Carbon Nitride Thin Films as All-In-One Technology for Photocatalysis

Stefano Mazzanti, Giovanni Manfredi, Alex J. Barker, Markus Antonietti, Aleksandr Savateev,* and Paolo Giusto*

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ABSTRACT: Organic π-conjugated polymers are promising heterogeneous photocatalysts that involve photoredox or energy transfer processes. In such settings, the materials are usually applied in the form of dispersion in liquid medium, which is bound to certain technological limits of applicability. Herein, we present an innovative approach using carbon nitride thin films prepared via chemical vapor deposition at different vessel walls and using them as batch and microfluidic photoreactors. This approach allows us not only to fabricate technologically relevant and reusable devices but also to improve photophysical properties of carbon nitride, such as the singlet−triplet energy gap and lifetime of triplet excited states, when the material is assembled in thin films. These morphological changes are employed to maximize the performance of the materials in photocatalytic reactions, in which the carbon nitride thin films show at least 1 order of magnitude higher activity per area unit compared to photocatalysis using suspended particles.

KEYWORDS: *carbon nitride, chemical vapor deposition, flow chemistry, photocatalysis, thin films*
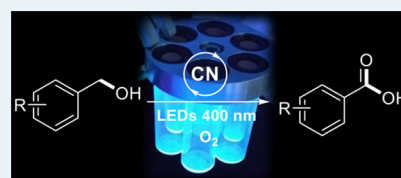
1. INTRODUCTION

Photoredox catalysis enables unique reaction pathways to high value-added products that are not available with classical thermal activation of the molecules.[1−4] Recently, visible light photocatalysis has gained high momentum, not only in academic research but also in the chemical industry as a new synthetic tool,[5,6] in the preparation of fine chemicals and active pharmaceutical ingredients.[7−10]

In general, photoredox catalysis can be divided into homogeneous and heterogeneous catalyses, both effectively mediating a number of photochemical transformations.[11] However, each of these approaches possesses unique advantages and disadvantages. For example, homogeneous photocatalysis provides very high density of redox sites per volume unit in solution. On the other hand, a unique feature of heterogeneous photocatalysis is tuning properties of the employed material, which typically is a semiconductor, by adjusting its morphology. In other words, semiconductor particles with essentially the same bulk chemical composition, but having, for example, variable diameter,[12] aspect ratio between different facets of the single crystal,[13] just to name a few,[14] possess different photophysical properties and therefore demonstrate different activities.

Despite an outcome of a certain photocatalytic reaction mediated by either the homogeneous or heterogeneous photocatalyst is the same, the underpinning mechanism is quite often different.[15] In homogeneous organic photoredox catalysis, represented, for example, by organic dyes, triplet excited states of the sensitizer with lifetime in the μs−ms range are often engaged.[16] While inorganic semiconductors do not possess triplet states, organic π-conjugated systems fall in between inorganic semiconductors, in terms of their heterogeneous nature and processability, and molecular sensitizers, due to similarities of their local structure. Carbon nitride (CN), a polymeric semiconductor with the ideal formula C_3N_4, constituted by heptazine or triazine units cross-linked via nitrogen bridges and stacked in a graphitic fashion, is one type of such materials.[17,18] It has been actively studied in organic photocatalysis.[19,20] For example, it has been shown that upon excitation, carbon nitrides undergo singlet−triplet intersystem crossing (ISC) and form triplet excited states with the lifetime of up to hundreds of microseconds.[21−23] In organic photocatalysis, triplet states in carbon nitrides have been employed in energy transfer (EnT) to O_2 in the synthesis of oxadiazoles-1,2,4[21] and sensitization of the Ni(II) co-catalyst in arylation of $C(sp^3)$-H bonds in amides.[24]

Semiconductor photocatalysis also offers multiple engineering solutions.[25] For example, coating of the photoreactor wall with semiconductor particles is an appealing feature in combination with flow technology.[26] In this regard, Wang et al. recently reported on a fixed-bed flow system employing CN supported on glass fibers and beads.[27] However, backscattering
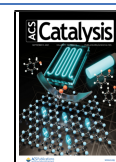
from the surface limits accessibility of photons and reduces efficiency of the reactor.

