

ChemSusChem

Chemistry-Sustainability-Energy-Materials



European Chemical Societies Publishing



Accepted Article

Title: Mesoporous P- and F-co-doped Amorphous Carbon Nitride: Nanocatalysts for Photocatalytic CO2 Reduction and Thermocatalytic Furanics Synthesis from Sugars

Authors: Subodh Kumar, Manoj B. Gawande, Josef Kopp, Štěpán Kment, Rajender S. Varma, and Radek Zboril

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemSusChem 10.1002/cssc.202001172

Link to VoR: https://doi.org/10.1002/cssc.202001172



RESEARCH ARTICLE

P- and F-co-doped Carbon Nitride Nanocatalysts for Photocatalytic CO₂ Reduction and Thermocatalytic Furanics Synthesis from Sugars

Subodh Kumar,^[a] Manoj B. Gawande,^{*[a, b]} Josef Kopp,^[a] Stepan Kment,^[a] Rajender S. Varma,^[a] and Radek Zbořil^{*[a]}

 [a] Dr. S. Kumar, Dr. M. B. Gawande, Josef Kopp, Prof. R. S. Varma, Prof. R. Zbořil Regional Centre of Advanced Technologies and Materials, Palacký University Olomouc Šlechtitelů 27, 783 71 Olomouc, Czech Republic E-mail: manoj.gawande@upol.cz; <u>radek.zboril@upol.cz</u>
 [b] Prof. Manoj B. Gawande

Institute of Chemical Technology, Mumbai-Marathwada Campus Jalna, Maharashtra 431213, India. Supporting information for this article is given via a link at the end of the document.

Abstract: A novel P- and F-co-doped amorphous carbon nitride (PFCN) has been synthesized via sol-gel mediated thermal condensation of dicyandiamide. Such synthesized P- and F-doped carbon nitride displayed a well-defined mesoporous nanostructure and enhanced visible light absorption region up to infrared with higher BET surface area of 260.93 m² g⁻¹; the highest recorded value for phosphorus doped carbon nitride materials. Moreover, the formation mechanism is delineated and the role of templates was found to be essential not only in enhancing the surface area but also in facilitating the co-doping of P and F atoms. Co-doping helped to narrow the optical band gap to 1.8 eV, thus enabling an excellent photocatalytic activity for the aqueous reduction of carbon dioxide into methanol under visible light irradiation, which is fifteen times higher (119.56 µmol g⁻¹ h⁻¹) than the bare carbon nitride. P doping introduced the Brønsted acidity into the material, turning it into an acid-base bifunctional catalyst. Consequently, the material was also investigated for the thermal conversion of common carbohydrates into furanics.

Introduction

Graphitic carbon nitride, a layered polymeric semiconductor material, is a suitable catalyst candidate due to its advantageous features including abundance, nontoxicity, stability, and chemical tenability.^[1] It is generally prepared by thermal condensation of nitrogen-rich precursors encompassing C-N bonded building blocks such as melamine, urea and dicyandiamide under inert or air atmosphere. However, the degree of condensation, surface properties and the yield of the final material vary with the precursor and conditions deployed. Carbon nitrides have shown promising applications in many fields including catalysis (thermal, photo-, and electrophotocatalysis).^[2] However, pristine g-C₃N₄ still suffers from its restricted visible-light harvesting capacity, ready recombination of charge carriers, and very low surface area, which is prerequisite for the efficient catalysis.^[3] In order to develop the carbon nitride material with extended visible light absorption and higher surface area, various modification

approaches, such as doping,^[4] exfoliation,^[5] templating,^[6] and homogeneous amorphization,^[7] have been implemented, although homogeneous amorphization appears to be the most effective. Although these results are important with respect to designing a material with defects to lower the band gap, they do not provide high surface area. Moreover, extended visible light absorption beyond 500 nm does not contribute to the photocatalytic activity of the material.^[8] Hence, in order to exploit the extended light absorption, it is necessary to create the midgap energy states by heteroatom doping,^[9] which is also important for the thermal catalysis, as carbon nitride has been exploited as a basic catalyst^[2a,6,10] or support^[11] owing to nitrogen framework in the polymeric carbon nanostructure. Therefore, in order to explore the catalytic activity (photo and thermal), suitable chemical doping (metal and nonmetal) is one of the effective strategies to manipulate electronic and chemical nature of the catalyst and concomitantly generating high surface area of the material. Until now, various heteroatom-doped carbon nitrides have been synthesized in diverse morphological forms via many techniques; ^[2b,4,12] every dopant bestows some typical characteristic properties on the material. For instance, phosphorus doping not only provides the reduction in band gap but also imparts the acidity to carbon nitride, turning it into a metal-free acid-base bifunctional catalyst.^[13] On the other hand, fluorine doping can improve the optical absorption (band gap reduction) and photocatalytic activity by facilitating the migration and separation of photogenerated charge carriers.^[14] We envisioned that codoping may be a promising approach and this unique combination of P- and F-co-doped carbon nitride with high surface area could generate an exceptionally good thermal as well as a photocatalyst. Interestingly, despite the reports on co-doped carbon nitrides with assorted combinations (B/F, B/S, P/O, S/O, and P/S),^[15] to the best of our knowledge, there is no report available on the powder synthesis of P- and F-co-doped amorphous carbon nitride until now. Zhang et al. synthesized the P-doped analogue using the same precursor (BmimPF₆) which lacked F doping.^[16]

