN trimer is mainly attributed to the combination of nitrogen p_z orbitals, while the LUMO mostly localizes in C–N bond orbitals [24,43]. In contrast, as shown in Fig. 5, the LUMO of CN40 exhibits a shift, which locates the copolymerized theobromine segment. Although the HOMO retains the tri-s-triazine subunit, it is no longer symmetrical. This loss of symmetry induces a slight down-shift of the HOMO. Consequently, the incorporation of

Fig. 4. UV-vis diffuse reflectance spectra (a) and plots of $(\alpha h\nu)^{1/2}$ versus $h\nu$ (b) of the PCN samples, together with VB-XPS spectra (c), Mott-Schottky plots (d), and schematic band structure evolution (e) of CN and CN40.

the theobromine molecules into the PCN framework adjusts the corresponding HOMO and LUMO energy levels by effectively relocating the π -conjugated electrons. The apparent down-shift

of the LUMO along with the slight down-shift of the HOMO makes CN40 possess the reduced band gap. The results of DFT calculations are consistent with those obtained from the MS plots and the VB-XPS spectra.

3.3. Charge separation and photoelectrochemical properties

To explore the recombination properties of the photogenerated charge carriers in the samples, photoluminescence spectra (PL) have been monitored and shown in Fig. 6(a). Obvious changes occur in the peak positions and emission intensities of CN and CNx. The shifts in the peak positions is ascribed to the reduction in their band gap values (Fig. 4). Significantly, the PL intensity gradually decreases as the theobromine amount is increased from 32 to 40 mg and then enhances with its further increase to 44 mg. It is indicated that the introduction of theobromine at a suitable amount leads to a reduction in charge recombination, meaning that more photogenerated carriers will transport to the surfaces of the photocatalyst to take part in the photocatalytic reactions. While, the enhancement in PL intensity at the high content of theobromine is probably attributed to the carbon deposition originating from the excessive amount of theobromine, which could act as the charge-carrier recombination centers. In addition, the lifetimes

Fig. 5. Electronic structure of polymeric trimer models including the optimized HOMO and LUMO for CN and CN40.

Fig. 6. (a) PL emission spectra (the inset is time-resolved fluorescence spectra of CN and CN40); (b) room-temperature solid-state EPR spectra of electron detected in the dark at atmospheric conditions; (c) transient photocurrent response (in 0.5 mol/L Na₂SO₄ electrolyte under visible light irradiation, $\lambda > 420$ nm); (d) EIS Nyquist plots in the dark, of the undoped and doped PCN samples.

of charge carriers in CN and CN40 have been measured, and the obtained results are shown in the inset of Fig. 6(a). The double-exponential function (Eq. (1)) was used to fit the decay curves [40], and the weighted mean lifetime was obtained from Eq. (2). The lifetime of the charge carriers in CN40 (4.53 ns) is obviously longer than that of the charge carriers in CN (2.32 ns). The extending in the lifetimes facilitates the transport of these charge carriers to the surfaces of CN40 for participating in the photocatalytic reactions [33,44].

$$I(t) = Ae^{(-t/t_1)} + Be^{(-t/t_2)} + I(0) \quad (1)$$

$$\tau = (At_1^2 + Bt_2^2) / (At_1 + Bt_2) \quad (2)$$

Moreover, the EPR spectra of the solid samples have been investigated. As shown in Fig. 6(b), all of the samples exhibit single Lorentzian centrosymmetric EPR peaks at 3505 G, which g-factor is 2.0024 and can be ascribed to the delocalized unpaired electrons on sp^2 carbon atoms within the π -conjugated aromatic rings [45,46]. The EPR intensities of all the CN_x samples are higher than that of CN, suggesting that the introduction of theobromine leads to an increase in the delocalized unpaired electrons. Specifically, CN40 exhibits the most intense EPR signal among all of the CN_x samples, revealing that this sample possesses the greatest delocalization and spin mobility of the lone-pair electrons and the highest charge-carrier density.

