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Covalent Functionalization of Carbon Nitride Frameworks through Cross-Coupling Reaction

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Abstract: Here we introduce a new and simple synthetic route to covalently functionalize the carbon nitride (CN) framework by the implementation of halogenated phenyl groups (Cl, Br and I), which serve as a chemically reactive center, within the CN framework. The covalent modification is demonstrated here by substituting phenyl and *tert*-butyl propionate onto the modified-CN framework through Suzuki and Reductive-Heck cross-coupling reactions, respectively. The effective functionalization leads to a facile exfoliation of the CN framework into thinner layers and greatly enhances the dispersibility in many solvents as well as the photocatalytic activity compared to the unmodified CN. The general covalent modification opens the possibility for tailor-made design of the CN materials dispersibility as well as the photophysical and chemical properties toward their exploitation in many fields, such as photocatalysis, bio-imaging, sensing and heterogeneous catalysis.

Two-dimensional (2D) carbon nitride (CN) based semiconductors possess a great promise in various fields as solar fuels production, bio-imaging, sensing, light-emitting diodes and solar cells due to their unique electronic, optical and structural properties.^[1] as well as to their low price, environmentally friendly nature and high stability to oxidation and harsh chemical condition.^[2,3] The synthesis of CN frameworks usually relies on the condensation of nitrogen-rich organic molecules such as urea, dicyandiamide or melamine at elevated temperatures.^[4] Their photophysical and electronic properties are derived from the carbon-to-nitrogen ratio and spatial organization in the final material. The traditional solidstate synthesis of bulk CN framework usually leads to disorganized textures with small grain sizes, poor electronic and catalytic properties, which limits their performance in different applications.^[5] Additionally, the dispersibility of CN frameworks in most solvents is relatively low owing to the strong van der Waals and hydrogen bonds interaction between their layers.^[6] The low dispersibility strongly restricts the use of CN frameworks in potential applications and hinders the elucidation of their local

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structures by liquid-based techniques (i.e. NMR).^[7] Moreover, the strong van der Waals interaction between the CN layers alongside with their low dispersibility impede their exfoliation into a stable 2D material.^[7]

Intensive efforts have been devoted to optimizing the photophysical and catalytic properties of bulk CN frameworks as well as to improving their dispersibility, including physical and chemical cleavage,^[8a] nanostructuring,^[8b-d] surface protonation,^[9] heteroatom incorporation,[10a-e] heterojunctions[10f] and other electronic structures construction,^[11] copolymerization of CN monomers prior to their condensation at high temperature^[12] and non-covalent interaction with different molecules.^[13] However, most of the modifications involve either the bottom-up approach condensation of molecules with different heteroatoms and molecular structure or by non-covalent post-modifications of the final CN frameworks.^[14] In contrast to the above-mentioned approaches, post-condensation, covalent functionalization is considered as more robust and permanent modification due to the establishment of a non-reversible chemical bond between the material and the selected molecule.[15] In addition, it allows the introduction of groups that would be decomposed or condensate during the calcination process (such as nitriles, esters, carboxylates, boronic acid, etc.). The nature of the introduced molecule can affect several properties of the modified material, e.g. its electronic properties, surface charge, charge separation under illumination, optical properties (i.e. band gap) and its dispersibility in different solvents.^[16] Several pioneering works demonstrated the covalent functionalization of graphene and other carbon allotropes such as carbon nanotubes.^[17] This successful approach paves the way for further development of functional graphene derivatives. However, a direct covalent modification of CN-based organic framework is challenging and rarely reported before,^[16,18] due to the chemical inertness of sp² carbon-nitrogen bonds within the CN framework and the strong interaction between its layers. Therefore, we envision that in order to overcome these obstacles, the CN framework should encompass a chemically reactive group that can be further covalently functionalized.

