FAST EXFOLIATION AND FUNCTIONALISATION OF 2D CARBON NITRIDE BY FRAMEWORK CHARGING

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ABSTRACT

Two-dimensional, layered graphitic carbon nitride (gCN) nanosheets are complementarity to graphene, offering tunable electronic and chemical properties. However, the inherent low solubility and limited chemical reactivity of gCN makes exfoliation and functionalisation for specific applications difficult. Here, a scalable one-pot reductive method is used to produce solutions of exfoliated single and few layer 2D gCN nanosheets (FL-CN) (82 % ≤ 4 layers) with exceptional monodispersity in a high yield (35 %) from polytriazine imide (PTI). The use of a framework charging method avoids intense sonication and related damage, preserving the lateral dimensions of the starting material; high resolution imaging of the intact crystalline layers confirms the atomic structure and identifies an AB stacking. The dissolved FL-CN can reach a high concentration of 1.2 mg•mL⁻¹ in organic solvent, with excellent stability, and can also be transferred to aqueous dispersion. By exploiting the negative charge, the first deliberate functionalisation of dissolved gCN is illustrated by alkylation with dodecyl bromide, providing a general route to adjust the properties of PTI.

INTRODUCTION

Two-dimensional graphitic carbon nitride (gCN) has triggered tremendous interest due to its 2D structure, analogous to graphene, but with complementary characteristics. In particular, it offers inherent semiconductivity with tunable band gap and optical absorption, whilst the different chemical valences of N and C create empty sites within the layers, lined with N lone pairs and/or N-H groups, enabling host/guest interactions, with potential applications for charge storage, ionic diffusion, and anchoring of (electro)catalysts. Monolayer/few layer carbon nitride nanosheets (FL-CN) have been isolated as a new family of 2D layered materials, motivated by their unique photocatalytic activity. Dispersions of these FL-CN provide routes to assemble porous thin films and high surface area 3D constructs, relevant to a wide range of potential applications in electrochemical devices, H₂O splitting photocatalysis, metal-free chemical catalysis, and nanomedicine.

The atomic structures of the sp² hybridised gCN layers are predominately based on either heptazine or polytriazine imide (PTI) ordered networks, and contain more nitrogen than carbon, in sharp contrast to N-doped graphenes. Due to the availability of the starting material, most work on gCN exfoliation has focused on heptazine-based gCNs, either by intense liquid-phase sonication in water/acid/organic solvents, thermal oxidation or lithium (Li)/liquid ammonia intercalation with prolonged sonication. Unfortunately, these processes damage the intrinsic structure, altering the properties of interest, they are also time-consuming and provide only low yields of dilute nanosheet suspensions. PTI is more crystalline than its heptazine-based counterpart, and its exfoliation into high quality 2D
FL-CN crystals is, therefore, attractive. Potassium vapour\textsuperscript{9} has been previously intercalated into PTI before reaction with water to improve dispersibility; although the exfoliated sheets had up to micrometer lateral sizes, the sheets were multilayered and generally damaged, since the water-exfoliation generates radicals.\textsuperscript{18} An improved, non-damaging and efficient route to prepare FL-CN at high concentration/yield is highly desirable.

Covalent functionalisation is a vital tool in tailoring the properties of carbon-based materials and is widely employed for graphene and carbon nanotubes (CNTs).\textsuperscript{19,20} However, to date, there has been little direct covalent functionalisation of PTI, although heptazine-gCNs have been protonated\textsuperscript{21} or oxidized by free radical reactions to form gCN quantum dots.\textsuperscript{22}

This paper demonstrates a simple, one-pot exfoliation, dissolution, and optional functionalisation of few-layered PTI (FL-PTI) \textit{via} a reductive charging route. Reductive charging has been used previously to dissolve a variety of nanomaterials, including fullerene,\textsuperscript{23} nanotubes,\textsuperscript{24,25} graphenes\textsuperscript{26} and other 2D materials\textsuperscript{27} \textit{via} metal-ammonia solutions and organic charge transfer agents. The use of sodium naphthalide (NaNp) dissolved in N,N-dimethylacetamide (DMAc) was recently found to be especially effective for the dissolution and functionalisation of single wall nanotubes in a single step.\textsuperscript{28} Here the methodology is adapted to gCNs, specifically PTIs.

