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Article

Donor-acceptor carbon nitride with electron-withdrawing chlorine group to promote exciton dissociation

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ABSTRACT

Carbon nitride (C_3N_4) is promising for photocatalytic hydrogen production, but photogenerated electrons and holes in C_3N_4 usually tend to exist as excitons due to intrinsic Coulomb interactions making its photocatalytic activity unsatisfactory. Herein, a well-designed intramolecular C_3N_4 -based donor-acceptor (D-A) photocatalytic system was constructed to promote exciton dissociation. Due to its good chemical compatibility with melamine and appropriate sublimation property, 2-amino-4,6-dichloropyrimidine unit was chosen as the monomer to react with melamine to construct intramolecular D-A system (CNCl_x). The hydrogen evolution rate of CNCl_{0.15} is 15.3 times higher than that of bulk C_3N_4 under visible light irradiation, with apparent quantum efficiency of 13.6% at 420 nm. The enhanced activity is attributed to introduced electron-withdrawing –Cl group as terminal group in the resulted CNCl_x samples, which can build internal electric field to promote the exciton dissociation into free electron and hole. In addition, lower work function value of CNCl_x samples indicates that internal electric field can help free electrons and holes transfer to the surface of CNCl_x samples for photocatalytic reaction.

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1. Introduction

Water splitting under visible light using polymer photocatalysts is a promising technology for sustainable hydrogen production [1,2]. Polymeric carbon nitride (C_3N_4) has emerged as an attractive photocatalyst for water splitting and pollutant degradation because of the ability to absorb visible light efficiently, chemical stability and non-toxicity [3]. Unfortunately, photogenerated electrons and holes in C_3N_4 usually tend to exist as excitons due to intrinsic Coulomb interactions making its photocatalytic activity unsatisfactory [4]. So, there have been a lot of efforts promoting exciton dissociation into free

electrons and holes to enhance the carriers separation efficiency of C_3N_4 [5]. Donor-Acceptor (D-A) system is an effective way to promote exciton dissociation because it can induce internal electric field which promotes the exciton to dissociate into free electrons and holes. And then free electrons and holes transfer to the surface of catalyst with the help of internal electric field [6–8].

In the past few years, various intramolecular copolymers have been constructed to form D-A systems based on C_3N_4 [9–12]. In 2009, Wang *et al.* [13] synthesized C_3N_4 with D-A structures by simple copolymerization with organic monomer (barbituric acid) for the first time. The resulted sample showed

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extended absorption region and enhanced hydrogen evolution rate. Inspired by this work, variety of organic monomers were exploited, like benzene [14,15], naphthalene [16], and so on [17]. The introduction of these monomers always resulted facilitated charge separation. Except for the organic monomers, -Se [18], -C≡N [19,20], oxygen group (C-O-C and C=O) [21] were also incorporated to C₃N₄ for constructing D-A copolymers.

Although a lot of efforts have been made to construct intramolecular copolymers with D-A structure, and these C₃N₄-based copolymers showed enhanced performance for photocatalysis, there are still several points that need paying more attention to: (1) the chemical compatibility of the monomer with the precursor molecule of C₃N₄; (2) the sublimation property and temperature of the introduced monomer which are very important for the copolymerization process; (3) the final position of the monomer in the copolymer. Herein, this work takes these three points into account and chooses 2-amino-4,6-dichloropyrimidine (C₄H₃Cl₂N₃) as the monomer. C₄H₃Cl₂N₃ has good chemical compatibility with melamine (C₃N₃(NH₂)₃, the precursor of C₃N₄), because their molecular structures are similar. During the copolymerization process, C₄H₃Cl₂N₃ sublimates at 219–222 °C and then melamine sublimates at 300 °C, resulting the sufficient gas-phase mixture for copolymerization. When the temperature continues to rise, the copolymerization process will take place. If the C₄H₃Cl₂N₃ molecules react with C₃N₃(NH₂)₃, the polymerization will end at this direction, thus the electron-withdrawing -Cl groups will all locate at the terminal of the copolymers which will be helpful for the construction of D-A system.

2. Experimental

2.1. Materials

Melamine (C₃N₆H₆), 2-amino-4,6-dichloropyrimidine (C₄H₃Cl₂N₃), and triethanolamine (TEOA) were purchased from Aladdin Industry Corporation. Chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O), methyl orange (MO) and rhodamine B (RhB) were obtained from Guangfu Institute, China. Phenol was purchased from J&K Chemical. All the chemicals were reagent grade and used without further purification. Milli-Q ultra-pure water was obtained from HYP-QX machine.

