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Photoluminescent carbon nitride films grown by vapor transport of carbon nitride powders†

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The thermal vapor transport of nitrogen-rich carbon nitride powders produces carbon nitride films on substrates that retain significant nitrogen content, have conjugated bond character, and show blue photoluminescent emission near 450 nm.

Organic polymers and conjugated molecular systems have made impressive inroads in recent years in the area of photo- and electro-luminescent materials for optical technologies.[1] Most of the well-developed systems are red to green light emitting materials based on polyphenylene and polyfluorene conjugated systems.[1] To produce a full color spectrum, blue emitting materials (*ca*. 440–480 nm) are also of interest. Many recent blue luminescent systems contain three coordinate nitrogen centers or nitrogen-containing aromatic rings;[1,2] for example, triazine-based dendrimers[3] and heterocyclic nitrogen-substituted superbenzenes[4] show luminescence in the blue-green region. One of the drawbacks of organic light emitting systems is lower thermal and air stability relative to inorganic light emitters such as GaAs, GaP, and GaN.[5]

Amorphous nitrogen-doped carbon films reportedly show luminescence near 540 nm (2.3 eV), but the emission intensity diminishes upon annealing at 300 °C.[6] Carbon nitride film growth has generally been accomplished by elemental gas phase processes producing films with low to moderate nitrogen contents, *e.g.* $CN_{0.2}$ to $CN_{1.0}$.[7] Recently triazine-based precursor approaches have produced high-nitrogen content powders and films.[8,9]

We have previously reported in detail on the synthesis and characterization of nitrogen-rich carbon nitride powders (C_3N_{4+x}) from the decomposition of energetic triazine precursors. Specifically, the rapid exothermic decomposition of $(C_3N_3)(NHCl)_3$, trichloromelamine or TCM, produces $C_3N_{4.5}H_{1.6}$ powder (TCM-C_3N_5) above 165 °C[10] and the slow decomposition of $(C_3N_3)(N_3)_3$, triazidotriazine or TAT, produces $C_3N_{4.8}H_{1.3}$ powder (TAT-C_3N_5) below 190 °C.[11] The major byproducts in the TCM and TAT decompositions are HCl and N_2 gas, respectively, and the hydrogen content in the TAT system results from passivation of reactive bonds during solvent workup. Depending on the synthesis conditions, the bulk compositions of these amorphous $C_3N_{4+x}H_y$ powders can vary somewhat by elemental analysis (CHN combustion methods), but are generally within the range of $x = 0.5–0.8$ and $y = 1–2$. These carbon nitride products have spectroscopic characteristics consistent with significantly cross-linked polymer-like networks containing triazine components and sp[2] carbon bonding.[10,11] Powders from either method are insoluble in all tested solvents and exhibit good thermal stability up to 500–600 °C where they evaporate or decompose. In the current study we examined the ability of these powders to produce carbon nitride films via vapor transport growth.

In a typical experiment, the carbon nitride powder (*ca*. 20 mg) was placed in an alumina boat in a horizontal silica flow tube and heated under flowing argon at 600 °C and 650 °C for TCM-C_3N_5 and TAT-C_3N_5, respectively (Fig. 1, see ESI† for details). At these temperatures, the carbon nitride powders volatilize and recondense on Si(111) and SiO_2 wafers placed near the furnace exit. The temperature in the substrate region was 250–350 °C. Both powders produce visibly smooth films that are pale yellow in color on SiO_2 and show multicolor interference fringes on silicon. Auger spectroscopic analysis of the films yields compositions of $C_3N_{4.8}$ and $C_3N_{4.6}$ for films from TCM-C_3N_5 and TAT-C_3N_5 powders, respectively (see ESI† for spectra). This indicates that the vapor phase species retain significant nitrogen content and transfer it to the growing film. While no attempt was made to control film thickness, scanning electron microscopy demonstrates that thickest film regions on Si are 300–500 nm thick, while the thinnest regions, nearest to the SiO_2 substrates, are about 100 nm thick.

The TCM-C_3N_5 powder is yellow-tan with distinct IR bands in the 1000–1700 cm^{-1} C–N bonding region (Fig. 2A). The TAT-C_3N_5 powder is dark brown with broad IR absorption in the C–N region, in addition to cumulated double bond absorption (*e.g.*, C=N=N) at 2160 cm^{-1} (Fig. 2B). Both vapor deposited films display sharp and very similar IR absorption peaks, indicating improved ordering at a local bonding level (Fig. 2C and 2D). The peaks are consistent with C=N linkages, and secondary/tertiary amine (C–N) motifs. There are also clear N–H stretching modes (3200–3400 cm^{-1}), slightly shifted from those in the powder spectra. The peak near 800 cm^{-1} is a

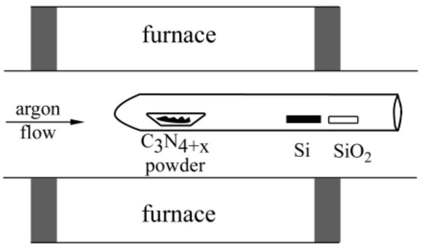

Fig. 1 Schematic for film growth by vapor transport of carbon nitride powder.

