Excellent Visible-Light Photocatalysis of Fluorinated Polymeric Carbon Nitride Solids

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Heterogeneous photocatalysis is a promising method to produce fuels/chemicals at the expense of solar energy.[1,2] As the selection of the photocatalysts offers special challenges, much effort is focused on the search for new photocatalysts. The creation of efficient, simple, and sustainable materials as photocatalysts working with visible light represents a central challenge of the field.[3-6]

Carbon nitrides are fascinating materials that have attracted worldwide attention.[7-13] They promise access to an even wider range of applications than carbon materials because the incorporation of nitrogen atoms in the carbon architecture can enhance the chemical, electrical, and functional properties.[14-16] For example, a weakly ordered graphitic carbon nitride (g-C_3N_4), the most stable allotrope at ambient conditions, was found to be active for reduction of carbon dioxide and as a metal free catalyst for Friedel–Crafts reactions.[17] Very recently, it was described that polymeric C_3N_4 exhibits an appealing electronic structure, being a wide-band gap, indirect semiconductor. This allows its direct use in heterogeneous photocatalysis, for example, in the hydrogen evolution from water.[18]

As this polymeric semiconductor is composed of carbon and nitrogen only (with a little residual hydrogen due to incomplete condensation) and can be made directly out of urea, g-C_3N_4 is obviously a most "sustainable" semiconducting polymer. In addition, the catalytic, electronic, and optical properties of the structure are by principle adjustable, using the rich chemistry of nitrogen and carbon.[19] Indeed, such protocols have been also widely used to control the performance of more traditional materials, for example, as an important modification method, fluorination has been used to modify the properties of graphite, activated carbons, carbon nanotubes, BN nanotubes, etc.[20-24] In this communication, fluorinated polymeric carbon nitride solids (CNF) was synthesized and employed as heterogeneous catalyst in the photochemical hydrogen generation from water containing an appropriate sacrificial reagent, as well as for the oxidization of benzene to phenol under visible light.

The synthesis of CNF samples has been carried out employing a directly incorporating of different amount of NH_4F (x = 0.05, 0.1, 0.5, 1.0, 2.0 g) into the classical carbon nitride condensation (For simplicity, the resulting samples are denoted CNF-x). The fluorination may be accomplished through the NH_4F reaction (see Scheme S1 in the Supporting Information) on the freshly thermally induced condensation of polymeric carbon nitride solids.

X-ray diffraction analysis (Figure 1a) reveals the graphite-like packing of practically all products, showing the typical (002) interlayer-stacking peak around 27.4°, e.g. corresponding to an interlayer distance of d = 0.33 nm for CNF-1.0, as is well-known for g-C_3N_4. However, the (002) peak becomes broader and gradually less intense with increasing amount of NH_4F, which indicates disturbance of graphitic structure, potentially by the fluorine

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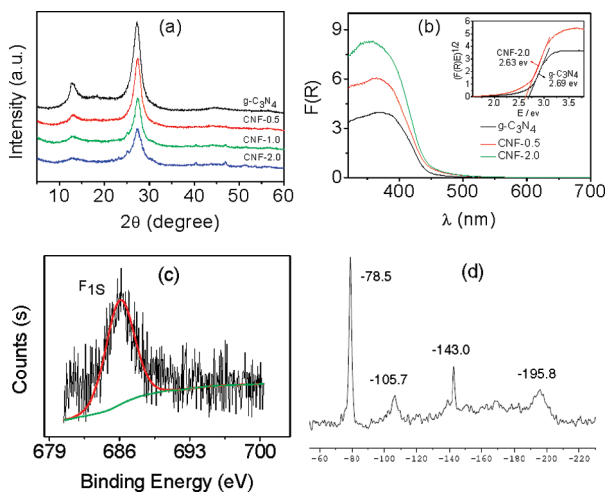
Figure 1. (a) XRD patterns; (b) UV−vis spectrum of g-C_3N_4 and CNF-x and (b, inset) optical band gap (E_g) of g-C_3N_4 and CNF-2.0; (c) XPS spectra of CNF-2.0; and (d) ^{19}F solid-state MAS NMR spectra of CNF-2.0.

Figure 2. Photocatalytic activity of Pt/CNF for the hydrogen evolution reaction with visible light ($\lambda > 420$).

functionality. The XRD peak at 13° corresponding to in-plane ordering of tri-s-triazine units which form 1D melon strands also slowly vanished with increasing amount of NH_4F. Because of the electronegativity of fluorine and nitrogen, the doped fluorine is most certainly not bound to the nitrogen, but to the carbon, resulting in a partial conversion of C-sp^2 to C-sp^3, which may lead to lower in plane order of the material (see Figure S1 in the Supporting Information).

The carbon and nitrogen stoichiometry determined by elemental analysis (Table S1) shows that the products are very close to the ideal value of C_3N_4 (theoretical C/N is 0.75). Both XPS and FTIR results indicate that fluorine atoms had been doped in the CN matrix as C−F. The XPS peak at 686.2 eV can indeed be assigned to the fluorine attached to carbon (Figure 1, c),[25] and the fluorine concentration is of ∼3 at % (i.e., a tentative sum formula of the structure is $C_3N_{4.2}F_{0.26}H_{1.6}$). In the FTIR spectra (see the Supporting Information, Figure S2), the fluorinated materials exhibit a new band at 1220 cm^{-1} compared with the unmodified parental material, which can be attributed to the stretching mode of C−F bond.[26] FTIR also features the typical C−N heterocycle stretches in the 1200−1600 cm^{-1} and the breathing mode of the tri-s-triazine units at 800 cm^{-1}, as the unmodified g-C_3N_4, which supports the formation of extended network of C−N−C bonds. A band at 2160 ($\nu_{C\equiv N}$) was also observed in CNF-x, which indicates the partly imperfect polymerization after introducing of NH_4F.