2.2. Fabrication of D-A copolymers

2.5224 g of melamine (0.02 mol) was mixed thoroughly with a certain amount of (0.001, 0.002, 0.003 and 0.004 mol) 2-amino-4,6-dichloropyrimidine (C₄H₃Cl₂N₃). The mixture was then calcined in air at 550 °C for 4 h, while the heating rate is 2.3 °C/min. The obtained products are denoted as CNCl_x, where the x values (0.05, 0.1, 0.15, and 0.2) represent the molar ratios of C₄H₃Cl₂N₃ to melamine. For comparison, bulk C₃N₄ (donated as BCN) was also fabricated by calcining melamine at 550 °C for 4 h [21].

2.3. Characterizations

X-Ray diffraction (XRD) characterizations were conducted on a X'Pert Pro X-ray diffractometer equipped with Cu K_α radiation at 40 kV and 40 mA. FT-IR spectra were recorded on a Bruker Vertex70 spectrometer. The morphologies of synthesized samples were obtained with Hitachi S-4800 FE-SEM (scanning electron microscope) and JEM-2100F TEM (transmission electron microscope). The chemical states were conducted on a Thermo Scientific K-Alpha X-ray photoelectron spectroscopy (XPS). Time-resolved photoluminescence spectra decays were recorded on an Edinburgh Instrument (FLS 980, λ = 375 nm). Steady-state photoluminescence (PL) spectra were taken on a HITACHI F-4600 instrument (λ = 375 nm). N₂ adsorption and desorption isotherms were conducted on a Quantachrome Instruments Quadrasorb EVO at 77 K. UV-vis diffuse reflectance spectra (DRS) were obtained on a SHIMADZU UV-2600 spectrometer using BaSO₄ as reference. Nuclear Magnetic Resonance (NMR) was performed with Bruker AVANCE III 600 MHz solid-state nuclear magnetic spectrometer. Electron paramagnetic resonance (EPR) measurement was performed with a JES FA200 spectrometer. Ultraviolet photoelectron spectrometer (UPS) measurements were performed with an American ThermoFischer, ESCALAB 250Xi instrument.

2.4. Photocatalytic hydrogen evolution and organics degradation performance

Photocatalytic hydrogen evolution performance was tested in a closed Pyrex top-irradiation vessel (280 mL). Firstly, 50 mg photocatalyst was dispersed in 100 mL triethanolamine solution (10 vol%) under ultrasonic treatment for 30 min. After that, 405 μL H₂PtCl₆ aqueous solution was added. Then, 3 wt% Pt as co-catalyst was introduced by *in-situ* photodeposition method. The reaction solution was purged with Ar for 30 min to completely remove air until the pressure up to 101 kPa. The reaction was conducted at 0.5 °C under a 300 W Xe-lamp (PLS-SXE300UV, Beijing Trusttech. Co. Ltd.) equipped with a 420 nm-cut-off filter. The evolved gas was analyzed on gas chromatography (Bruker 450-GC) equipped with a thermal conductive detector (TCD) and a 5 Å molecular sieve column, using Ar gas as the carrier gas.

The apparent quantum yield (AQY) was calculated as $AQY = Ne/Np \times 100\%$, where *Ne* is the amount of reaction electrons, *Np* is the amount of incident photons. The irradiation area was 20 cm². The intensity of incident light was measured using a UV-A radiometer (Photoelectric Instrument Factory, Beijing Normal University, model UV-A). For 420 nm monochromatic light, the intensity was 7.51 mW/cm². *Ne* is calculated based on the average amount of hydrogen produced per hour.

Photodegradation of organics (RhB, phenol, and MO) was conducted in an opening quartz chamber (150 mL) under the vertical irradiation of a 300 W high-pressure Xenon lamp. The detailed reaction conditions are listed as follows: the reaction temperature 25 ± 0.2 °C, the weight content of photocatalyst 0.2 g/L, C₀(RhB) = 20 μmol·L⁻¹, C₀(MO) = 120 μmol·L⁻¹, C₀(Phenol) = 400 μmol·L⁻¹. Before the photodegradation reaction, the suspension composed of organic solution and photo-

catalyst was stirred for 20 min in black to achieve adsorption equilibrium. For comparison, the self-degradation of RhB, phenol, and MO was conducted without any catalysts under light irradiation. The concentrations of organics were analyzed by UV-vis spectrometer.