For high-throughput screening (HTS) in photocatalysis and flow technology, an ideal solution would be a thin transparent layer of the semiconductor deposited at the inner wall of the photoreactor. Thermal chemical vapor deposition (CVD) offers an elegant solution to grow such thin films by reacting precursors in the gas phase followed by deposition at the surface of the desired substrate.[28] Indeed, the approach has been validated in the preparation of CN thin films.[29,30] Carbon nitride thin films deposited at conductive substrates by CVD are applied mainly as photoelectrodes demonstrating current densities of several hundreds μA cm^{-2}, IPCE > 12%, and faradaic efficiency toward O_2 of 40.3−51% at +1.23 V, which underlines robustness, reproducibility, and operational simplicity of the method.[31−34]

Very recently, our group reported a method to obtain highly homogeneous CN thin films over areas of several dozens of cm^2 on different substrates, regardless of their shape and surface topology by means of CVD under highly controlled conditions of vacuum, gas flow, and temperature.[35,36] High homogeneity and flatness allowed for applying these CN thin films in optics, showing that they have a very high refractive index comparable to that of diamond in the visible range.

In the last decade, CN as a material in general has been studied in water splitting, production of hydrogen,[37] conversion of CO_2 into valuable products,[38] and synthesis of fine chemicals.[39−44] Due to the exciting properties of CN, the scope of applications for this material spans beyond photocatalysis, for example, to optoelectronics,[45,46] energy and membrane separation,[47] among others.[48,49]

Rich experimental data of using CN particulates in photocatalysis, as well as unique opportunities offered by this class of materials in combination with the CVD, enabled us to explore the highly homogeneous thin and transparent CN film as active coating in photoreactors.

Herein, we present an innovative approach in photocatalysis using nanometer-thick CN films deposited on different glass surfaces, such as standard glass vials and the microfluidic reactor plate, by means of CVD. The glassware with the photocatalytically active layer is tested in the oxidation of benzyl alcohols under light irradiation.

2. RESULTS AND DISCUSSION

We coated standard 4 mL glass vials that are also used by many research groups working in the field of automated photoredox catalysis across the world, with the CN thin film using CVD similar to the earlier reported procedure.[35,36] In this way, visible batch wall reactors (Vis-BWR) were fabricated (Figure 1a). Deposition of the CN film on the reactor wall after the CVD is seen with naked eye by its typical yellowish color, photonic reflections, and the deep blue fluorescence when the Vis-BWR is exposed to UV light (Figure 1b).[50] The CN film strongly absorbs photons with wavelength ≤420 nm as confirmed by the UV−vis absorption spectrum (Figure S1a). In the steady-state photoluminescence spectrum, the maximum is observed at 460 nm (Figure S1b).

A CN film with a thickness of about 111 nm was obtained as evidenced by atomic force microscopy (AFM) (Figure S2). CN coating in the Vis-BWR is homogeneous and flat, while surface roughness is <1 nm over the field of view 5 × 5 μm^2, as confirmed by AFM (Figure S3) and scanning electron microscopy (SEM, Figure 2a). Despite the fluorescence
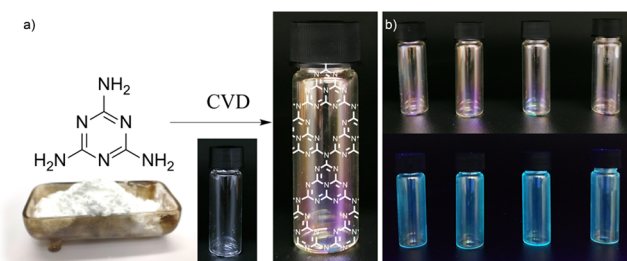

Figure 1. Fabrication of Vis-BWR and their appearance. (a) Schematic representation of the CVD process of vial coating with CN, showing the ideal heptazinic structure. (b) Vis-BWR under visible and 365 nm light.