The growing demand for energy and continuous depletion in fossil fuel reserves insinuate an urgent need to substitute the

RESEARCH ARTICLE

petroleum-based feedstock with renewable resources of energy, the major renewable energy resources being biomass, hydropower, geothermal, wind, and solar. Moreover, abundant carbon dioxide, a greenhouse gas with climate change implications, is a safe and inexpensive C₁ source that needs to be viewed as an inexhaustible renewable resource. Amongst these, biomass and carbon dioxide can exclusively generate liquid fuels and chemicals, thus offering a potential substitute for fossil fuels. In this context, methanol and furanic compounds (5-hydroxymethyl-2-furaldehyde (HMF) and furfural) are quite important and can be produced photochemically and thermally from the carbon dioxide and carbohydrates (glucose/fructose and xylose), respectively.^[17]

We report here, for the first time, a novel synthetic protocol that provides P-, F-co-doped mesoporous carbon nitride (PFCN) with high surface area and lower band gap. Inspired by its extended visible light absorption and acid-base bi-functional nature, we explored this new class of catalyst for the aqueous photocatalytic reduction of CO₂ into methanol and conducted thermal catalytic conversion of carbohydrates (glucose and xylose) into high-value furanics compounds (HMF and furfural). dicyandiamide might have also weakened the in-plane hydrogen bonding between the strands of polymeric melon units during calcination, imparting amorphous nature to the final material. These results highlight the significant role of the templates used to produce a material with distinctive textural properties. The above-mentioned outcomes indicate that using



Scheme 1. Stepwise synthesis of porous phosphorus- and fluorine-co-doped carbon nitride.

Results and Discussion

High surface area P- and F-co-doped carbon nitride (PFCN) was synthesized with enhanced optical absorption via a simple thermal condensation of dicyandiamide and 1-butyl-3methylimidazolium hexafluorophosphate (BmimPF₆) in presence of hexadecyltrimethylammonium bromide (CTAB) and tetraethyl orthosilicate (TEOS) at 550 °C. Templates roles were investigated by the controlled polycondensation of dicyandiamide and BmimPF₆ using CTAB, TEOS, CTAB+TEOS, and in the absence of templates to synthetize PCN-C, PCN-T, PFCN, and PCN, respectively. under the same reaction conditions. Thermogravimetric analysis (TGA) was used to monitor the progress (Figure S1). In addition, poly-condensation of pure dicyandiamide and decomposition of CTAB and TEOS were also recorded. CTAB template seemed to enhance the polycondensation of dicyandiamide and BmimPF₆ mixture (PCN-C) and lose more weight at the same temperature. It might be because of the ion exchange^[18] between CTAB and BmimPF₆, which leads to the formation of less thermally stable [Bmim]Brspecies^[19] during the micelle formation. These micelles thermally decompose into hydrocarbons and other volatile intermediates, thus allowing to generate pores to produce mesoporous carbon nitride. However, the PCN-C sample showed comparatively low surface area and no fluorine doping (Table S1 and S2). It might be because of the higher decomposition temperature of dicyandiamide than micelles; consequently, the pores generated were occupied with uncondensed dicyandiamide. However, in case of the PFCN sample, the TEOS polymerized around the micelles during the sol-gel process becomes transformed into silica matrix on thermal treatment. The silica matrix not only prevents the structural pores to collapse but concurrently traps the PF₆ species to react with amino groups of uncondensed carbon nitride precursor to join the C-N framework; the removal of the silica template by subsequent washing with ammonium fluoride solution generates the silica-free, P-, F-co-doped materials with high surface area (Scheme 1). Moreover, the micelles surrounded by the TEOS throughout the matrix of

the combination of TEOS and CTAB templates successfully leads to co-doping of P and F and higher surface area with a significant change in the matrix network of PFCN.

SEM and TEM images of PFCN revealed a rough, agglomerated and crumpled structure with 3-20 nm pores on its surface indicating that the multilayered sheets are mesoporous in nature (Figure 1a; Figure S2a-c). The HR-TEM image displays the interpenetrating carbon nitride networks with long-range disorder suggesting amorphous nature of the material (Figure 1b; Figure S2d), which is further confirmed by the SAED pattern (Figure S2e). However, local ordering with lateral dimension of 1 to 3 nm and lattice spacing of 3-5 A° can also be seen along with the curly ribbons. EDX spectra and corresponding HAADF images of PFCN confirmed the presence of carbon, nitrogen, phosphorus, and fluorine elements and their uniform distribution all over the surface (Figure 1c-f; Figure S2f and S3). Carbon nitride has less folded nanosheets with comparatively smooth surface, which clearly indicates that phosphorus doping changes the structural features of the material while different templates are used (Figure S4a).



RESEARCH ARTICLE

Figure 1. a) TEM image; b) HR-TEM image; c) HAADF image; and d–f) STEM elemental mapping images of PFCN.