2.5. Photoelectrochemical measurements

The photoelectrochemical measurements were performed on a CHI 660e electrochemical system. Firstly, 20 mg sample was dispersed in 2 mL ethanol and then 20 μ L Nafion was added. Secondly, the dispersion was sonicated for 2 hours and dip-coated on an F-doped tin oxide (FTO) glass electrode (2×2 cm²), which was ultrasonically in acetone solution to remove surface impurities before using. Thirdly, the FTO glass electrode was heated to 150 °C and maintained at 150 °C for 12 h. A standard three-electrode cell was composed of the prepared FTO glass electrode coated with sample (working electrode), a platinum wire counter electrode, an Ag/AgCl reference electrode. Electrolyte is 0.2 M Na₂SO₄ solution. The electrochemical

impedance spectroscopy (EIS) were tested with a sinusoidal ac perturbation of 0.1 V applied over the frequency range of 0.01–10⁵ Hz.

3. Results and discussion

3.1. Structure and morphology

The crystal structures of prepared C₃N₄ materials were firstly investigated by XRD. As shown in Fig. 1(a), BCN and CNCl_x show two typical diffraction peaks at 13.2° and 27.4°. The peak at 13.2° is attributed to the in-plane intervals of periodic tri-s-triazine units (100) plane. And the peak at 27.4° arises from the interplanar stacking of aromatic systems (002) plane of graphitic C₃N₄ (JCPDS No. 87-1526), while the peak of (002) plane tends to be broadened and weakened from BCN to CNCl_{0.2}, indicating the reduced size and/or the decreased thickness of C₃N₄ nanosheets. The SEM images and TEM images of synthesized C₃N₄ materials were displayed in Figs. 1(b–f) and Figs. 2(a–e). As shown in Fig. 1(b), the nanosheets are

Fig. 1. (a) The XRD pattern BCN and CNCl_x; SEM images of BCN (b), CNCl_{0.05} (c), CNCl_{0.1} (d), CNCl_{0.15} (e), and CNCl_{0.2} (f).

Fig. 2. The TEM images of BCN (a), CNCl_{0.05} (b), CNCl_{0.1} (c), CNCl_{0.15} (d), CNCl_{0.2} (e); (f) BET surface area of bulk C₃N₄ and CNCl_x.

densely packed in form of bulk particles without obvious porosity in BCN. While CNCl_x samples show less compact and porous structures with variable ordering (Figs. 1(c–f)), among which $\text{CNCl}_{0.15}$ shows the most ordered structure. Moreover, the nanosheets become smaller and thinner with increasing the amount of $\text{C}_4\text{H}_3\text{Cl}_2\text{N}_3$, which can also be confirmed by the TEM images (Figs. 2(b–e)) and is consistent with the result of XRD. N_2 adsorption-desorption measurements were performed to further investigate the porous structures of copolymers (Figs. 2(f) and S1). The surface area increases from bulk C_3N_4 ($16 \text{ m}^2 \text{ g}^{-1}$) to $\text{CNCl}_{0.15}$ ($24 \text{ m}^2 \text{ g}^{-1}$). But it decreases for $\text{CNCl}_{0.2}$ ($21 \text{ m}^2 \text{ g}^{-1}$) because the sheets tend to aggregate, which can be proved by the TEM image of $\text{CNCl}_{0.2}$ (Fig. 2(e)).

The FT-IR spectras of BCN and CNCl_x samples demonstrate typical aromatic C–N heterocycle stretches at $1200\text{--}1700 \text{ cm}^{-1}$ and the triazine units breathing mode at 806 cm^{-1} (Fig. 3(a)). The broad peak at $2800\text{--}3400 \text{ cm}^{-1}$ arises from the N–H of the residual uncondensed amino groups and O–H bands of the absorbed H_2O molecules [22]. The vibrations of C–Cl group are hardly observed in CNCl_x , presumably because its content is low and its vibration is overlapped with those of C–N heterocycle [23]. Even if the molar ratio of $\text{C}_4\text{H}_3\text{Cl}_2\text{N}_3$ to melamine is raised up to 0.5, the vibrations of C–Cl groups are still not visible (Fig. S2). As shown in Fig. 3(b), the ^{13}C NMR spectrum of BCN and $\text{CNCl}_{0.15}$ both display two typical signals at 164.92 and 157.05 ppm, which correspond to C atoms bonded to external groups (C–NH) and C atoms linked trigonally to three N atoms

(C–N₃), respectively [24,25], indicating that –Cl groups don't influence the chemical shift of intrinsic lattice C. Combined with the results of FT-IR, we can conclude that the –Cl groups don't disturb the intrinsic structure of C_3N_4 , confirming that –Cl groups don't substitute the lattice C or N atom.