Here, we demonstrate a new and facile strategy to covalently functionalize CN organic framework by the insertion of a halogen-(Cl, Br and I) substituted phenyl into the CN framework. Prior to the covalent functionalization, the reactive CN framework is prepared by the calcination of a new series of derivatives based on modified 2,4-diamino-6-phenyl-1,3,5-triazine where the phenyl group is substituted with different halogens. The introduction of the halogenated phenyl group significantly improves the dispersibility of the new CN framework in various solvents and facilitates the exfoliation of the CN material into 2D sheets, most likely because these bulky groups sterically hinder the interaction between the layers. The great potential of this method is exemplified here by functionalizing the CN organic framework with a phenylboronic acid and a *tert*-butyl acrylate through Suzuki

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and Reductive-Heck cross-coupling reactions, respectively. The final products after the covalent modification present ultrathin sheet-like structure and enhanced dispersibility in many solvents, such as DMSO, THF, n-hexane and diethyl ether. The advantage of the enhanced dispersibility is exemplified here by the efficient photooxidation of benzyl alcohol as a model reaction.

The new 2,4-diamino-6-phenyl-1,3,5-triazine derivatives (DPT-X, X = CI, Br, I) were synthesized by reacting dicyandiamide with nitriles under microwave irradiation (Figure 1a).^[19] The chemical structure of the new monomers was confirmed by gas chromatography–mass spectrometry (GC-MS), X-ray Diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR) spectra (Figure S1 and S2).



Figure 1. (a) Illustration of the synthesis of DPT-X and the corresponding CN-Ph-X. TEM images of (b) CN-Ph, (c) CN-Ph-CI, (d) CN-Ph-Br and (e) CN-Ph-I. SEM mapping of (f) CN-Ph-Br. (g) XRD patterns and (h) FTIR spectra of CN-Ph, CN-Ph-CI, CN-Ph-Br and CN-Ph-I.

The modified carbon and nitrogen based frameworks (referred here as CN-Ph and CN-Ph-X, X= CI, Br, I) were acquired by the calcination of DPT and DPT-X for 4 h at 350 °C under nitrogen atmosphere. We note that the condensation of the precursors into organic CN framework takes place between 250-350 °C as suggested by TGA measurement (Figure S3-S4) and elemental analysis (EA), as detailed below. Different from the commercial DPT, weight loss is observed below 100 °C for the synthesized DPT-X, due to the desorption of moisture. Furthermore, the decomposition slightly shifted compared to DPT owing to the different intramolecular interactions. The high amount of carbon in the starting materials leads to the formation of a semiconductor already at 350 °C, while at higher calcination temperatures a more nitrogen-doped carbon is obtained (Figure S5). EA data of the CN frameworks is shown in Table S1. Compared to the original CN-Ph, the relative amount of hydrogen in all three halogenated materials is significantly reduced and the C/N ratio increases from 1.54 to ~1.64. The EA data together with the TGA measurements indicate that the DPT-X condensed during the thermal treatment with the release of amino groups, which is similar to the condensation progress of melamine.^[20] Simultaneously, the amount of halogen groups remained steady, underpinning their preservation after 4 h calcination at 350 °C.

Sheet-like CN-Ph and CN-Ph-X morphologies were observed via TEM and SEM (Figure 1b-e and Figure S6a-d). Energy-dispersive X-Ray spectroscopy (EDXS) elemental mapping of CN-Ph-X (Figure 1f and Figure S6e, f) displays a homogeneous halogen distribution, further confirming the successful incorporation of the phenyl-halogen groups within the framework. Additional evidence for the layered structure of CN-Ph and CN-Ph-X framework is given by the XRD patterns (Figure 1g). Identical predominant diffraction at ~27° is detected in all samples, speaking for the graphitic stacking feature,^[13] in accordance with the TEM images. The halogen incorporation leads to a small increase of the distance between the CN frameworks layers, which facilitates their exfoliation.



Figure 2. XPS spectra of (a) C 1s, (b) N 1s and (c) Br 3d in CN-Ph-Br. (d) Band structure diagram of CN-Ph and CN-Ph-X. (e) Digital photograph images of bulk CN (calcination from melamine) and CN-Ph (calcination from DPT) suspensions in diverse solvents. (f) Pictures of CN-Ph and CN-Ph-X powder as well as the corresponding suspension in DMSO.