FT-IR spectroscopy ascertained the functional groups present in the synthesized material (Figure S5a). A peak at 807 cm⁻¹ as well as a series of vibrations ranging between 1200 and 1650 cm⁻¹ were observed in the spectrum of the material, which can be attributed to the characteristic bending vibration of tri-s-triazine units and stretching vibrations of C-N heterocycles of dicyandiamide, respectively.^[20] Compared to the CN sample, PFCN shows no obvious change in the peak position but the merging of peaks presumably indicates the overlapping stretching vibrations corresponding to C=C and C-F. Moreover, there are two new peaks of P-related group at 950 and 1055 cm⁻¹ which can be assigned to P-N stretching mode and P=O, respectively that appears exclusively for the PFCN sample, pointing to the high P doping.[21] In addition, broadening of the band in the range of 3200-3500 cm⁻¹ indicates the presence of absorbed water molecule and uncondensed/free N-H stretching of the amine groups.

The BET analysis was executed to learn about the textural properties of the synthesized material, and the N2 adsorptiondesorption isotherms with pore size distribution (Figure 2a). The synthesized material showed a type IV nitrogen adsorptiondesorption isotherm with a H3-shaped hysteresis loop signifying the well-defined mesoporous nanostructure with slit-like pores, derived from the overlapping and stacking of nanosheets. N₂ absorption at low pressure is related to the filling of micropores indicating the presence of a very weak microporosity. However, the contribution of micropore surface area to the total surface area is found to be zero, calculated by the T-plot method. The isotherm of PFCN presents high absorption at a high relative pressure (P/P₀), which suggests the existence of large mesopores. Furthermore, the above-mentioned observations are also supported by the respective pore size distribution results, which may be due to the random pore formation induced by the decomposition of CTAB and subsequent removal of silica template; a very broad pore size distribution in the 3-30 nm region is observed (Figure S5b). These results are in agreement with the TEM results and confirm the purely mesoporous nature of the material. PFCN showed higher surface area of 260.93 m² g⁻¹ which is the highest value, reported so far for phosphorus- and fluorine-doped carbon nitride materials.

Deviations in the crystal structure and phase of the synthesized materials (CN and PFCN) were revealed by the XRD technique (Figure 2b). CN exhibited mainly two reflections at 15.23° and 31.9°, while the PFCN sample showed only one broad reflection at around 31.4°. The reflections at 20 value of 15.23° and 31.9° correspond to the [100] and [002] graphitic planes arising from the in-plane structural packing motif of the heptazine units and interlayer stacking of conjugated aromatic systems, respectively. The disappearance and broadening of the peaks at 15.23° and 31.4°, respectively, in PFCN indicate a change in the graphitic structure or absence of a long-range order in the atomic arrangements of the materials after doping.[7a] In comparison to CN, using the combination of CTAB and TEOS templates to synthetize the PFCN sample leads to the shift in [002] reflection towards lower 20 value, indicating an increase in the interlayer distance after P doping, which is attributed to the larger radius of the doped P atom (100 pm) than that of the replaced C atom (70 pm).[9]

In addition to XRD, Raman spectra were obtained to recognize the templates-dependent structural changes in the skeleton of carbon nitride after doping with P and F; mainly, two bands appeared at around 1329 cm⁻¹ (the D band) and 1611 cm⁻¹ (the G band) for the synthesized material (Figure S5c). The shape, position, and relative intensity of these D and G bands (I_D/I_G) are used to estimate the structural changes including surface disorder. However, weak intensity of the G bands in the Raman spectrum of PFCN compared to the native carbon nitride alone suggests that the use of templates significantly altered the structural arrangement in the form of defects, thus increasing the I_D/I_G ratio from 1.35 to 1.44 for CN and PFCN, respectively. CN and PFCN show nitrogen-doped carbon-type Raman spectra with 2D bands, which suggests a multilayer structure. Moreover, broadening of peaks indicates an increase in the amorphous nature of the material.

The main objective of XPS analysis is to interpret the atomic concentration and chemical interactions of C. O. N. P. and F atoms in the synthesized materials (CN and PFCN). A survey scan of CN showed mainly three peaks centered at 288.31, 398.65, and 531.72 eV corresponding to C1s, N1s, and O1s, respectively. The appearance of two new peaks in PFCN centered at 133.51 and 686.31 eV. corresponding to P2p and F1s atom, confirms that phosphorus and fluorine doping was successful (Figure S5d); notably, fluorine doping along with the P has been elusive in previous reports even using the same precursor. This may be because of the lack of reaction between fluorine species with the melem unit in view of the higher decomposition temperature of BmimPF₆ ionic liquids. The removal of PF6 at higher temperature presumably leads to no doping of F. In our case, BmimPF₆ could have taken part in the micelles formation with CTAB and generated less thermally stable [Bmim]Br species; the formed micelles are further surrounded by the silica due to the polymerization of TEOS during sol-gel reaction, thus limiting the escape of fluorine species unreacted. In order to study the bonding states of P and F atoms, highresolution C1s, N1s, O1s, F1s, and P2p XPS spectra were recorded and de-convoluted (Figure 2c,d; Figure S6a-f).