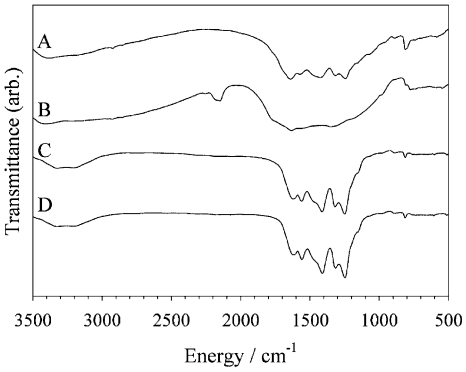

Fig. 2 Infrared spectra for (A) TCM-C_3N_5 powder, (B) TAT-C_3N_5 powder, (C) film on Si from TCM-C_3N_5 powder, (D) film on Si from TAT-C_3N_5 powder.

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† Electronic supplementary information (ESI) available: complete experimental procedures, characterization information, Auger spectra. See http://www.rsc.org/suppdata/cc/b2/b207041c/.

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triazine ring mode, suggesting that the triazine precursor motif translates from the powder to the growing films.

While IR indicates that the vapor deposited C_3N_{4+x} films are more structurally ordered than the powders, they show no crystallographic ordering by powder X-ray diffraction and no active molecular or graphitic modes (D and G) by Raman spectroscopy. Several layered C_3N_{4+x} structures have been previously proposed that are based on interconnected triazine rings, in some cases bridged by secondary amine linkages (> NH),[9–11] and our films may contain ordered regions that are consistent with these structures.

The UV-vis optical absorption properties of both deposited films on silica are consistent with their pale yellow color (Fig. 3). An extrapolation of each curve's maximum slope to zero transmittance corresponds to cutoff wavelengths of 320 nm (3.88 eV) and 300 nm (4.14 eV) for the TCM-C_3N_5 and TAT-C_3N_5 films, respectively.

While the TCM-C_3N_5 powder shows blue photoluminescence,[10] the more structurally disordered TAT-C_3N_5 powder does not show any detectable emission in the visible region. In contrast, the carbon nitride films deposited from both of these powders show clear emission in the blue region (Fig. 4). The room temperature photoluminescence spectra for the films from TCM-C_3N_5 and TAT-C_3N_5 are broad and have peak emission at 455 nm and 450 nm, respectively. Under illumination by a handheld UV lamp, the films are pale greenish-yellow in color, possibly because the broad-spectrum lamp activates additional yellow emission modes.

In summary, this report demonstrates that thermally robust nitrogen-rich carbon nitride powders (C_3N_{4+x}), synthesized from triazine-based precursors, are useful starting materials for the vapor transport growth of carbon nitride films that exhibit blue photoluminescent emission. We are currently examining the effect of chemical influences (*e.g.*, protonation and metal complexation) on carbon nitride film luminescence, for potential chemical sensor and color tuning applications.

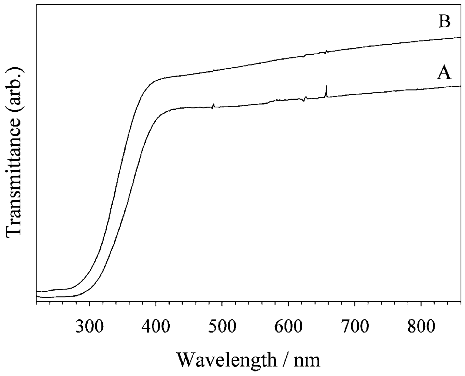

Fig. 3 UV-visible spectra for films on SiO_2 deposited from (A) TCM-C_3N_5 powder and (B) TAT-C_3N_5 powder.

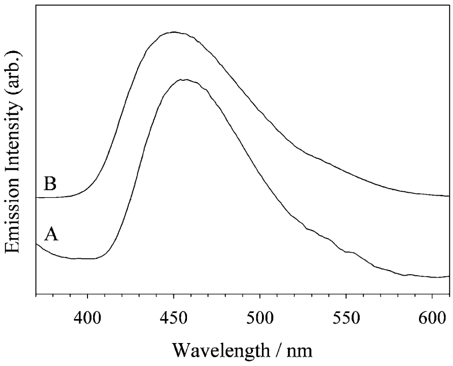

Fig. 4 Photoluminescent emission (340 nm excitation) from films on Si deposited from (A) TCM-C_3N_5 powder and (B) TAT-C_3N_5 powder.

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