The framework charging exfoliation process of PTI is depicted in Figure 1. Sodium is used as the electron source to form naphthalide ions in solution, which act as a charge transfer agent. DMAc is an excellent room temperature solvent for naphthalene, naphthalide, and pure nanocarbons, and can be expected to be a good solvent for FL-PTI.\textsuperscript{28} NaNp/DMAc solution has a characteristic dark green color which simplifies reaction monitoring. NaNp/DMAc solutions were added into carefully dried PTI powders at controlled stoichiometry. The reduction and exfoliation process was observed by the color change from the initial brown of PTI suspension to dark green after addition of NaNp/DMAc, before finally forming a brilliant orange dispersion of FL-PTI (FL-PTI\textsuperscript{ν}) within minutes. After removing the remaining insoluble PTI fragments by centrifugation (5000 g, 30 min), a homogeneous clear golden FL-PTI\textsuperscript{ν} solution with a concentration up to 1.2 mg·mL\textsuperscript{-1} was obtained, which was stable under N\textsubscript{2} for at least 1 year. Deposited FL-PTI\textsuperscript{ν} nanosheets display hexagonal geometry with a height of 1-2 nm, indicating that they comprise only a few PTI layers, based on a 3.52 Å layer thickness.\textsuperscript{5} The negative charges from the naphthalide are likely to be transferred to the PTI, where they remain counterbalanced by both solvated and intercalated Na\textsuperscript{+}. The partially dissociated Na\textsuperscript{+} leaves a net unscreened negative charge on the PTI\textsuperscript{ν}, leading to short range Coulombic repulsions and hence exfoliation of PTI into solvated FL-PTI\textsuperscript{ν} sheets (Figure 1). This mechanism is analogous to that proposed for nanotubides and graphenides.\textsuperscript{25,27} Upon air exposure, the FL-PTI reagglomerates slowly (~2 months); the reduced rate compared to charged SWCNTs,\textsuperscript{25} likely relates to the lower aspect ratio and localisation/low mobility of the charges on the framework.\textsuperscript{30}

![Figure 1: Schematic illustration of the framework charging exfoliation process from the pristine PTI to FL-PTI\textsuperscript{ν} nanosheets.](image)

The charging ratio (PTI framework atom:Na, using an average atomic weight for PTI of 13.14) and initial PTI loading (total PTI mass over volume of DMAc) are two vital factors affecting the exfoliation process, controlling both the yield and concentration of solubilised FL-PTI\textsuperscript{ν} nanosheets. Increasing the degree of charging (\textit{i.e.} lower PTI:Na ratios), at a static PTI loading, initially led to an improved yield of FL-PTI\textsuperscript{ν} (from 4.1\% to 34.5\%) due to the enhanced Columbic repulsion (Figure 2a). However, further increasing charge density (PTI:Na < 7) reduced the yield. Similar effects have been observed in charged nanotubide and graphenide sus suspensions, attributed to Na\textsuperscript{+} condensation and
screening of the repulsive negative charge.\textsuperscript{28,31} The optimum Na concentration for exfoliation of PTI is 15 mM (corresponding to a 7:1 PTI:Na ratio, Figure 2a), comparable to the value identified for the exfoliation of Na-reduced graphite intercalation compounds (~10 mM) with similar geometry.\textsuperscript{31} At the highest charge regimes, the negative charge on the PTI saturates (at PTI:Na ratio of ~5), as observed by the green tinge of unreacted NaNp (Figure 2a). The optimum PTI:Na ratio of 7:1 produced a yield of 34.5 wt\% from an initial PTI loading of 1.4 mg mL\textsuperscript{-1} (Figure 2a). On varying the PTI loading, the concentration of dissolved FL-PTI\textsuperscript{a} scales linearly, giving a consistent yield between 31 and 35 wt\%, indicating that there may be an intrinsically soluble portion of the starting material (most effectively dissolved at PTI:Na = 7); the residue, isolated after centrifugation may contain defects that bind the layers. The maximum concentration of FL-PTI\textsuperscript{a} is \textasciitilde1.2 mg mL\textsuperscript{-1}, at a PTI loading of 3.5 mg mL\textsuperscript{-1}; further increase in PTI loading does not increase the concentration continually, indicating the solution is saturated (Figure 2b).