Solid-state MAS NMR investigation on the ^{19}F shows four well-resolved signals between −60 and −220 ppm, which correspond to four different positions in the framework structure (see Figure S1 in the Supporting Information). Thus the fluorine heteroatoms most probably connected to the corner or bay carbon forming C−F
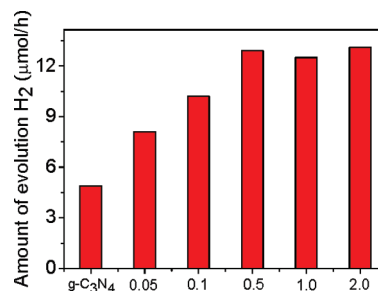
bonding in the modified C_3N_4 framework, which has four positions, considering neighbor effects to the next layers (ABA stacking).

To gain a better understanding of the variation of the electronic structure with the incorporation of F into the C/N scaffold, DFT calculations have been done using model unit. Indeed, the fluorination essentially adjusted the HOMO and LUMO positions of uncodensed form (see Figures S1 and S3 in the Supporting Information). It is worth noticing that the incorporation of F at the bay carbon shifts both the LUMO and HOMO to higher energy values. However, incorporation of F at the corner carbon shifts the LUMO to higher energy and the HOMO to lower energy values (see Figure S3 in the Supporting Information). The HOMO and LUMO orbitals in an extended system are defined as the conduction band and the valence band, therefore, this remarkable LUMO and HOMO energy changes brought by fluorine doping are expected to modify the redox properties and promote heterogeneous photocatlysis.

UV−vis spectrum (Figure 1b) indicate that the optical band gap and thereby the semiconductor properties of the CNF materials have indeed slightly been changed, with an extension of the spectrum toward absorption in the visible range. The fluorine doping gives rise to a decrease in band gap from 2.69 eV of g-C_3N_4 to 2.63 eV of CNF-2.0 (as estimated from the UV−vis spectrum). The red shift of UV−vis spectrum indicated that fluorination is different from protonation in which the spectrum was blue-shifted,[27] which supports our view that fluorine is not bound as a counterion F$^-$ but indeed doped into the C−N matrix.

It is interesting to follow how the fluorination influences the photochemical properties. Figure 2 shows the photocatalytic activity of CNF-x samples toward hydrogen evolution from water/triethanolamine mixture with visible light ($\lambda > 420$) and Pt (3 wt %) as a cocatalyst. Indeed, the CNF-x samples show an improvement in H_2 evolution activity over g-C_3N_4. For example, the H_2 evolution on CNF-0.5 was about 2.7 times higher than that of unmodified, polymeric g-C_3N_4.

To further investigate the photocatalytic acitivity, we then employed CNF-x as a metal free catalysts in direct oxidation of benzene to phenol under mild conditions

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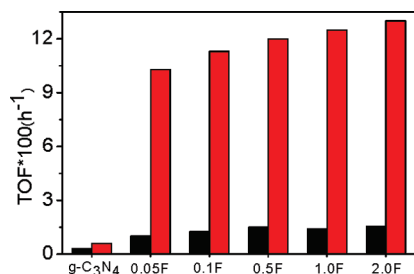
Figure 3. Catalytic oxidation of benzene using CNF-x. TOF: turnover frequency, n(phenol) per n(melem units) per hour. Black column, without illumination; red column, illumination with visible light, $\lambda > 420$. For reaction conditions, see the Supporting Information.

(60 °C, using H_2O_2 as a clean oxidant). Figure 3 indicates turnover frequency of the reaction increases with increasing fluorine content. With $g\text{-}C_3N_4$ as catalyst, phenol was formed under visible light irradiation ($\lambda > 420$) with a very low turnover frequency (TOF = 0.006 h^{-1}), which can be enhanced to TOF = 0.125 h^{-1} using CNF-2.0 as photocatalyst, and there was no detectable side product according to GC-MS in both cases. Modification with fluorine therefore greatly enhanced the catalytic/photocatalytic activity of the system for the oxidation of benzene to phenol.

In addition, the catalysts can easily be separated from the reaction solution by simple filtration. They are highly stable and can be reused for several cycles without losing of activity (see Figures S7 and S8 in the Supporting Information), which is a prerequisite for practical applications. Furthermore, CNF-x was also found to be capable of oxidizing other hydrocarbons, such as toluene and cyclohexane, with excellent selectivity toward aldehyde and ketone. Work focused on more detailed photocatalytic oxidation studies of CNF material is ongoing.

In conclusion, we have shown here a simple fluorination route of polymeric carbon nitrides, using ammonium fluoride as a cheap fluorine source. Fluorination not only provides a modified texture but also enables the effective adjustment of the electronic band gaps to a given problem, which was demonstrated by improved activities both for the photocatalytic hydrogen production from water/TEA and oxidization of benzene to phenol under visible light. We anticipate a wide range of potential applications of CNF in photochemistry in general.

Supporting Information Available: Experimental details and more characterization results (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.