Fig. 6(c) and (d) shows the transient photocurrent response and electrochemical impedance spectra of the samples. Significantly, all the CN_x samples exhibit greater photocurrent densities than CN (Fig. 6(c)), which is related to their enhanced optical absorption and reduced PL emission. Specifically, the photocurrent density of CN_x increases as the amount of theobromine is increased from 32 to 40 mg, which is due to the increased optical absorption (Fig. 4(a)) as well as the decreased PL intensity (Fig. 6(a)). By contrast, when the amount of theo-

bromine is greater than 40 mg, a decrease in the photocurrent density is observed. Since the optical absorption does not decrease with the theobromine amount (Fig. 4(a)), this decrease is certainly associated with the enhancement in the PL intensity of the corresponding samples (Fig. 6(a)). Consequently, CN40 exhibits the highest photocurrent density, suggesting that this sample possesses the maximum number of the photoinduced charge carriers to participate photocatalytic reactions [19,47]. Furthermore, all of the samples show a reversible and reproducible transient photocurrent after several repeated ON/OFF irradiation cycles, implying their good photoelectrochemical stability. In addition, under dark conditions, CN40 exhibits the smallest semicircular Nyquist curves among all of the samples (Fig. 6(d)), suggesting that it has the lowest charge-transport resistance. It is revealed that introducing an appropriate amount of theobromine in PCN could facilitate charge transport, thus favoring the improvement in photocatalytic activity. The decreased PL emission, the enhanced photocurrent density, and the reduced charge-transport resistance can be attributed to the strong electron-receptor effect of the pyrimidine and imidazole ring in theobromine, which induces the photoinduced electrons transfer from PCN to the pyrimidine and imidazole ring.

3.4. Photocatalytic activity and mechanism

First, the optimal amount of the cocatalyst for the photocatalytic oxygen evolution (OER) has been determined for CN40. As shown in Fig. 7(a), the OER of CN40 increases with the mass fraction of the cobalt cocatalyst ranging from zero to 3 wt%. However, with a further increase in the cobalt amount, the OER decreases. This decrease is possibly due to the excess

cobalt, which deposits onto the surface of the photocatalyst and forms surface charge-carrier recombination traps. Consequently, the optimal loading of the cocatalyst is approximately 3 wt%, consistent with the results of Wang [48]. The OER of all the samples have been investigated at a fixed cocatalyst loading of 3 wt% under the LED white-light irradiation. As plotted in Fig. 7(b), a gradual enhancement in the OER is observed as the theobromine amount is increased from 32 to 40 mg. This trend agrees with that of the photocurrent density. However, when the addition amount of theobromine is further increased to 44 and 48 mg, the obtained samples exhibit an obvious decrease in OER, especially for CN48. Note that CN48 does not exhibit the lowest photocurrent density (Fig. 6(c)). The obvious decrease in the OER of CN48 is largely associated with its large charge-transport resistance, very close to that of CN. The excess theobromine has been carbonized during the calcination, resulting in the formation of charge-carrier recombination centers. Furthermore, note the photocatalytic reaction for oxygen evolution occurs at a high oxidation potential. As a result, the VB holes may induce the self-oxidation of the PCN polymers, causing a decrease in the O_2 evolution selectivity and activity. Consequently, the degree of self-oxidation has been evaluated by measuring the amount of N_2 evolved. As shown in Fig. 7(b), the amount of N_2 evolved for all of the samples is too low for the self-oxidation of PCN, and thus the self-oxidation can be neglected. Apparently, the highest OER ($\sim 295.4 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$) is achieved by CN40, which is approximately 4.43 times higher than that of CN ($66.6 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$). It is suggested that the doping of theobromine at a suitable amount into PCN can lead to the enhancement in photocatalytic oxygen evolution. This improvement can be attributed to the following reasons. One is the slight positive shift in the valence position of

CN40 as compared with that of CN, which makes an increase in the oxidizing ability of the photoinduced holes for CN40. The other reason is associated with more amount of h^+ generated from CN40 than from CN, since CN40 exhibits enhanced optical absorption, reduced charge recombination and better charge transport than CN.