Aqueous FL-PTI dispersions are desirable for easy and environmentally benign processing; however, pristine PTI are poorly soluble in water due to their strong interlayer interactions (6 h probe sonication was found to give a concentration of <0.2 mg mL\textsuperscript{-1}). The framework charging process overcomes the strong interlayer interactions and solubilisation in DMAc allows the removal of the intrinsically insoluble fraction of the pristine PTI. The FL-PTIs are then recovered from the DMAc solution by (i) quenching with dry oxygen and collecting the FL-PTI wet-cake via vacuum filtration; (ii) sequential washing with tetrahydrofuran and ethanol to remove naphthalene and sodium salts, respectively; and (iii) re-dispersion in water by brief bath sonication (1 minute). The resultant FL-PTI aqueous system has a saturated concentration of 3.5 mg mL\textsuperscript{-1}, more than an order of magnitude greater than sonicated samples. However, as for their sonication-exfoliated counterpart,\textsuperscript{8} these FL-PTI aqueous dispersions are highly stable both at low (\textlesssim3) and high (\textgtrsim8) pH ranges, where $\zeta$ \textgtrsim30 mV, generally considered sufficient to sustain mutual repulsion in colloids.\textsuperscript{32} Zeta potential measurements also show that the surface charge switches from negative (-49.5 \pm 1.6 mV) to positive (+43.9 \pm 3.3 mV) on decreasing the pH from 12 to 2, with an isoelectric point of pH 3.9, corresponding to the ionization and protonation of the bridged imide moieties within the PTI framework, respectively.\textsuperscript{8,21} Adjusted the effective charge provides a feasible route to make PTI multifunctional macro-constructs via electrostatic self-assembly.\textsuperscript{33}

Atomic force microscopy (AFM) confirms an excellent dispersion of FL-PTI nanosheets in water (Figure 3a), and the corresponding height estimates range from 0.33-3.2 nm (avg. 1.11 nm, Figure 3b), suggesting that the exfoliated nanosheets mostly comprise \textasciitilde3 PTI layers, although some monolayers are present. Representative energy dispersive X-ray spectroscopy (EDX) maps show uniform dispersion of C and N throughout the whole hexagonal area of the exfoliated FL-PTI nanosheet (Fig 3c-e). High-resolution transmission electron microscopy (HRTEM) micrographs show intact PTI crystallites with regular hexagonal geometry and clear facets (Figure 4a). Notably, no defect holes or dislocations were observed, confirming the non-destructive nature of the framework charging.
exfoliation, as well as the high quality of the starting material. The fast Fourier transform (FFT) of the unfiltered HRTEM image shows a hexagonal lattice, demonstrating a single crystal exfoliated FL-PTI (Fig 4a). The minimum reciprocal lattice vector, $g_{\text{min}}$, is $1.4 \text{ nm}^{-1}$, which gives a lattice constant $a = 2/\sqrt{3}g_{\text{min}} = 8.2 \text{ Å}$, consistent with the reported value of 8.5 Å observed by HRTEM for bromide ion intercalated PTI, within error. Two possible stacking models can be considered for the FL-PTI nanosheets: AB stacking, where the voids in two adjacent layers overlap with a 180° rotation leaving pore channels through the crystal, and AC stacking, where the voids in one layer overlay triazine units in the next layer leaving no channels. Comparing simulated electron diffraction patterns of these two models with the experimental selected area electron diffraction (SAED) data, the AB stacking structure is the better fit for the FL-PTI nanosheets (Figure 4b-d).