Figure 2. a) N_2 Abs-Desorption isotherm with pore size distribution; b) XRD spectrum; c) P2p; d) F1s XPS spectra of PFCN.

RESEARCH ARTICLE

The high-resolution C1s spectrum of PFCN sample mainly revealed two wide peaks attributed to different types of chemical interaction of carbon. These peaks can be further deconvoluted into six associate peaks at 284.76, 285.89, 286.44, 287.34, 288.73, and 289.40 eV, corresponding to the C-C/C=C, C-CF, C-O/C-N, N-C=N, C-F, and O=C-O functional groups, respectively. An actual indication of fluorine doping of carbon nitride was deduced by the presence of one peak with shoulder in F1s core level spectra, which on deconvolution splits into three peaks centered at 686.16, 687.13, and 688.41 eV. The first peak represents the semi-ionic C-F, while the other two peaks represent the covalently bound fluorine to carbon (C-F_X). It is worth mentioning here that the intensity of the peak attributable to C-C/C=C in high-resolution C1s XPS spectrum of CN is very low, while in the PFCN samples is higher, demonstrating a significant increase in the conjugation forming C=C bonds. This may possibly be due to the carbonizing of templates.[22] Moreover, appearance of a new peak at 399.69 eV in N1s XPS spectrum



Figure 3. Solid-state NMR spectra of PFCN sample. a) ³¹P CPMAS; b) ¹⁹F; c) ¹H nuclei and d) ¹H-³¹P heteronuclear correlation (HETCOR) 2D NMR.

suggests the formation of N-P bonds in the PFCN sample after doping. We identified only one strong broad peak at 133.42 eV position in P2p spectrum, which represents N=P-N bonds formation and can be deconvoluted into two signals, assigned to two different chemical environments of phosphorus atom in N=P-N. The peaks positioned at 133.29 and 134.42 eV represent the phosphorus atom forming phosphonic acid moiety (P-OH) and phosphates (P=O), respectively. Additional evidence for this comes from the O1s XPS spectrum; it displays a broad peak with a shoulder, which can be deconvoluted into five different peaks. Peaks at 530.87, 532.09, and 534.1 eV are due to the absorbed oxygen, -N-C-O, and absorbed water, respectively. The additional two peaks at 530.31 and 533.08 eV represent the O=P and HO- P, respectively. It is important to note that no peak for C-P bond is observed in neither P2p nor C1s high-resolution, indicating that P replaced the carbon in carbon-nitride skeleton forming P-N bond. However, the marginal shifting in the peak positions in PFCN spectra is due to the doping. Based on the compositional information of C, O, N, P, and F, we observed P and F doping level at 4.3 and 1.4 atom % for PFCN (Table S2).

Furthermore, solid-state magic angle spinning nuclear magnetic resonance (MASNMR) analyses were performed to confirm the chemical environment of the elements in the synthesized material network. ¹³C, ¹⁵N, ³¹P, ¹⁹F, and ¹H MAS and CPMAS NMR spectra of PFCN material are shown in Figure 3 and Figure S7. ¹³C CPMASNMR displays four peaks that suggest the presence of four types of carbon (Figure S7a). The peaks at 160.0 (C₃) and 168.1 (C₄) ppm are the characteristic peaks for carbon atoms in carbon nitrides due to the C-NH₂ or C-NH- bond.^[23] A peak with very low intensity at 98.0 (C₁) ppm occurs due to the fluorine doping, confirming the F-C covalent bonding and a little shoulder at 148.9 (C₂) ppm corresponds to the graphitic carbon.

Additionally, ¹⁹F spectrum shows a wide peak at -147.6 ppm, which corresponds to the C-F units, excluding the probability of absorbed fluorine. Moreover, ¹⁵N CPMAS spectrum exhibits five peaks between 0-300 ppm, which correspond to five different types of nitrogen environments. The peaks at 97.25, 135.14, 153.08, and 204.98 ppm are assigned to the -NH₂, -NH-, N-C₃, and -N=C groups, respectively, and are consistent with the existing reports.^[23] However, a new peak arises at 48.54 ppm, which could be assigned to N-P bond. ³¹P CPMASNMR spectrum further confirms the successful phosphorus doping displaying two intense peaks at -3.63 and 6.40 ppm, indicating that there are possibly two types of P doping (P-OH and P=O) in the final material.^[13] We presume that all the doped P atoms replace the corner and bay C atoms during the polymerization of carbon nitride skeleton. Significantly, ¹H MASNMR evidence the actual association of protons with the respective nuclei; ¹H MASNMR spectrum clearly shows four peaks at 4.1, 5.9, 8.8, and 11.3 ppm represented as H₁, H₂, H₃, and H₄, respectively (Figure 3c). The peaks at 4.1 and 5.9 ppm correspond to the proton associated without hydrogen-bonded -NH₂ and -NH- groups, respectively, while an intense broad peak at 8.83 ppm indicates proton associated with the hydrogen-bonded -NH2 groups. A new peak at 11.38 ppm could be assigned to the acidic proton (P-OH). In order to support our assignment, we also performed ¹H-³¹P heteronuclear correlation (HETCOR) 2D MASNMR (Figure 3d). There is a clear cross peak between P₂ peak of ³¹P and H₄ peak of ¹H nuclei, suggesting the presence of phosphorus in the form of P-OH. However, no cross peak was observed for the peak P1, which indicates deprotonated phosphorus probably in the form of P=O. Moreover, the existence of characteristic peaks in the ¹³C and ¹⁵N solid-state NMR confirms that the melem unit structure remained intact after the phosphorus doping.