XPS spectra were studied to investigate the chemical states. The XPS spectra of C 1s and N 1s orbitals are displayed in Fig. 4. As shown in Fig. 4(a), the peak at 284.8 eV corresponds to carbon impurities from carbon contamination [26]. The peaks at 288.1 eV corresponds to sp^2 -hybridized C in the N-containing aromatic ring, which is the major aromatic carbon species of C_3N_4 . The peak attributed to the C–NH_x species is at 285.7 eV of bulk C_3N_4 , while the binding energy shifts towards the high energy side after introducing the –Cl group due to the decrease of electron density of C–NH_x [27,28]. This result proves that different terminal groups (electron-donating group C–NH_x and electron-withdrawing group –Cl) change the electron distribution of the heptazine heterocyclic structure, which can build internal electric field in the CNCl_x samples. The internal electric field helps the exciton dissociation into free electrons and holes. The high-resolution N 1s XPS spectrum (Fig. 4(b)) shows that the main species is at 398.6 eV attributed to sp^2 -hybridized nitrogen (C–N=C) center involved in triazine rings. And the weak peak at 400.4 and 401.2 eV is attributed to the tertiary nitrogen N–(C)₃ groups and amino groups (C–N–H), respectively [29]. As for the content of Cl, XPS result shows that the overall concentration in $\text{CNCl}_{0.15}$ is 0.2 mol%, but the result is

Fig. 3. (a) The FT-IR spectra and NMR spectra of bulk C_3N_4 and CNCl_x ; (b) NMR spectra of bulk C_3N_4 and $\text{CNCl}_{0.15}$.

Fig. 4. (a,b) High-resolution XPS spectra of the BCN and CNCl_x ; (c) The structure of CNCl_x copolymer.

Fig. 5. (a) UV-vis absorption spectra; (b) Room-temperature EPR spectrum; (c) Time-resolution fluorescence spectra; (d) Electrochemical impedance spectroscopy of BCN and CNCl_x.

not convincing when the atomic percentage content is less than 1%. Hence, we investigated the content of Cl in the prepared CNCl_{0.5} sample, in which the atomic percentage content of Cl is 1.5% (Fig. S3 and Table S1), indicating that –Cl group can be incorporated into C₃N₄ through the co-calcination of C₄H₃Cl₂N₃ and melamine [30].

Both C 1s and N 1s spectra results are consistent with the result of FT-IR spectra that basic heptazine heterocyclic structure doesn't change after introducing –Cl group into C₃N₄, except the electron density of C–NH_x species. From the above results, the structure of CNCl_x is proposed in Fig. 4(c). As indicated, the incorporated –Cl groups are located at the terminals of the copolymer.

Fig. 5(a) shows the UV-vis absorption spectra. With increasing the amount of –Cl groups, the absorption band edge of the CNCl_x sample has a red shift and the light absorption value gradually increases. This is because when the electron donating group and the electron withdrawing group exist at the same time, the intramolecular charge-transfer absorption can occur [31]. This result further confirms the existence of the internal electric field [32]. Based on the UV-vis absorption spectra, the optical band gaps of as-prepared samples were evaluated by a classical Tauc approach [33]. Fig. S4(b) shows the band gap of BCN is 2.7 eV. As shown in Figs. S4(c–f), the band gap decreases from 2.67 to 2.61 eV with increasing the terminal –Cl group from CNCl_{0.05} to CNCl_{0.2}, indicating that the introduction of terminal –Cl group can regulate the electronic structure of C₃N₄.