Figure 3: (a) AFM image of FL-PTI nanosheets deposited on mica from aqueous solution. (b) Statistical analysis of the thickness of ~200 FL-PTI nanosheets measured in AFM images. Mean value is derived from a lognormal distribution. (c) STEM image and EDX elemental maps of C (d) and N (e) on a FL-PTI nanosheet. The background C signal in (d) is due to the carbon TEM support.

Figure 4: (a) HRTEM image (with average background subtraction filter applied) of a FL-PTI nanosheet. Inset: FFT of the unfiltered HRTEM image, showing a single crystal hexagonal structure. (b) SAED pattern of a FL-PTI nanosheet. (c) Schematic of the AB stacking in a bilayer. (d) Simulated electron diffraction pattern from the AB crystal structure.

The FL-PTI® synthesised in DMAc solution provides an excellent platform for covalent functionalisation of PTIs, comparable to negatively-charged carbon-only and boron nitride nanotube
counterparts. Functionalisation can be performed via simple addition of an alkyl halide to the reduced nanomaterial. Pristine PTI powders and FL-PTI nanosheets are thermally stable up to ~700 and 670 °C, respectively (Figure 5a); the slightly depressed decomposition temperature for FL-PTI nanosheets reflects its few-layered character. After functionalisation by reaction with dodecyl bromide, a 5 wt% mass loss can be observed in thermogravimetric analysis/evolved-gas mass spectrometry (TGA-MS), relative to controls; the weight loss correlates with a m/z peak at 57, attributed to C\textsubscript{8}H\textsubscript{15} from the grafted C\textsubscript{12}H\textsubscript{25} alkyl chain (Figure 5a). Controls of air-quenched FL-PTI mixed with C\textsubscript{12}H\textsubscript{25}Br and FL-PTI\textsuperscript{\textregistered} with unreactive C\textsubscript{12}H\textsubscript{26} showed similar TGA curves to the unfunctionalised FL-PTI nanosheets, excluding a contribution from physisorption\textsuperscript{\textregistered}, and confirming the alkylation of FL-PTI\textsuperscript{\textregistered}. The successful functionalisation can be readily identified with the color changing from a clear golden, for FL-PTI\textsuperscript{\textregistered} and ‘FL-PTI\textsuperscript{\textregistered}+C\textsubscript{12}H\textsubscript{26}’ control, to a slightly turbid pale yellow for alkylated FL-PTI, as the depletion of the negative charges progresses (Figure 5b).

Figure 5: (a) TGA of pristine PTI, FL-PTI nanosheets, alkylated FL-PTI (FL-PTI\textsuperscript{\textregistered}+C\textsubscript{12}H\textsubscript{25}Br) and two control samples of ‘FL-PTI\textsuperscript{\textregistered}+C\textsubscript{12}H\textsubscript{26}’ and ‘FL-PTI+C\textsubscript{12}H\textsubscript{25}Br’ (solid lines) and corresponding TGA-MS curves (dashed line). (b) Photographs of control sample (top) and alkylated FL-PTI (bottom), respectively.

CONCLUSIONS

In summary, controlled framework charging provides a new and straightforward route for exfoliation and functionalisation of PTI nanosheets, via NaNP/DMAC reduction. By avoiding damage, the intrinsic properties of the PTI structure can be retained and high resolution images obtained. AFM and TEM indicate highly exfoliated hexagonal, highly crystalline and intact FL-PTI nanosheets, averaging 1.1 nm thick (~3 layers) with an AB stacking. The as-prepared FL-PTI nanosheet solutions had a high concentration (~1.2 mg·mL\textsuperscript{-1}) and yield (35 wt%), as well as excellent stability in DMAC under inert conditions and after dispersion in both acidic (pH≤3) and basic (pH ≥8) water. The FL-PTI\textsuperscript{\textregistered} was successfully functionalised with alkyl chains via the framework charge, suggesting a route to a wide range of functionalised species, adapting electrophilic reagents applied to charged nanocarbons. Functionalisation provides a route adjusting surface chemistry and functional properties. Stabilised dispersions of high surface area FL-PTIs are useful feedstocks for a wide range of promising multifunctional applications.

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