quantum yield of the CN films is relatively low (<0.6%), emission can be observed even by naked eye. For further analysis, the CN film was completely removed from the selected area of the vial by mechanical treatment. By comparing the cleaned area of the vial with the untreated area after the CVD, the presence of the CN film on the glass surface was confirmed by energy-dispersive X-ray spectroscopy (EDX) mapping (Figure 2b−d).[51] At the nanoscale, the film reveals the presence of a layered structure, where each shade of gray represent a stack of layers in graphitic-like fashion (Figure 2e). The graphitic-like structure was further confirmed by X-ray diffraction, where we identified the $\pi−\pi$ stacking peak at 27.4° (Figure S5). Based on the interlayer distance of 0.33 nm and film thickness of 111 nm, we estimate the average number of layers in the CN film to be ca. 350. Electron energy loss spectroscopy (EELS) reveals the presence of carbon (as a peak at 287 eV) and nitrogen (400 eV), which are integrated in the strongly sp^2−conjugated structure as confirmed by the pronounced π* peak (Figure 2f). The surface of the CN film is free of oxygen contaminations as concluded from the absence of a peak at ca. 532 eV (Figure 2f), which is in good agreement with previous results.[35,52] In the present study, EELS provides a qualitative analysis on the type of bonds and conjugation. The measurement is not quantitative because in anisotropic systems, the response depends not only on the magnitude of the applied energy but also on the orientation of the sample.[53,54]

The high quality of the deposition achieved on the vials provides a solid evidence to transform, in principle, every piece of lab glassware, such as vials, test tubes, and flasks, into a Vis-BWR, according to the reaction requirements.