Moreover, the photocatalytic activity of CN $_x$ has been also evaluated by degrading RhB under the 5-W LED white-light irradiation. As shown in Fig. 7(c), all of the samples achieved an adsorption-desorption equilibrium within 30 min in the dark. The adsorption ability gradually increases with their specific surface area. Under the LED white-light irradiation, the self-degradation of RhB in the absence of a photocatalyst is too small to be considered [49]. After the irradiation lasting for 15 min, the photocatalytic RhB degradation ratios have been calculated to be 48.2%, 83.6%, 87.4%, 90.0%, 85.5%, and 68.3% for CN, CN32, CN36, CN40, CN44, and CN48, respectively. Obviously, all the CN $_x$ samples exhibit higher photocatalytic activity than CN. Furthermore, to enable an intuitive comparison in the photocatalytic activities of the investigated catalysts, the rate constants obtained from the kinetic curves for the degradation of RhB are listed in Table 1. The rate constants for CN, CN32, CN36, CN40, CN44, and CN48 are 0.02966, 0.1309, 0.1409, 0.1506, 0.1317, and 0.07468 min^{-1} , respectively. The highest rate constant is achieved by CN40, whose rate constant is 5.1 times greater than that of CN. These results further evidence that the introduction of theobromine into PCN has the function of improving the photocatalytic activity of the obtained samples. This improvement can be attributed to the enhancement in optical absorption, the reduction in charge recombination, and the facilitation for charge transport.

In addition, the stability of CN40 has been tested by repeat-

Fig. 7. (a) The effect of Co loading on the O_2 evolution rate of CN40; (b) OER of the PCN samples under the LED white light irradiation; (c) Degradation curves of RhB over different photocatalysts; (d) Degradation curves of RhB over CN40 with the addition of different radical scavengers. ESR spectra of DMPO/ O_2^- (e) and DMPO/ OH (f) adducts over the different PCN samples in aqueous solution before and after 5 and 10 min under visible light irradiation ($\lambda > 420 \text{ nm}$).

ing the photodegradation of RhB four times (Fig. S8). Almost no attenuation is observed from the results of the four experiments. Moreover, in the XRD patterns and FT-IR spectra of the fresh and used CN40, no distinct changes can be found for the used CN40, verifying that the structure of the catalyst has not been altered during the photocatalytic reaction (as shown in Fig. S9(a) and (b)).

To elucidate the photocatalytic mechanism of the doped PCN, IPA, AO, and BQ have been added into the reaction system containing CN40 for trapping $\cdot\text{OH}$, h^+ , and $\cdot\text{O}_2^-$, respectively. As shown in Fig. 7(d), the obvious decrease in the degradation ratio of RhB is found for the reaction systems containing BQ, AO, and IPA, suggesting that $\cdot\text{O}_2^-$, h^+ , and $\cdot\text{OH}$ are the active species playing a role in the photocatalytic degradation reaction. The highest reduction ratio in the activity is achieved by the addition of BQ, indicating that $\cdot\text{O}_2^-$ is the most important active species in the photocatalytic system containing CN40. The importance of $\cdot\text{O}_2^-$ can be further verified by the enhancement in the photocatalytic activity of the oxygenated system and the reduction in the degradation ratio for the one that has been filled with N_2 . Although the integration of theobromine into PCN led to a remarkable positive shift in the CB, as illustrated in Fig. 4, the CB position of CN40 is still negative enough for generating $\cdot\text{O}_2^-$. Moreover, the generation of $\cdot\text{O}_2^-$ has been also confirmed via the spin-trapping ESR/DMPO technique. As shown in Fig. 7(e), no obvious ESR signal is detected under dark. By contrast, characteristic peaks appear in the systems containing CN and CN40, when irradiated with visible light. These peaks, which exhibit a relative intensity ratio of 1:1:1:1, are attributed to the formation of a DMPO/ $\cdot\text{O}_2^-$ adduct. Significantly, the DMPO/ $\cdot\text{O}_2^-$ ESR signal intensity for the system containing CN40 is greater than that based on CN, reflecting that more amount of $\cdot\text{O}_2^-$ has been generated in the system based on CN40. The increase in $\cdot\text{O}_2^-$ could be attributed to more photogenerated electrons existing in CN40, since it exhibits enhanced optical absorption, reduced charge recombination and better charge transport, as compared with CN. Notably, the photocatalytic activity in the presence of AO is lower than that with the addition of isopropanol (IPA). This result means that the role of h^+ is more important than that of $\cdot\text{OH}$ in the photocatalytic reaction. Note that $\cdot\text{OH}$ is recognized as the useful species in the photocatalytic reaction. The ESR/DMPO spin-trapping of $\cdot\text{OH}$ has been also carried out. As shown in Fig. 7(f), four ESR peaks with a relative intensity of 1:2:2:1, corresponding to the characteristic peaks of DMPO/ $\cdot\text{OH}$, are observed for both CN and CN40 under the visible-light irradiation. The signal intensity of CN is stronger than that of CN40 in the dark, which may be attributed to the slight positive shift in the valence position for CN40 as compared with that for CN (Fig. 4). More significantly, under the visible light irradiation, CN40 exhibits higher signal intensity than CN, implying that more amount of $\cdot\text{OH}$ can be generated from CN40. Since the potential for generating $\cdot\text{OH}$ (1.99 eV vs. NHE) is larger than the valence band position of CN40, $\cdot\text{OH}$ is formed via the intermediate H_2O_2 that can be generated according to the equation: $\text{O}_2 + 2 \text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O}_2$ (0.68 eV vs. NHE) [35]. The more photogenerated electrons existing in CN40 are responsible for the more amount of