The chemical structure of CN-Ph-Xs was further elucidated by FTIR and XPS analysis as shown in Figure 1h, Figure 2a-c and Figures S7-S9. The characteristic FTIR vibration peaks of CN framework at 3400 cm⁻¹, between 1000 and 1700 cm⁻¹ or at 800 cm⁻¹, corresponding to the N-H, C-N and C=N, as well as the breathing mode of triazine units,^[21] respectively, were detected. The C 1s XPS analysis of CN-Ph-Br shows the intrinsic sp² C-C and N=C-N species together with C-Br bond at binding energies (BEs) of 286.20 eV (Figure 2a).[22] The peaks at 400.3 eV and 398.6 eV in N1s XPS spectra can be assigned to N-(C)₃ and C=N-C^[23] (Figure 2b). The missing N-H peak implies the loss of N-H groups during the condensation process. The existence of N-(C)₃ indicates the fusion of the amine group by the formation of heptazine unit as previously described for carbon nitride materials.^[24] The Br 3d core-level spectrum exhibits two peaks centered at 70.4 eV and 71.5 eV, corresponding to the Br 3d_{5/2} and Br 3d_{3/2}, respectively (Figure 2c). More evidence for the successful introduction of Br can also be deduced from the appearance of three additional signals with BEs at about 70, 189 and 256 eV in the wide-scan spectrum (Figure S7), attributable to Br 3d, Br 3p, and Br 3s, respectively.^[25] Additionally, the integration of CI and I atoms in the CN framework was also confirmed by the XPS measurements (Figures S8-S9). The Cl 2p peaks can be resolved into two peaks, centered at BEs of 200.5

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and 201.8 eV, belonging to the CI $2p_{3/2}$ and CI $2p_{1/2}$ species.^[22] Likewise, the I 3d spectrum entails two multiple peaks centered at 621.5 and 633.3 eV, corresponding to I $3d_{5/2}$ and I $3d_{3/2}$, respectively.^[26] Having all data at hand we can safely conclude that the halogen-phenyl groups are fully integrated into the final CN organic framework structure.

To investigate the effect of the halogens on the optical and electronic properties of the final CN framework, UV-vis absorption and Mott-Schottky analysis were performed (Figure S10 and S11). The high amount of carbon in the starting monomers leads to the formation of semiconductors with bandgaps ranging from 2.5 to 2.05 eV already at 350 °C. The redshift of the optical absorption edge can be attributed to the withdrawing character of the halogen groups. Similar to other carbon nitride materials, the conduction band (CB) edge position of the new materials is highly negative, indicating their strong reducing properties. Interestingly, the halogen groups mainly affect the CB edge while the valence band (VB) position for all materials is similar (Figure 2d). Verv importantly, the new CN frameworks are much more readily dispersed (1 mg/ml) in a variety of solvents, such as DMSO, DMF, THF, MeOH, NMP, toluene and IPA (Figure 2e, f). We note that bulk CN, calcinated from melamine at 550 °C, is almost insoluble in these solvents.



Figure 3. (a) Illustration of the post-covalent functionalization of CN-Ph-Br via Suzuki and Reductive-Heck reaction. TEM images of CN-Ph-Br after the (b) Suzuki reaction and (c) Reductive-Heck reaction. (d) FTIR spectra of CN-Ph-Br, CN-Ph-Suzuki and CN-Ph-RHeck.

The existence of halogen in the CN-Ph framework, alongside with its positive effect on the dispersibility of the material in various solvents, opens a unique possibility to covalently functionalize the material by the replacement of the halogen groups with other molecules. Brominated aromatics are particularly conducive to take part in a series of organic reactions, especially in cross-coupling reactions such as Suzuki and Reductive-Heck reaction.^[27] Thus, here we chose CN-Ph-Br as a substrate for further chemical modifications. With the assistance of Pd(OAc)₂ and K₂CO₃ as catalyst and base, a Suzuki cross-coupling reaction conducted with phenylboronic acid and *tert*-butyl acrylate was selected to react with CN-Ph-Br for a typical Reductive-Heck reaction, in both cases under microwave irradiation (Figure 3a). The estimated weight percent of Br in CN-Ph-Br is around 30 %,

as calculated from the EA results. Therefore, here we introduced 30-40 mg phenylboronic acid or *tert*-butyl acrylate, around three molar equivalents of Br for 25 mg CN-Ph-Br. Using similar reaction conditions, both coupling reaction were shown to fully substitute the bromophenyl group when conducted on small molecules.^[28]