CVD allows growing CN thin films, while at the same time, the technique does not alter substantially the positions of the highest occupied molecular orbital and lowest unoccupied molecular orbital,[35] which in combination with numerous earlier reports using the suspended CN particulate, enables us to consider such films as very promising candidates for using them as photocatalysts in net oxidative reactions under visible light. Taking into account the innovative approach used in this work, we have chosen oxidation of benzyl alcohols to benzoic acid as a benchmark reaction to compare the performance of the CN thin films and Vis-BWRs with other photocatalysts and photocatalytic systems. Acetonitrile was chosen as a solvent due to its polarity and high capacity toward dissolution of oxygen and high chemical stability against reactive oxygen species, such as superoxide radicals and singlet oxygen.[55] Thorough optimization of reaction conditions is given in the Supporting Information (Table S1). Control experiments confirmed that the reaction is purely photocatalytic. Thus,
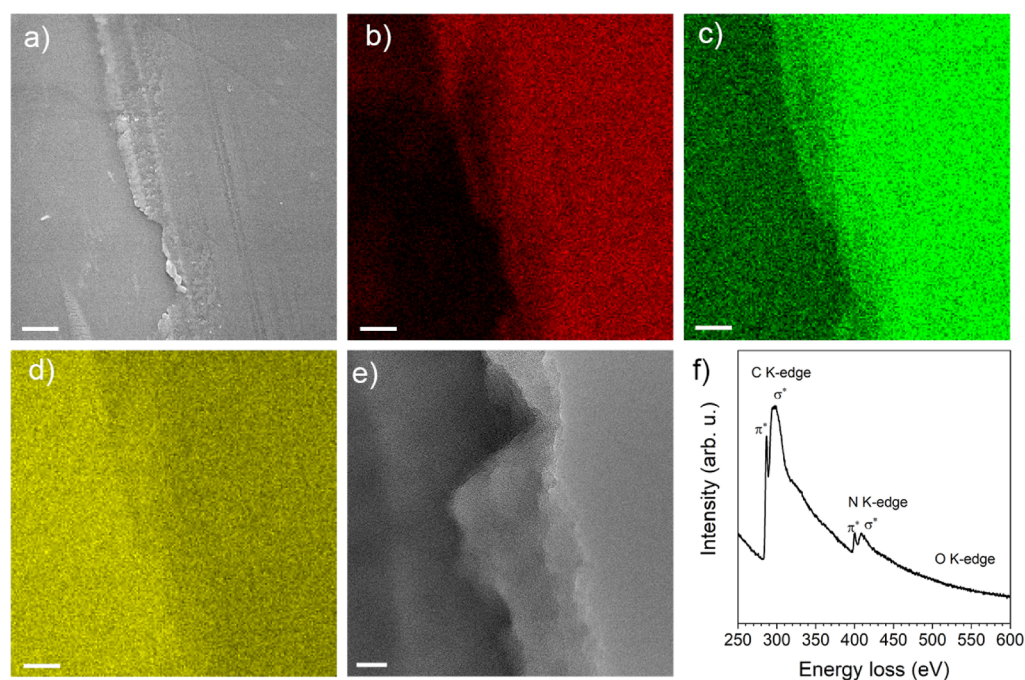
Figure 2. CN film characterization. (a) SEM image of a scratched area of the coated vial. (b−d) SEM−EDX mapping of carbon (in red), nitrogen (in green), and silicon (in yellow); scale bar 2 μm. (e) TEM image of the CN thin film (scale bar 20 nm) and (f) EELS core loss spectrum.
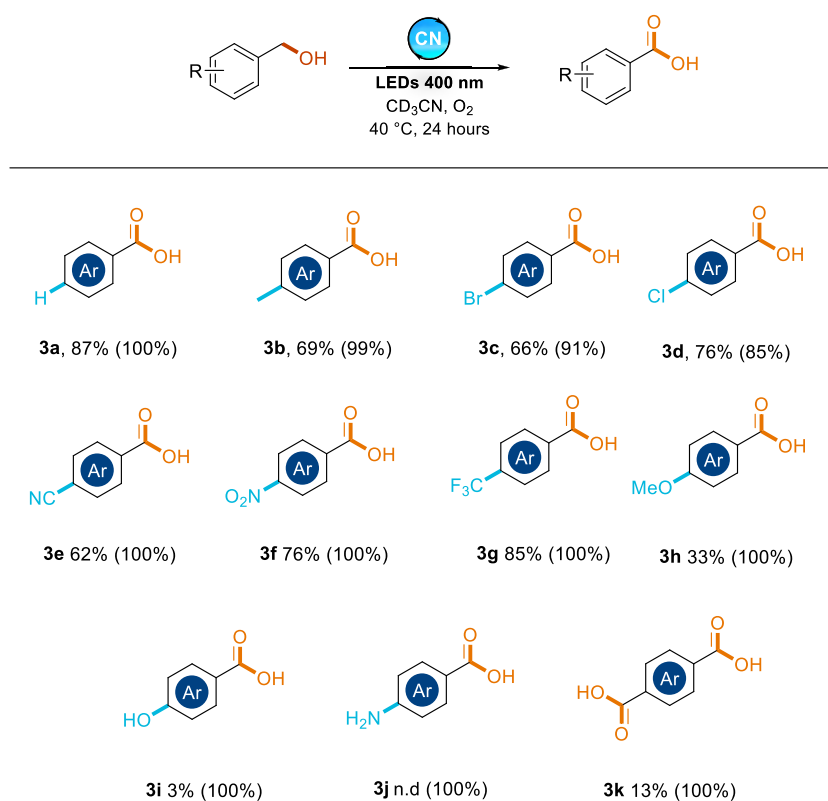

Figure 3. Scope of benzyl alcohols. Reaction conditions: alcohol (0.01 mmol), CD_3CN (3 mL), O_2 (1 bar), reaction was conducted in 4 mL Vis-BWR. See the experimental procedure for details in the Supporting Information. Yields and conversions (in parentheses) have been determined using 1,3,5-trimethoxybenzene as an internal standard by ^1H NMR.

no benzoic acid was obtained in the absence of the CN films, excluding the thermal effects induced by heating originating from the light source as a potential driving force (entry 14). Reaction did not proceed in the dark either (entry 15). Under optimized conditions, benzoic acid was obtained in 87% yield along with the quantitative conversion of benzyl alcohol under illumination with 400 nm LED for 24 h. Recently, Hutchings et al. showed that benzyl alcohol acts as a quencher of the radical species in the thermal oxidation of benzaldehyde to benzoic acid, even at very low concentrations, which explains

the formation of benzaldehyde in our case at lower conversions (Table S1, entries 1−12, Figure S7).[56]