$\cdot\text{OH}$. Consequently, the more amounts of $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ make CN40 exhibit much higher photocatalytic activity than CN.

4. Conclusions

In this work, the doping of PCN with theobromine has been explored, aiming at introducing a strong electron receptor into the framework of PCN. Compared with CN, the optimized theobromine doped PCN sample, CN40, displays enhanced visible light harvesting, narrowed bandgap, along with a positive shift in the CB position and a positive shift in the VB position. The decreased PL emission, the enhanced photocurrent density, and the reduced charge-transport resistance reveal that CN40 possesses good charge separation and transport efficiency. More significantly, CN40 exhibits a photocatalytic oxygen evolution rate of $295.4 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, approximately 4.43-fold greater than that of CN ($66.6 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$) under the LED white-light irradiation. Moreover, the photocatalytic degradation ratio of RhB could reach 90.0% after irradiation for 15 min in the presence of CN40, which is 5.1-fold greater than the degradation ratio achieved by CN. The improved photocatalytic oxygen evolution originates from the positive shift in the VB position and the enhanced optical absorption and charge separation and transport of the theobromine doped PCN sample.

References

- [1] S. W. Cao, J. X. Low, J. G. Yu, M. Jaroniec, *Adv. Mater.*, **2015**, 27, 2150–2176.
- [2] Y. Wang, X. C. Wang, M. Antonietti, *Angew. Chem. Int. Ed.*, **2012**, 51, 68–89.
- [3] W. K. Ho, Z. Z. Zhang, W. Lin, S. P. Huang, X. W. Zhang, X. X. Wang, Y. Huang, *ACS Appl. Mater. Interfaces*, **2015**, 7, 5497–5505.
- [4] J. Wen, J. Xie, H. Zhang, A. Zhang, Y. Liu, X. Chen, X. Li, *ACS Appl. Mater. Interfaces*, **2017**, 9, 14031–14042.
- [5] Z. Z. Kong, X. Z. Chen, W. J. Ong, X. J. Zhao, N. Li, *Appl. Surf. Sci.*, **2019**, 463, 1148–1153.
- [6] K. He, J. Xie, X. Luo, J. Wen, S. Ma, X. Li, Y. Fang, X. Zhang, *Chin. J. Catal.*, **2017**, 38, 240–252.
- [7] S. Sahar, A. Zeb, Y. Liu, N. Ullah, A. Xu, *Chin. J. Catal.*, **2017**, 38, 2110–2119.
- [8] Q. Liu, T. X. Chen, Y. R. Guo, Z. G. Zhang, X. M. Fang, *Appl. Catal. B*, **2017**, 205, 173–181.
- [9] Q. Liu, Y. R. Guo, Z. H. Chen, Z. G. Zhang, X. M. Fang, *Appl. Catal. B*, **2016**, 183, 231–241.
- [10] Z. H. Li, W. L. Wang, Q. Liu, Z. G. Zhang, X. M. Fang, *Mater. Res. Bull.*, **2018**, 106, 152–161.
- [11] Q. Liu, X. L. Wang, Q. Yang, Z. G. Zhang, X. M. Fang, *Appl. Surf. Sci.*, **2018**, 450, 46–56.
- [12] W. Ding, S. Liu, Z. He, *Chin. J. Catal.*, **2017**, 38, 1711–1718.
- [13] L. S. Zhang, N. Ding, M. Hashimoto, K. Iwasaki, N. Chikamori, K. Nakata, Y. Z. Xu, J. J. Shi, H. J. Wu, Y. H. Luo, D. M. Li, A. Fujishima, Q. B. Meng, *Nano Res.*, **2018**, 11, 2295–2309.
- [14] T. Xiong, W. L. Cen, Y. X. Zhang, F. Dong, *ACS Catalysis*, **2016**, 6, 2462–2472.
- [15] Z. A. Lan, G. G. Zhang, X. C. Wang, *Appl. Catal. B*, **2016**, 192, 116–125.
- [16] F. Chen, H. Yang, W. Luo, P. Wang, H. Yu, *Chin. J. Catal.*, **2017**, 38, 1990–1998.
- [17] S. C. Yan, Z. S. Li, Z. G. Zou, *Langmuir*, **2010**, 26, 3894–3901.

Graphical Abstract

Chin. J. Catal., 2019, 40: 875–885 doi: S1872-2067(19)63337-1

Enhanced photocatalytic performance of polymeric C₃N₄ doped with theobromine composed of an imidazole ring and a pyrimidine ring

Zehao Li, Qian Yang, Chengcheng Chen, Zhengguo Zhang, Xiaoming Fang *

South China University of Technology

The oxygen evolution rate and photocatalytic degradation ratio of RhB for C₃N₄ doped with imidazole ring and pyrimidine ring are 4.43 times and 5.1 times higher than those of the undoped PCN, respectively.