To further confirm the electronic structure of CNCl_x, EPR was conducted. As shown in Fig. 5(b), all samples exhibit one single Lorentzian line with a *g* value of 2.0034, attributing to

the unpaired electrons in the CB of C₃N₄ [34]. Compared with the pristine C₃N₄, the EPR signals are much enhanced for CNCl_x samples and the highest for CNCl_{0.2} samples. Note that the higher EPR intensity is an indication of the higher concentration of unpaired electrons [34,35]. It could be then deduced that the introduction of –Cl offers internal electric field, which has a strong ability to delocalize electrons and thus benefits the photoinduced generation of charge carriers for photocatalytic reaction. Time-resolved photoluminescence (PL) spectra was measured to investigate the lifetime of charge carriers. As revealed in Fig. 5(c), the lifetimes (τ) are 1.89, 2.23, 2.46, 3.88, 4.06 ns for BCN and CNCl_x samples, which shows the same trend in the steady-state PL spectra (Fig. S5), indicating the enhanced exciton dissociation efficiency with the increased amount of –Cl group. This result suggests that the intensity of internal electric field enhances with the amount of –Cl group [36].

3.2. Photocatalytic performance

The photocatalytic performances of the composites were evaluated by degrading organic pollutants and hydrogen evolution reaction (HER) under visible light irradiation ($\lambda > 420$ nm). In Fig. 6(a), it is obvious that CNCl_x shows an enhanced rate by a factor of 6–15 over 168.7 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ of bulk C₃N₄. Especially, the H₂ evolution rate of CNCl_{0.15} reaches 2585.3 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, which is about 15.3-fold of bulk C₃N₄. In order to distinguish the contribution of surface area and –Cl terminal groups to the overall activity, the HER rate is normalized by the surface area. As shown in Fig. 6(a), CNCl_x samples show higher normalized

Fig. 6. (a) Photocatalytic hydrogen evolution rates of CN and CNCl_x samples under visible light irradiation; cycling stability test (b) and wavelength-dependent apparent quantum yield (c) of CNCl_{0.15}; (d) Degradation of organic pollutants of CN and CNCl_x samples under visible light irradiation.

activity than bulk C₃N₄, indicating that surface area is not the inherent reason for the improvement of the performance. The proposed schematic illustration of charge transfer in CNCl_x under visible-light irradiation is shown in Fig. 7. And the improvement of activity is mainly due to the enhancement of photoabsorption and exciton dissociation efficiency with the increase of terminal –Cl groups (Figs. 5(a–c)). However, –Cl groups can also act as the trap sites for electrons, thus decreasing the efficiency of charge transfer. This is testified by the Nyquist plots of EIS, transient photocurrent response and UPS results. The smallest arc radius and highest transient photocurrent response of CNCl_{0.15} among all the samples suggested the minimum resistance and highest carrier transfer efficiency (Figs. 5(d) and S6). The work function values of BCN and CNCl_x samples (Fig. S7) investigated by UPS measurement. Referring to the calculation method in previous report [37], the work function values (difference between the Fermi and vacuum level) for BCN, CNCl_{0.05}, CNCl_{0.1}, CNCl_{0.15} and CNCl_{0.2} are calculated to be 4.4, 4.39, 4.11, 3.75 and 4.28 eV, respectively. Because work function is defined as the minimum amount of thermodynamic work (i.e. energy) required to remove an electron from a solid to a point in the vacuum immediately outside the solid surface [38], smaller work function values of CNCl_x indicates that electrons are easier to move to the surface under the influence of internal electric field [39], while excess –Cl groups increase the work function values of CNCl_{0.2}. So, excess –Cl groups can result in the decrease of photocatalytic activity

for CNCl_{0.2} sample.

The stability of optimized catalyst CNCl_{0.15} was also tested. It shows a stable HER rate after 5 cycling trips (Fig. 6(b)). Furthermore, the wavelength dependent apparent quantum yield (AQY) of CNCl_{0.15} reaches up to 13.6 % at 420 nm (Fig. 6(c)).

The photocatalytic degradation of organic pollutants under visible light irradiation is shown in Figs. 6(d) and S8. After introducing –Cl groups, CNCl_x samples show superior activity to bulk C₃N₄, demonstrating internal electric field can also improve the photocatalytic pollutant degradation performance. Among the CNCl_x samples, CNCl_{0.15} exhibits the highest activity, which is 5.8, 7.9 and 9.5 times of bulk C₃N₄ for the degradation of RhB, MO and phenol, respectively (Fig. 6(d) and Table S1).

Fig. 7. Schematic illustration of proposed charge transfer in CNCl_x under visible-light irradiation.

Especially, $\text{CNCl}_{0.15}$ can remove 97% of RhB within 60 minutes.