Optical properties of PFCN were studied by the UV-Vis diffuse reflectance (DRS) spectra as shown in Figure 4a. Based on the spectra, the band gaps of the samples were acquired from the transformed Kubelka–Munk equation (Figure S8a): $[F(R)\cdot hv]^2 = A(hv - Eg)$, where $F(R) = \alpha = (1 - R)^2/2R$, R is the percentage of reflected light, hv is the incident photon energy, Eg is the band gap energy and A is constant (value depends on the transition probability).^[24] In contrast to CN, PFCN shows a red shift in the absorption edge, which suggests the narrowing band gap. In fact, the co-doping narrows the band gap of PFCN to 1.83 eV

RESEARCH ARTICLE

compared with CN (2.83 eV), enhancing the light-harvesting capability of PFCN in the visible-light region (700 nm > λ > 420 nm). However, PFCN displays a very strong tail absorption in the visible-light region; the tail, also known as Urbach tail, appeared due to the photoexcitation from the valence band (VB) to the midgap electronic states. In other words, the photogenerated electron can easily jump from the VB to the midgap state or from the midgap states to the conduction band (CB). These midgap states are generated as a result of P doping by the hybridization of C 2s2p, N 2s2p and P 3s3p and appear below the conduction band (CB) of PFCN (Figure 4d). In order to recognize the narrowing of bandgap for PFCN material, XPS valence band spectra of CN and PFCN were studied and the position of valence bands were determined by extrapolating the edges of spectra (Figure 4b, c). CN and PFCN showed band tail with its end at 1.72 and 1.47 eV respectively, which are higher than their respective dominant edges value. This could be due to the amorphous nature and presence of dangling bonds.^[7a] These values imply that CB edge is shifted towards VB by 0.75 eV and VB shifts towards the CB by 0.25 eV, thus narrowing the band gap by 1.0 eV. In order to reveal the position of middap states in the band gap, the transition energy (Et) from VB to the midgap states for PFCN was calculated to be 1.52 eV by the Kubelk-Munk method (Figure S8a).^[25] The exact position of midgap states for PFCN was determined to be at -0.05 V vs. NHE, which is higher than the [2H+/H₂ (0.0 V), CO₂/CH₃OH (0.03V) and H₂O/O₂ (1.23 V)] and thus still satisfying the thermodynamic requirements (Figure 4d).



Figure 4. a) UV-vis spectra; b) and c) valence band XPS spectra; d) Band alignments of CN and PFCN.

This result encouraged us to test its photocatalytic prowess for the reduction of carbon dioxide under visible light irradiation at room temperature using blue LED light source (Kessil 150N, 34W) with the light density of 22 mW/cm². Initially, glass tube was charged with water (20 mL), PFCN (100 mg) and then carbon dioxide was purged for 30 min in the mixture with continuous stirring. The tube was then sealed, connected with a carbon dioxide balloon through the needle and exposed to the light

source for 24 h. The highest methanol yield obtained was 119.56 µmol h⁻¹g⁻¹, which was higher in comparison with previously reported heteroatom doped and undoped carbon nitride catalyzed photoreduction of CO₂ to methanol.^[26] There are two possible reasons for PFCN's higher photocatalytic activity: lower band gap and more existing defects in the structure.^[27] Lower band gap corresponds to broadened light response, so that electrons could be generated upon irradiation. Incorporation of F in the C₃N₄ network can modify its electronic structure by converting C sp² to C sp³ hybridization thus narrowing the band gap.^[14] Moreover, F atom has lone-pair electrons and C₃N₄ has a large π-conjugated system. The incorporation of F into the C/N scaffold could promote the formation of $p-\pi$ conjugation, which might increases the charge density on the HOMO thus reducing the photocarrier transfer barrier^[28] and enabling the enhanced photocatalytic activity of PFCN for the aqueous reduction of CO₂ to methanol. On the other hand, defects (structural and chemical) facilitate the charge separation. For this, photoluminescence (PL) emission analyses of PFCN and CN samples were performed under an excitation wavelength of 390 nm to study the recombination of photogenerated charge carriers. Evidently, there is no peak for PFCN unlike the CN sample at 440 nm (Figure S8b) in the PL spectrum, which indicates inhibition of charge carrier recombination due to their trapping in the defects associated with long-range disorder.^[7a] Moreover, midgap states generated on P doping also act as an electron reservoir to trap the unstable electrons thus inhibiting the direct recombination of electron-holes and providing a shorter path length for electron excitation to the CB; the electrons residing at the midgap states are known to have a prolonged lifetime as compared to free excitons.[28b,29] Consequently, PFCN can provide more charge carriers for the photocatalytic reduction of CO₂ in comparison with CN. PFCN absorbed the visible light efficiently and generated electron (e⁻) and holes pair (h⁺). Holes oxidize the water molecules to give protons (H⁺) and hydroxide radicals (OH). The hydroxide radicals react further with water molecules to produce oxygen (O₂) and protons. These protons and CO2 adsorbed on the catalyst surface was then reduced to methanol by photo-generated electrons. Shifting the conduction band towards redox potential of CO₂/CH₃OH limits the formation of liquid side products such as HCOOH and HCHO. We believe that these studies will help to design other possible catalysts for the photocatalytic applications in the future.