- [18] C. Yang, B. Wang, L. Z. Zhang, L. Yin, X. C. Wang, *Angew. Chem. Int. Ed.*, **2017**, 56, 6627–6631.
- [19] X. Q. Fan, L. X. Zhang, R. L. Cheng, M. Wang, M. L. Li, Y. J. Zhou, J. L. Shi, *ACS Catal.*, **2015**, 5, 5008–5015.
- [20] K. Li, W. D. Zhang, *Small*, **2018**, 14, e1703599.
- [21] K. Li, M. Sun, W. D. Zhang, *Carbon*, **2018**, 134, 134–144.
- [22] Z. H. Chen, P. Sun, B. Fan, Q. Liu, Z. G. Zhang, X. M. Fang, *Appl. Catal. B*, **2015**, 170, 10–16.
- [23] Z. Li, S. Zhou, Q. Yang, Z. Zhang, X. Fang, *J. Phys. Chem. C*, **2019**, 123, 2228–2237.
- [24] J. S. Zhang, G. G. Zhang, X. F. Chen, S. Lin, L. Möhlmann, G. Dołęga, G. Lipner, M. Antonietti, S. Blechert, X. C. Wang, *Angew. Chem. Int. Ed.*, **2012**, 51, 3183–3187.
- [25] J. J. Tian, L. X. Zhang, X. Q. Fan, Y. J. Zhou, M. Wang, R. L. Cheng, M. L. Li, X. T. Kan, X. X. Jin, Z. H. Liu, Y. F. Gao, J. L. Shi, *J. Mater. Chem. A*, **2016**, 4, 13814–13821.
- [26] M. W. Zhang, X. C. Wang, *Energy Environ. Sci.*, **2014**, 7, 1902–1906.
- [27] J. S. Zhang, X. F. Chen, K. Takanabe, K. Maeda, K. Domen, J. D. Epping, X. Z. Fu, M. Antonietti, X. C. Wang, *Angew. Chem. Int. Ed.*, **2010**, 49, 441–444.
- [28] M. K. Bhunia, S. Melissen, M. R. Parida, P. Sarawade, J. M. Basset, D. H. Anjum, O. F. Mohammed, P. Sautet, T. L. Bahers, K. Takanabe, *Chem. Mater.*, **2015**, 27, 8237–8247.
- [29] Y. Chen, J. S. Zhang, M. W. Zhang, X. C. Wang, *Chem. Sci.*, **2013**, 4, 3244–3248.
- [30] A. D. Becke, *J. Chem. Phys.*, **1993**, 98, 5648–5652.
- [31] Q. Liu, X. L. Wang, Q. Yang, Z. G. Zhang, X. M. Fang, *Appl. Catal. B*, **2018**, 225, 22–29.
- [32] S. C. Yan, Z. S. Li, Z. G. Zou, *Langmuir*, **2009**, 25, 10397–10401.
- [33] Y. R. Guo, Q. Liu, Z. H. Li, Z. G. Zhang, X. M. Fang, *Appl. Catal. B*, **2018**, 221, 362–370.