After finding optimal reaction conditions, we expanded the scope of benzyl alcohols (Figure 3). The method provides a simple procedure for the preparation of substituted benzoic acids. Substrates bearing poorly electron donating or electron withdrawing groups at the aromatic ring have been converted into the corresponding benzoic acids in good and high yields (3a−g). On the other hand, alcohols bearing strong electron donating groups were fully consumed, but the corresponding acids were obtained in poor or no yields (3h−k). Lower tolerance of the functional groups to reactive oxygen species is apparently responsible for lower selectivity in these cases (Figure S8 and S9).[57]

The conventional CVD method allows for fabricating several vials at once with high reproducibility, which makes the technology highly relevant to the needs of high-throughput photocatalysis (Figure 4a).[58] In addition, Vis-BWR coated with the CN thin film are stable and can be reused many times, here proven only for three to five catalytic cycles (Figure 4b).

To evaluate the performance of the CN films and compare it with that of other photoredox catalysts, we determined the apparent quantum yield (AQY). Vis-BWR showed an AQY of 1.8%, which is higher compared to that of commonly used Ir and Ru sensitizers (Figure S11). The AQY of Vis-BWR is comparable to that of mesoporous graphitic-CN (mpg-CN)

and it is higher than for potassium poly(heptazine)imide (K-PHI).[39,59] Additionally, Vis-BWR shows higher activity per area unit compared to dispersions of semiconductor particles (see Figure S12 and the relevant discussion therein). Explanation of enhancement of the activity is given below taking into account the results of time-resolved spectroscopic characterization of the CN thin films.

Vis-BWRs having different thicknesses of the CN film (123, 111, and 55 nm) were also prepared to investigate the influence of this parameter on the photocatalytic activity (Figure S13). The data show that the thicker the CN film, the faster is kinetics, which in turn leads to higher selectivity toward benzaldehyde (Figure S14a). This study agrees with the fact that the number of available excitons correlates with the number of absorbed photons, and thus, it is proportional to the number of photoactive layers. Although the geometric surface area of the CN films is the same, the efficiency is improved by increasing the number of layers (thickness). The steady-state fluorescence spectra of Vis-BWRs show that there are fewer recombination events in thinner films, which probably stems from the fact that excitons are more likely to reach the film surface (Figure S14b). Nevertheless, faster kinetics of benzyl alcohol oxidation in case of thicker films indicates that recombination of excitons as a side process does not contribute significantly to the overall efficiency.

We also investigated the possible chemical modifications of the carbon nitride surface of the BWR during the reaction. The steady-state UV−vis absorption spectrum of the BWR after five photocatalytic cycles showed a shift of the absorption edge to shorter wavelengths, but no additional features in the visible range evolved (Figure S15a). A slight shift of the emission maximum in the PL spectrum was observed in the case of the BWR (Figure S15b). Such observations are explained bythe partial exfoliation of the thin films from the vessel walls after five catalytic experiments rather than chemical modification of the carbon nitride film. This conclusion is also in agreement with the investigation of a series of films of variable thickness, where photoluminescence and catalytic activity decrease by decreasing the number of photoactive layers (Figure S14).