The final morphology of the composed materials (denoted as CN-Ph-Suzuki and CN-Ph-RHeck) are shown in Figure 3b, c and Figure S12a, b. An ultrathin sheet-like morphology of CN-Ph-Suzuki and CN-Ph- RHeck indicates their good exfoliation to few layers. A broader XRD peak at ~27° was observed for the CN-Ph-Suzuki and CN-Ph-RHeck compared to the original CN-Ph-Br (Figure S12c), supporting the improved exfoliation to a few layers.^[13]

The successful Suzuki and Reductive-Heck reactions and the final chemical structure were investigated by FTIR and ¹H NMR measurements (Figure 3d and Figure 4). New absorption peaks of CN-Ph-Suzuki around 780 and 750 cm⁻¹ were attributed to the introduction of another substituted phenyl group. Meanwhile, after the Reductive-Heck reaction, a C=O absorption peak at 1725 cm⁻ was detected (Figure 3d).^[29] Furthermore, the successful covalent modification of the CN-Ph-Br was supported by ¹H NMR measurements of CN-Ph-Br. CN-Ph-Suzuki and CN-Ph-RHeck in DMSO-d₆ as shown in Figure 4 and Figure S13-S15. In contrast to the starting material, CN-Ph-Br, the covalently modified CN-Ph-Br samples show new ¹H NMR signals belonging to the aromatic (consistent with the formation of a new biphenyl moiety) or aliphatic (consistent with the addition of the tert-butyl and methylene groups) regions for the CN-Ph-Suzuki and CN-Ph-RHeck materials, respectively. The ¹H NMR and FTIR measurements strongly support the successful covalent functionalization of the CN-Ph-Br framework.



Figure 4. ¹H NMR of CN-Ph-Br, (a) CN-Ph-Suzuki and (b) CN-Ph-RHeck (400 MHz, DMSO- d_{6} , details with chemical shift are shown in the SI).

The functionalization of CN organic framework with bromo, phenyl group and *tert*-butyl propionate lead to further enhancement of their dispersibility in serious of organic solvents, e.g., THF, n-hexane, diethyl ether and DMSO as shown in Figure 5a. The high dispersibility of these CN materials enables their exploitation for various applications such as catalysis in organic solvents. Especially in THF and DMSO, CN-Ph-Br, CN-Ph-Suzuki and CN-Ph-RHeck, were spontaneously dispersed and formed a clear yellow solution with a concentration of 1 mg/mL. Upon standing for more than one month, all materials in THF and DMSO were extremely stable without any observable aggregation. Even

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in less or non-polar solvents such as diethyl ether and n-hexane, CN-Ph-Suzuki and CN-Ph-RHeck are well dispersed.

The introduction of phenyl group and tert-butyl propionate results in the alteration of the photophysical properties. A strong fluorescent quenching (Figure 5a and Figure S16b) for both materials was observed, implying that the relaxation of a fraction of photocarriers occurs via a non-radiative pathway, probably from the charge transfer of electrons and holes to the new surface states.²¹ Figure S16a displays the UV-vis absorption spectra of CN-Ph-Br, CN-Ph-Suzuki and CN-Ph-RHeck powders. For both materials, the new group leads to a color change and a redshift of the absorption edge. The absorption properties of the corresponding materials in THF and DMSO were also investigated (Figure 5b, c). The absorption edge of the modified CNs in solution is strongly blue-shifted compared to the solid materials, speaking for the successful exfoliation of the CN framework into freestanding sheets.^[30] In both solvents, there is a notable redshift and increased absorption ranging from 330 to 430 nm, due to the introduced conjugative effect from phenyl group and tert-butyl propionate compared to the CN-Ph-Br.^[31] The different absorption spectra of the materials in THF and DMSO indicate the strong interaction between the material and the solvent. The sharp peak at 256 nm is attributed to the aromatic π $\rightarrow \pi^*$ transition whereas another peak at 295 nm can be assigned to the nitrogen nonbonding orbital to the aromatic nonbonding (n $\rightarrow \pi^{*}$) transition.^[32] As a polar aprotic organic solvent, DMSO can reduce both the energies of excited states in $\pi \rightarrow \pi^*$ transition and the ground-state energy in $n \to \pi^* transition,$ resulting in a redshift of the absorption and the disappearance of the fine electronic structure compared to the one in THF. The good dispersibility of the functionalized CN materials in other solvents as THF opens the possibility to improve their dispersibility in water by using THF as co-solvents as shown in Figure 5d. The functionalized CN materials can be well-dispersed in a THF/H₂O mixture (v/v ratio = 1:1) to form a colloidal suspension with a significant Tyndall effect without showing any aggregation after 3 days at room temperature. Once the mixture was further diluted with double amount of H₂O, tiny floccules could be slowly collected. After a gentle vacuum drying, the precipitate revealed a homogeneous highly-ordered morphology as shown in Fig. S17. This phenomenon opens new opportunities to prepare colloids of carbon and nitrogen based materials in different solvents and to hybridize it with other materials for a broader range of applications.