Since PFCN catalyst contains Brønsted acid sites as revealed by the XPS and ¹H SSNMR analysis, we further explored this new class of catalyst for the thermal catalytic conversion of sugars (glucose and xylose) into high-value furanic compounds (HMF and furfural). In a typical experiment, glucose or xylose (0.2 mmol) and PFCN catalyst (50 mg) were put into water/THF mixture (3.0 mL) and the resulting mixture was heated at 130 °C in a sealed pressure reactor under nitrogen atmosphere for 5 h. The highest yields of the HMF and furfural under above conditions were found to be 68 and 91%, respectively (Scheme 2). As suggested in the literature,^[30] the presence of both acidic and basic sites facilitates the conversion of carbohydrates into the furanics. Lewis bases are particularly important for the isomerization step, whereas Brønsted acidity is required for the dehydration step, which could be the reason for enhancement of the reaction rate. In analogy with the existing reports, we assume that the reaction probably involves the isomerization of glucose and xylose to fructose and xylose, followed by their dehydration to HMF and furfural,

RESEARCH ARTICLE

respectively. Furthermore, to ascertain the acidity generation on phosphorus doping, we determined the total acid content of the PFCN material by titration,^[31] which is found to be 931 μ mol g⁻¹ (see associated text in Supporting Information).



Scheme 2. PFCN-catalyzed synthesis of furanics.

Recycling of the catalyst is a critical step toward developing a greener and sustainable catalytic system for chemical transformations. After completion of the respective substrate reaction, the catalyst was separated by filtration, washed with water, ethanol and dried at 80 °C. The recovered catalyst was then regenerated by stirring in 1M HCl solution followed by heating at 400 °C for one hour before next run. The recovered catalyst was reused for five subsequent runs. In all experiments, the yield of the products remained almost the same, indicating that the developed catalyst can be recycled efficiently without significant loss in catalytic activity. Moreover, the spent catalyst was also analyzed by TEM and FT-IR to see any possible morphological changes and functionality of the catalysts (Figure S9); barely any noticeable change was discerned in peak features, indicating that the catalyst is quite stable and truly heterogeneous in nature during the reaction. The comparison of textural and electronic properties, catalytic activity of dual template-assisted synthesized PFCN material with the earlier documented methods is shown in Tables S3 and S4, Supporting Information.

Conclusion

We have synthesized P- and F-co-doped porous carbon nitride (PFCN) with enhanced visible light absorption and surface area using dicyandiamide, BmimPF₆⁻ ionic liquid taking CTAB and TEOS as templates via sol-gel mediated thermal condensation process. The presence of both soft and hard templates not only resulted in the high surface area of 260.93 m² g⁻¹ but also revealed unprecedented results for the P, F co-doping. High surface area and co-doping results in higher activity of the material towards visible light photoreduction of carbon dioxide into methanol. The activity of the nanocatalyst was found to be impeccable compared to most of the documented protocols with the added advantage that it could also be used as a thermal catalyst for the conversion of glucose and xylose into HMF and furfural, respectively. The high activity of the catalyst is due to its high surface area as well as the presence of Lewis base (nitrogen in carbon nitride) and Brønsted acid (doped phosphorus). Notably, this bi-functional catalyst described herein provides clear advantages in terms of environmental impact due to no use of metal and other additives, which bodes well for its adoption in industrial processes. The obtained results are important for

improvement of sustainable protocols for fine chemicals from biobased resources, particularly for large-scale reactions.

Acknowledgements

The authors gratefully acknowledge the support by the Operational Program Research, Development and Education -European Regional Development Fund, project no. CZ.02.1.01/0.0/0.0/15_003/0000416 of the Ministry of Education, Youth and Sports of the Czech Republic. The authors thank to Dr. V. Ranc for Raman analysis, Ms. J. Stráská and Ms. P. Bazgerová for SEM/TEM analysis, Dr. Juri Ugolotti and Mr. I. Popa for solidstate NMR analysis, and Dr. S. Kalytchuk for PL analysis. The authors also thank Mr. O. Tomanec and Mr. M. Petr for HRTEMmapping data and HR-XPS elemental measurements. respectively.