- [34] Y. R. Guo, T. X. Chen, Q. Liu, Z. G. Zhang, X. M. Fang, *J. Phys. Chem. C*, **2016**, 120, 25328–25337.
- [35] X. L. Wang, Q. Liu, Q. Yang, Z. G. Zhang, X. M. Fang, *Carbon*, **2018**, 136, 103–112.
- [36] G. G. Zhang, J. S. Zhang, M. W. Zhang, X. C. Wang, *J. Mater. Chem.*, **2012**, 22, 8083–8091.
- [37] Y. Sakata, K. Yoshimoto, K. Kawaguchi, H. Imamura, S. Higashimoto, *Catal. Today*, **2011**, 161, 41–45.
- [38] Y. Wang, M. K. Bayazit, S. J. A. Moniz, Q. Ruan, C. C. Lau, N. Martsinovich, J. Tang, *Energy Environ. Sci.*, **2017**, 10, 1643–1651.
- [39] Y. Chen, B. Wang, S. Lin, Y. F. Zhang, X. C. Wang, *J. Phys. Chem. C*, **2014**, 118, 29981–29989.
- [40] F. X. Wang, W. Septina, A. Chemseddine, F. F. Abdi, D. Friedrich, P. Bogdanoff, R. van de Krol, S. D. Tilley, S. P. Berglund, *J. Am. Chem. Soc.*, **2017**, 139, 15094–15103.
- [41] F. X. Wang, A. Chemseddine, F. F. Abdi, R. van de Krol, S. P. Berglund, *J. Mater. Chem. A*, **2017**, 5, 12838–12847.
- [42] N. Tian, Y. H. Zhang, X. W. Li, K. Xiao, X. Du, F. Dong, G. I. N. Waterhouse, T. R. Zhang, H. W. Huang, *Nano Energy*, **2017**, 38, 72–81.
- [43] X. C. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, *Nat. Mater.*, **2009**, 8, 76–80.
- [44] Q. Liu, T. X. Chen, Y. R. Guo, Z. G. Zhang, X. M. Fang, *Appl. Catal. B*, **2016**, 193, 248–258.
- [45] L. H. Lin, H. H. Ou, Y. F. Zhang, X. C. Wang, *ACS Catal.*, **2016**, 6, 3921–3931.

- [46] G. G. Liu, G. X. Zhao, W. Zhou, Y. Y. Liu, H. Pang, H. B. Zhang, D. Hao, X. G. Meng, P. Li, T. Kako, J. H. Ye, *Adv. Funct. Mater.*, **2016**, 26, 6822–6829.
- [47] G. G. Zhang, X. C. Wang, *J. Catal.*, **2013**, 307, 246–253.
- [48] Z. A. Lan, Y. X. Fang, Y. F. Zhang, X. C. Wang, *Angew. Chem. Int. Ed.*, **2018**, 57, 470–474.
- [49] C. Han, Y. D. Wang, Y. P. Lei, B. Wang, N. Wu, Q. Shi, Q. Li, *Nano Res.*, **2015**, 8, 1199–1209.