Furthermore, the photocatalytic activity of synthesized CN-Suzuki was evaluated using oxidation of benzyl alcohol as a model reaction, which is a fundamental transformation in organic chemistry and has wide application in flavour and fragrance industry.^[33] As shown in Fig. S18, the CN-Suzuki produces approximately 100 µmol of benzaldehyde in 24 h under white LED irradiation at 40 °C, almost twice higher than that of the traditional $g-C_3N_4$ as well as good recyclability (Fig. S19). This activity enhancement is mainly contributed from two aspects. First, compared to the g-C₃N₄, more carbon was introduced into the CN-Suzuki framework via the covalent functionalization, deducing a narrower band gap. Therefore, once under light irradiation, the CN-Suzuki would generate more electron and hole pairs, which benefits the photo-induced oxidation reaction. Secondly, unlike g-C₃N₄ which tends to aggregate and attaches to the wall of reactor in the organic solvent, CN-Suzuki can be uniformly dispersed in the reaction system (toluene) and further increase the reaction kinetics. TEM images and FTIR measurements of the CN-Suzuki after the recycle tests indicate the stability of the catalyst (Fig. S20 and S21). The similar morphology and chemical structure suggest that the CN-Suzuki is chemically stable and can be reused without noticeable change.



Figure 5. (a) Pictures of 1 mg/ml of CN-Ph-Br, CN-Ph-Suzuki and CN-Ph-RHeck in THF, n-hexane, diethyl ether, DMSO and corresponding solutions under UV light, 365 nm. UV-vis absorption spectra of CN-Ph-Br, CN-Ph-Suzuki and CN-Ph-RHeck in (b) THF and (c) DMSO. (d) A colloidal suspension of CN-Ph in THF/water 1:1 mixture and their Tyndall effect. In higher water concentration the formation of floccules is obtained.

In summary, we present a straightforward synthetic strategy to covalently functionalize carbon nitride frameworks through the implementation of chemically reactive groups, i.e. a halogenated phenyl group, within the material framework prior to the materials condensation at high temperature. The introduction of the chemically reactive groups was allowed by the synthesis of a series of halogen modified 2,4-diamino-6-phenyl-1,3,5-triazine molecules that serve as the CN monomers and can be fully preserved after calcination at 350 °C. The new CN materials demonstrate a good dispersibility in a wide range of solvents thanks to the weakened interaction between CN layers. The strength of this method is exemplified here by the postmodification of CN framework with phenyl group and tert-butyl propionate through Suzuki and Reductive-Heck cross-coupling reactions, respectively. The successful integration of the new groups into the CN framework significantly improves the dispersibility of the modified CN in various solvents and facilitates its exfoliation into 2D materials with different photophysical properties. The potential of this approach is exemplified here by the efficient photooxidation of benzyl alcohol as a model reaction in an organic solvent. This new, simple approach paves the way for tailored design of the chemical, photophysical and electronic properties as well as the dispersibility in various solvents of carbon nitride based materials toward their utilization in various applications such as bio-imaging, sensing, photocatalysis and electronic devices.

Experimental Section

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Details of synthetic methodology, characterization techniques, and photocatalytic analysis are given in the Supporting Information.

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Keywords: Carbon nitride • covalent functionalization • benzyl alcohol oxidation • 2D materials exfoliation

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A new, general synthetic route to covalently functionalize carbon nitride based semiconductors by the implementation of halogenated phenyl groups (Cl, Br and I), which serve as a chemically reactive center, within the CN framework is reported. The effective functionalization greatly enhances its dispersibility in many solvents as well as the photocatalytic activity.



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Covalent Functionalization of Carbon Nitride Frameworks through Cross-Coupling Reaction