Immobilization of the CN films at the glass surface simplifies the work-up procedure and more importantly eliminates the necessity of photocatalyst separation. These features prompted us to study the CN films in combination with flow technology. Microfluidic reactors are a promising class of chemical reactors, which offer significant advantages as compared to batch reactors, such as larger scale production (seamless scalability), precise control over the residence time, and local stoichiometry.[60] Here, two mirror parts of a microfluidic reactor (channel diameter 250 μm) were coated homogeneously with the CN thin films on the channel walls to obtain a visible (microfluidic) flow wall reactor (Vis-FWR) (Figure 4c). The Vis-FWR was again tested with the oxidation of benzyl alcohols 1a−c, 1g, and 1k under illumination with 400 nm. In this setting, the main products are benzaldehydes 2a−c, 2g, and 2k in excellent yields 86−100% with much shorter reaction time, applying recirculation of the reaction mixture (Figure 4c). In this configuration, the reaction proceed at higher conversion rates due to the higher surface area/volume ratio in the microchannels, preventing the consecutive oxidation of aldehyde to the corresponding acid. Oxidation of 1a in flow to benzaldehyde 2a follows quasi zero order kinetics, probably due to the photon limited regime (Table S3, Figure S16).
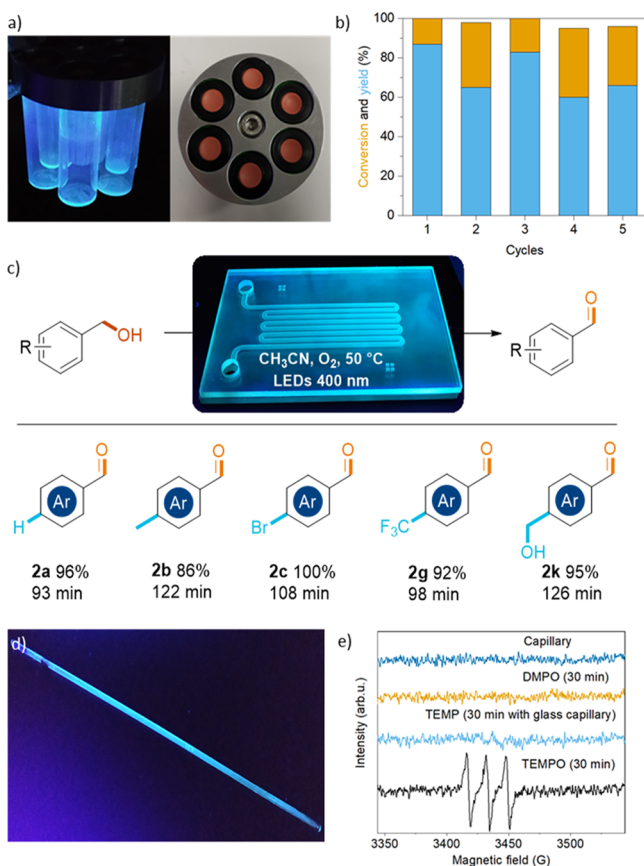

Figure 4. Application of the CN thin film in photocatalysis. (a) Vis-BWR for high-throughput screening. (b) Recyclability of Vis-BWR. (c) Scope of benzyl alcohols in flow (inset shows the half cell of Vis-FWR coated with the CN film under 365 nm light, see Supporting Information for more details). (d) Coated capillary. (e) TEMPO generation and detection via in situ EPR.

To gain insights into the nature of reactive oxygen species in the photocatalytic oxidation of benzyl alcohol and to propose a mechanism, we applied in situ EPR spectroscopy using a glass capillary coated with the CN film by CVD, in the same way as the Vis-BWR and Vis-BFR were produced (Figure 4d). The capillary was charged with the solution of 2,2,6,6-tetramethyl-piperidine in the O_2 saturated solution of MeCN followed by irradiation with 415 nm in the cavity of the EPR spectrometer. Appearance of the TEMPO signal indicates that in this set of experiments, CN films sensitize singlet oxygen ($^1O_2$) (Figure 4e, see Supporting Information for further details).

Eventually, we applied time-resolved spectroscopy to gain insights into the changes of CN excited-state dynamics, which result from the assembly of this material into thin films. Thus, photophysics of the excited state was investigated using time-correlated single photon counting time-resolved photoluminescence (tr-PL) and transient absorption spectroscopy (TAS). PL decay is well fitted ($R^2 > 0.99$) using a single stretched exponential function with a time exponent of half and a lifetime of ~0.6 ns (Figure S17, Table S4). Such behavior is common for polymer systems that present defects and traps (primary and secondary amines as terminal groups in this case),[61,62] in good agreement with the recorded relatively low internal quantum efficiency of 0.6% (Figure S1b).[63]

According to the TAS data acquired under N_2 (Figure S18), excitation of the CN film leads to the appearance of a broad band in the observed wavelength range (500−750 nm) ascribed to excited state absorption (ESA).[64] Such behavior of the CN thin films is significantly different from the dispersion of CN in the liquid phase reported earlier.[21,61] Therein, a negative photoinduced ΔOD signal in the visible range was attributed to ground-state bleaching (GSB) of the CN, whereas we observe a positive ΔOD signal from the CN thin films, indicating a transient photoinduced absorption.[61] Therefore, in case of the CN film, the net signal composed of the CN GSB and ESA is positive.