Keywords: Amorphous carbon nitride • Bi-functional catalysts • Biomass upgradation • P- and F-co-doping • Photocatalytic reduction of carbon dioxide

- a) W. Iqbal, B. Yang, X. Zhao, M. Rauf, M. Waqas, Y. Gong, J. Zhang, Y. Mao, *Catal. Sci. Technol.* **2018**, *8*, 4576-4599; b) A. Thomas, A. Fischer, F. Goettmann, M. Antonietti, J.-O. Müller, R. Schlögl, J. M. Carlsson, *J. Mater. Chem.* **2008**, *18*, 4893-4908.
- [2] a) Y. Gong, M. Li, H. Li, Y. Wang, *Green Chem.* 2015, *17*, 715-736; b)
 W.-J. Ong, L.-L. Tan, Y. H. Ng, S.-T. Yong, S.-P. Chai, *Chem. Rev.* 2016, *116*, 7159-7329; c) J. Liu, H. Wang, M. Antonietti, *Chem. Soc. Rev.* 2016, *45*, 2308-2326; d) L. Zhou, H. Zhang, H. Sun, S. Liu, M. O. Tade, S. Wang, W. Jin, *Catal. Sci. Technol.* 2016, *6*, 7002-7023; e) N. Mansor, T. S. Miller, I. Dedigama, A. B. Jorge, J. Jia, V. Brázdová, C. Mattevi, C. Gibbs, D. Hodgson, P. R. Shearing, *Electrochim. Acta* 2016, *222*, 44-57; f) A. Wang, C. Wang, L. Fu, W. Wong-Ng, Y. Lan, *Nano-micro lett.* 2017, *9*, 47; g) F. K. Kessler, Y. Zheng, D. Schwarz, C. Merschjann, W. Schnick, X. Wang, M. J. Bojdys, *Nature Rev. Mater.* 2017, *2*, 17030; h) S. Cao, J. Low, J. Yu, M. Jaroniec, *Adv. Mater.* 2015, *27*, 2150–2176.
- [3] a) J. Zhu, P. Xiao, H. Li, S. A. Carabineiro, ACS Appl. Mater. Inter. 2014, 6, 16449-16465; bS. Cao, J. Low, J. Yu, M. Jaroniec, Adv. Mater. 2015, 27, 2150-2176.
- [4] L. Jiang, X. Yuan, Y. Pan, J. Liang, G. Zeng, Z. Wu, H. Wang, Appl. Cata. B. Environ. 2017, 217, 388-406.
- [5] a) H. Xu, J. Yan, X. She, L. Xu, J. Xia, Y. Xu, Y. Song, L. Huang, H. Li, *Nanoscale* **2014**, *6*, 1406-1415; b) X. She, H. Xu, Y. Xu, J. Yan, J. Xia, L. Xu, Y. Song, Y. Jiang, Q. Zhang, H. Li, *J. Mater. Chem. A* **2014**, *2*, 2563-2570.
- [6] K. S. Lakhi, D.-H. Park, K. Al-Bahily, W. Cha, B. Viswanathan, J.-H. Choy, A. Vinu, *Chem. Soc. Rev.* 2017, 46, 72-101.
- a) Y. Kang, Y. Yang, L. C. Yin, X. Kang, G. Liu, H. M. Cheng, *Adv. Mater.* 2015, *27*, 4572-4577; b) M. Z. Rahman, P. C. Tapping, T. W. Kee, R. Smernik, N. Spooner, J. Moffatt, Y. Tang, K. Davey, S. Z. Qiao, *Adv. Funct. Mater.* 2017, *27*, 1702384.
- [8] A. B. Jorge, D. J. Martin, M. T. Dhanoa, A. S. Rahman, N. Makwana, J. Tang, A. Sella, F. Corà, S. Firth, J. A. Darr, *J. Phys. Chem. C.* 2013, *117*, 7178-7185.
- [9] J. Ran, T. Y. Ma, G. Gao, X.-W. Du, S. Z. Qiao, *Energ Environ. Sci.* 2015, 8, 3708-3717.
- [10] X. Jin, V. V. Balasubramanian, S. T. Selvan, D. P. Sawant, M. A. Chari, G. e. Q. Lu, A. Vinu, Angew. Chem. Int. Ed. 2009, 48, 7884-7887.
- [11] a) Z. Chen, Q. Zhang, W. Chen, J. Dong, H. Yao, X. Zhang, X. Tong, D. Wang, Q. Peng, C. Chen, *Adv. Mater.* 2018, *30*, 1704720; b) Z. Chen, E. Vorobyeva, S. Mitchell, E. Fako, M. A. Ortuño, N. López, S. M. Collins, P. A. Midgley, S. Richard, G. Vilé, *Nature Nanotechnol.* 2018, *13*, 702.
- [12] Y. Zheng, J. Liu, J. Liang, M. Jaroniec, S. Z. Qiao, *Energy Environ. Sci.* 2012, 5, 6717-6731.