含咪唑环与嘧啶环的可可碱掺杂的氮化碳聚合物及其增强的光催化性能

李泽浩^a, 杨 茜^a, 陈成成^a, 张正国^{a,b}, 方晓明^{a,b,c,*}

^a华南理工大学化学与化工学院传热强化与过程节能教育部重点实验室, 广东广州510640

^b华南理工大学化学与化工学院广东省高效蓄热与应用工程技术研究中心, 广东广州510640

^c华南理工大学化学与化工学院广东省燃料电池技术重点实验室, 广东广州510640

摘要: 氮化碳聚合物(PCN)是一种有潜力的聚合物型半导体光催化剂, 具有原料廉价、物理化学稳定性好以及合适的带边等优点, 使其在光催化分解水产氢产氧、降解染料以及抑菌等方面具有很大的潜力。但是由于高电负性的N原子被低电负性的C原子均匀地取代, 增加了PCN内部电子传输的难度, 使得光生电子-空穴对的复合度增加, 进而光催化活性降低。由于PCN的分子结构可调控, 所以可以通过分子掺杂来改变氮化碳分子结构, 提高光催化活性。常用的分子有机分子, 比如吡啶类化合物、嘧啶类化合物以及噻吩类化合物。研究发现, 强电负性元素的引入可以改变氮化碳的电子分布, 所以含有两个N原子的咪唑类化合物理论上对氮化碳的光催化活性提升帮助更大。由于此类化合物还未见有报道。因此, 本文将同时含有咪唑环和嘧啶环的可可碱与尿素反应, 生成了咪唑环与嘧啶环共掺杂的氮化碳聚合物, 并通过一系列的表征方法验证了咪唑环与嘧啶环成功引入到氮化碳聚合物结构中; 然后利用紫外可见光谱(UV-vis), 荧光发射光谱(PL), 电子顺磁共振(EPR)等实验与DFT理论计算共同验证了咪唑环与嘧啶环共掺杂的氮化碳光学性能; 最后通过光催化分解水产氧和降解罗丹明B(RhB)来评价改性后氮化碳的活性。

UV-vis测试结果表明, 改性后的PCN不仅本征吸收发生红移, 而且在波长450到550 nm之间有一个明显的吸收峰, 这是由于引入咪唑环和嘧啶环后本征 $n \rightarrow \pi^*$ 电子跃迁所致。并且改性后的PCN的禁带宽度相比于未改性有所降低, 说明其可利用的可见光范围增加。PL和EPR结果表明, 改性后的PCN不仅光生载流子的复合得到了极大地抑制, 而且能够产生更多的孤对电子。通过XPS价带谱, 莫特-肖特基曲线以及DFT理论计算推断出改性前后PCN的带边位置, 发现改性后PCN的价带位置更正, 说明其产生的空穴氧化能力更强。光催化分解水产氧和降解RhB发现, 最优改性样品CN40的产氧和降解RhB活性分别是未改性氮化碳的4.43倍和5.1倍。这说明通过咪唑环和嘧啶环共掺杂改性后的氮化碳的光催化活性确实得到了大幅度提升。最后通过添加各种牺牲剂和ESR/DMPO表明 $\cdot\text{O}_2^-$ 和空穴是降解RhB的主要因素。

综上所述, 通过咪唑环和嘧啶环共掺杂改性氮化碳聚合物, 不仅提高了其光吸收能力, 抑制了光生载流子的复合, 产生更多的孤对电子, 而且使得价带位置正移, 提高了价带空穴的氧化能力, 光催化活性显著提高。

关键词: 氮化碳聚合物; 分子掺杂; 可可碱; 光催化产氧; 染料降解

收稿日期: 2018-11-13. 接受日期: 2019-02-26. 出版日期: 2019-06-05.

*通讯联系人. 电话: (20)87112997; 传真: (20)87113870; 电子邮箱: cexmfang@scut.edu.cn

基金来源: 国家自然科学基金(21276088, U1507201); 广东省自然科学基金(2014A030312009); 中国博士后科学基金(2018M640784).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).