Tailoring Carbon Nitride Dimensionality via On-Surface Reactions of CN-Based Precursors

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Graphitic carbon nitrides (1) are promising porous, low-dimensional materials with tunable electronic and photochemical properties. Their structural diversity can be explored through complementary synthetic approaches (2), including solution-based reactions and on-surface polymerization under ultrahigh-vacuum (UHV) conditions.

Here, we investigate the synthesis of carbon nitride nanostructures using novel halogenated CN-based precursors (Fig. 1a). Following molecular characterization by Raman and infrared spectroscopy, solution-phase Fittig coupling was employed to produce two-dimensional (2D) porous carbon nitride flakes (Fig.1b), as confirmed by transmission electron microscopy (TEM) and atomic force microscopy (AFM). Presence of occasional one-dimensional (1D) wires suggests incomplete reaction.

To explore alternative reaction pathways, we deposited the same precursors onto Ag(111) under UHV conditions, using both thermal post-annealing and hot-substrate deposition to activate intermolecular coupling. Scanning tunnelling microscopy (STM) revealed the formation of self-assembled molecular layers (Fig. 1d) at room temperature, which evolved into 1D carbon nitride nanoribbons (Fig. 1c,e) upon thermal activation. These structures differ markedly from the 2D porous networks obtained through solution-phase synthesis, demonstrating how the molecular design, substrate nature, reaction environment and activation strategy can direct the dimensionality and morphology of carbon nitride materials.

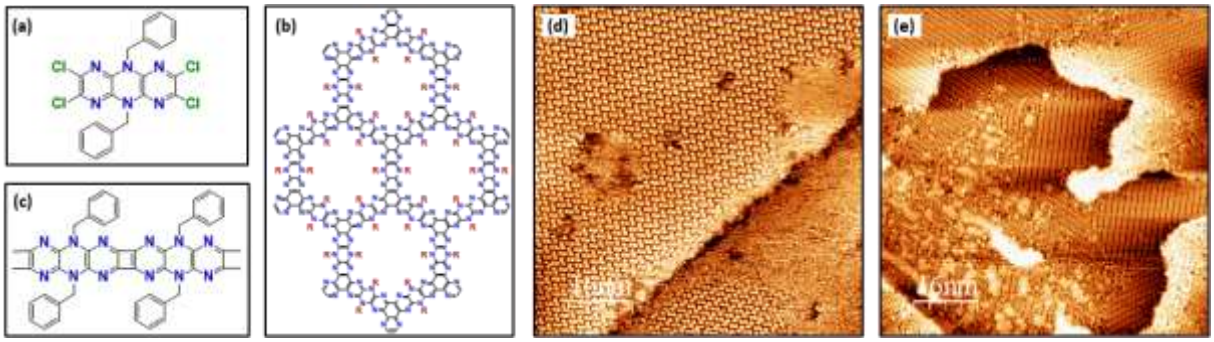

Fig. 1. (a) CN-based tetrachloro precursors that can form either (b) 2D porous carbon nitride networks via solution-phase Fittig reaction, or (c) 1D nanoribbons via on-surface synthesis under UHV condition. (d, e) STM images of (d) molecular assembly and (e) covalently bonded nanoribbons formed on Ag(111) at RT or at 400 °C.

REFERENCES

1. A.I. Cooper *et al.*, *Mater. Today*, **17**, 468 (2014); G. Algara-Siller *et al*., *Angew. Chem.*, **126**, 7580 (2014); J. Mahmood *et al*., *Nat. Commun.*, **6**, 6486 (2015)
2. C.M. Da Silva *et al*., *Sci. Rep.*, **13**,15423 (2023); J.J. Gammelgaard *et al*., *ACS Nano*, **17**, 17489 (2023)