RESEARCH ARTICLE

- [13] D.-H. Lan, H.-T. Wang, L. Chen, C.-T. Au, S.-F. Yin, *Carbon* 2016, 100, 81-89.
- [14] a) Y. Wang, Y. Di, M. Antonietti, H. Li, X. Chen, X. Wang, *Chem. Mater.* **2010**, *22*, 5119-5121; b) M. Xu, B. Chai, J. Yan, H. Wang, Z. Ren, K.-W. Paik, *Nano* **2016**, *11*, 1650137.
- [15] a) Y. Wang, J. Zhang, X. Wang, M. Antonietti, H. Li, *Angew. Chem. Int. Ed.* 2010, *49*, 3356-3359; b) H. Ma, Y. Li, S. Li, N. Liu, *Appl. Surf. Sci.* 2015, 357, 131-138; c) L. Jiang, X. Yuan, G. Zeng, X. Chen, Z. Wu, J. Liang, J. Zhang, H. Wang, H. Wang, *ACS Sustainable Chem. Eng.* 2017, *5*, 5831-5841; d) P. Babu, S. Mohanty, B. Naik, K. Parida, *ACS Appl. Energy Mater.* 2018, *1*, 5936-5947; e) Y.-C. Lu, J. Chen, A.-J. Wang, N. Bao, J.-J. Feng, W. Wang, L. Shao, *J. Mater. Chem. C* 2015, *3*, 73-78.
- [16] Y. Zhang, T. Mori, J. Ye, M. Antonietti, J. Am. Chem. Soc. 2010, 132, 6294-6295.
- [17] a) D. S. Simakov, Renewable Synthetic Fuels and Chemicals from Carbon Dioxide: Fundamentals, Catalysis, Design Considerations and Technological Challenges, Springer, 2017; b) K. Li, B. Peng, T. Peng, ACS Catal. 2016, 6, 7485-7527; c) H. Li, Q. Zhang, P. S Bhadury, S. Yang, Curr. Org. Chem. 2014, 18, 547-597.
- [18] Y. Zhou, W. Lin, H. Wang, Q. Li, J. Huang, M. Du, L. Lin, Y. Gao, L. Lin, N. He, *Langmuir* **2010**, *27*, 166-169.
- [19] Y. Cao, T. Mu, Ind. Eng. Chem. Res. 2014, 53, 8651-8664.
- [20] M. Gao, J. Feng, Z. Zhang, M. Gu, J. Wang, W. Zeng, Y. Lv, Y. Ren, T. Wei, Z. Fan, ACS Appl. Nano Mater. 2018, 1, 6733-6741.
- [21] S. Hu, L. Ma, J. You, F. Li, Z. Fan, F. Wang, D. Liu, J. Gui, *RSC Adv.* 2014, 4, 21657-21663.
- [22] S. Zhang, K. Dokko, M. Watanabe, *Mater. Horizons* **2015**, *2*, 168-197.
- [23] X. Li, I. V. Sergeyev, F. Aussenac, A. F. Masters, T. Maschmeyer, J. M. Hook, Angew. Chem.Int. Ed. 2018, 130, 6964-6968.
- [24] T. Zhang, I. P. A. F. Souza, J. Xu, V. C. Almeida, T. Asefa, *Nanomaterials* 2018, 8, 636.
- [25] H.-B. Fang, X.-H. Zhang, J. Wu, N. Li, Y.-Z. Zheng, X. Tao, Appl. Cata. B: Environ. 2018, 225, 397–405
- [26] a) F. R. Pomilla, A. Brunetti, G. Marcì, E. I. García-López, E. Fontananova, L. Palmisano, G. Barbieri, ACS Sustainable Chem. Eng. 2018, 6, 8743-8753; b) J. Mao, T. Peng, X. Zhang, K. Li, L. Ye, L. Zan, Catal. Sci. Technol. 2013, 3, 1253-1260.
- [27] Q. Tay, P. Kanhere, C. F. Ng, S. Chen, S. Chakraborty, A. C. H. Huan, T. C. Sum, R. Ahuja, Z. Chen, *Chem. Mater.* **2015**, *27*, 4930-4933.
- [28] a) W. Che, W. Cheng, T. Yao, F. Tang, W. Liu, H. Su, Y. Huang, Q. Liu, J. Liu, F. Hu, Z. Pan, Z. Sun, S. Wei, *J. Am. Chem. Soc.* 2017, *139*, 3021–3026; b) H. Yaghoubi, Z. Li, Y. Chen, H. T. Ngo, V. R. Bhethanabotla, B. Joseph, S. Ma, R. Schlaf, A. Takshi, *ACS Catal.* 2015, *5*, 327–335.
- [29] J.-Y. Tang, X. Y. Kong, B.-J. Ng, Y.-H. Chew, A. R. Mohamed, S.-P. Chai, *Catal. Sci. Technol.*, **2019**, *9*, 2335.
- [30] a) F. Parveen, S. Upadhyayula, *Fuel Process. Technol.* 2017, 162, 30-36; b) X. Cao, S. P. Teong, D. Wu, G. Yi, H. Su, Y. Zhang, *Green Chem.* 2015, *17*, 2348-2352; c) P. Zhao, Y. Zhang, Y. Wang, H. Cui, F. Song, X. Sun, L. Zhang, *Green Chem.* 2018, *20*, 1551-1559.
- [31] S.-H. Chai, H.-P. Wang, Y. Liang, B.-Q. Xu, Green Chem., 2007, 9, 1130-1136

RESEARCH ARTICLE

Entry for the Table of Contents



A novel synthetic protocol that provides P-, F-co-doped mesoporous carbon nitride (PFCN) with high surface area and lower band gap. Inspired by its extended visible light absorption and acid-base bi-functional nature, we explored this new class of catalyst for the photocatalytic reduction of CO_2 into methanol and conducted thermal catalytic conversion of carbohydrates into high-value furanics compounds.