4. Conclusions

In this work, three important points that can influence the construction of intramolecular D-A system are explicated. To meet the requirements of ideal monomer, $\text{C}_4\text{H}_3\text{Cl}_2\text{N}_3$ is chosen as the monomer to react with melamine to construct intramolecular D-A copolymers (CNCl_x). Introduction of $-\text{Cl}$ group would change the distribution of the electron density over the heptazine rings, thus building an internal field in the D-A system. The internal field can not only promote exciton dissociation into free electron and hole but also help free electrons and holes transfer to the surface of CNCl_x , thus improving photocatalytic efficiency. The hydrogen evolution rate of $\text{CNCl}_{0.15}$ is 15.3 times higher than that of bulk C_3N_4 under visible light irradiation, with apparent quantum efficiency of 13.6% at 420 nm. And it also presents 5.82, 7.93 and 9.53 times of bulk C_3N_4 for the degradation of RhB, MO and phenol.

Electronic supporting information

Supporting information is available in the online version of this article.

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Graphical Abstract

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Donor-acceptor carbon nitride with electron-withdrawing chlorine group to promote exciton dissociation

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Compared with bulk C_3N_4 , donor-acceptor carbon nitride catalysts exhibit much higher photocatalytic performance by incorporating electron-withdrawing $-\text{Cl}$ group as terminal group, which can build internal electric field to promote the exciton dissociation and charge carrier transfer.

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带有吸电子-Cl基团的供体-受体氮化碳的构建及其光催化性能

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摘要: 聚合物氮化碳(C_3N_4)因具有可见光响应特性、良好的化学稳定性、无毒性等优点而成为一类极具吸引力的光催化剂。遗憾的是, 由于本征库仑相互作用, C_3N_4 中的光生电子和空穴通常以激子的形式存在, 导致迁移到表面的光生电子和空穴数量减少, 从而降低了光催化活性, 因此人们做了大量的研究工作来促进激子解离成自由电子和空穴。D-A体系可以诱导内部电场的产生, 从而促进激子解离成自由电子和空穴, 因此, 构建供体-受体(D-A)体系是一种有效地促进激子解离的方法。然后在内电场作用下, 自由电子和空穴也能够更加容易地转移到共聚物表面, 从而发生相应的光催化还原和氧化反应。

本文选择了2-氨基-4,6-二氯嘧啶($C_4H_3Cl_2N_3$)作为单体, 与三聚氰胺共聚形成分子内共聚物($CNCl_x$)来构建D-A体系。由于分子结构相似, $C_4H_3Cl_2N_3$ 与 $C_3N_3(NH_2)_3$ 分子具有良好的化学相容性。在共聚过程中, $C_4H_3Cl_2N_3$ 在219~222 °C升华, 三聚氰胺在300 °C升华, 在温度继续升高到550 °C的过程中, 气相混合物充分混合并发生共聚反应。在共聚过程中, 如果 $C_4H_3Cl_2N_3$ 分子与 $C_3N_3(NH_2)_3$ 反应, 那么三聚氰胺沿着这个方向的聚合将终止, 因此吸电子-Cl基团将全部位于共聚分子的末端。

相较于体相 C_3N_4 , $CNCl_x$ 样品活性均有所提高, 且随着-Cl基团数量的增加, $CNCl_x$ 样品活性先提高后降低, 其中 $CNCl_{0.15}$ 样品活性最高。 $CNCl_{0.15}$ 在可见光下的析氢速率是体相 C_3N_4 的15.3倍, 在420 nm处的表观量子效率为13.6%。对RhB, MO和苯酚的降解速率分别为体相 C_3N_4 的5.82, 7.93和9.53倍。构建分子内D-A体系以后, C_3N_4 活性提高主要是因为随着末端-Cl基团的增加, 材料的吸光能力和激子解离效率提高。而且-Cl基团也可以充当电子的俘获位点, 浓度进一步升高会降低电荷转移的效率使活性降低。EIS的奈奎斯特图和*i-t*曲线结果表明, $CNCl_{0.15}$ 的电弧半径最小, 光电流最大, 说明其具有最低的电阻和最高的载流子传输效率。紫外光电子能谱测试结果表明, $CNCl_x$ 功函数值较小, 电子更容易在内部电场的作用下移动到表面, 而过量的-Cl基团增加了 $CNCl_{0.2}$ 的功函数值, 导致 $CNCl_{0.2}$ 样品的光催化活性降低。

关键词: 氮化碳; 供体-受体; 内电场; 激子; 产氢

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