Analysis of the ESA decay in the femto- to microsecond time scale suggests that the process is characterized by two lifetimes (Figure S19). The faster process is described by the same parameters ($\beta = 1/2$ and $\tau = 0.6$ ns) as tr-PL, which suggest that the singlet excited states (S_1) of the CN possess broad absorption in the visible range (Table S5). We assume that the depopulation of S_1 in the CN film proceeds via three pathways: (i) radiative relaxation, (ii) singlet−triplet ISC, and (iii) nonradiative recombination. Taking into account extremely low fluorescence quantum yields, <0.6% (Figure S1b), the first pathway is not dominant. The second, slower process, of the CN ground-state recovery corresponds to the depopulation of the triplet excited states (T_1) in the CN film. Furthermore, a channel by which T_1 is converted back into S_1, such as triplet−triplet annihilation (TTA, which would exhibit a density-dependent rate), explains the intensity dependence of the TA recombination rate in the nano- to microsecond time scale (Figure S20) and the longer time constants obtained, when the CN film was in degassed acetonitrile (Table S6).[22] TTA also contributes to the tail of long-lived emission seen in tr-PL, although the significant stretching rates of both PL and TA kinetics is likely due more to disorder in the excitonic landscape of CN materials.[65] The absence of the noticeable peak shift in the TAS indicates a vanishingly small singlet−triplet energy gap, which might be the additional pathway of S_1−T_1 interconversion.

Overall, different photophysics of the CN thin films, compared to the reported earlier, obviously stems from different synthesis conditions—polycondensation of the precursor in bulk at atmospheric pressure (used earlier)[61] and polycondensation−deposition of carbon nitride in thin layers from vacuum under the controlled conditions in the CVD system (gas-to-solid reaction in this work). Apart from being indispensable to create durable technological devices, CVD also produces the CN material with narrow ΔE_{ST}, which facilitates singlet−triplet ISC. Until now, CN materials prepared by condensation of the precursors in bulk have been reported to have a ΔE_{ST} value of 0.243−0.248 eV.[21,22] Furthermore, the absence of voids in the structure of the CN thin film is also beneficial to suppress the nonradiative recombination of triplet excited states (vibrational relaxation) by decreasing free volume in the crystal lattice and surface defects.[66,67] These differences strongly point that a strict control over preparation conditions of the photocatalysts defines the nanostructure of the sensitizer and influences the material photophysical properties to achieve high activity in photocatalytic reactions that involve EnT.

We combine the results of the spectroscopic study with experimental data and propose the following mechanism of benzyl alcohol oxidation by the CN thin films (Figure 5a).
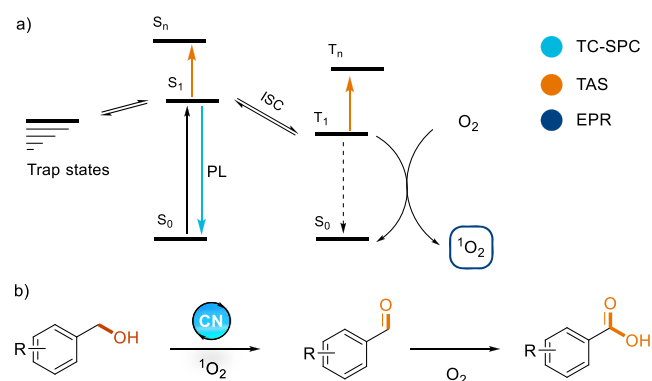

Figure 5. Mechanism of benzyl alcohol oxidation using thin CN films. (a) Proposed photophysical mechanism. (b) Photocatalytic mechanism of benzyl alcohol oxidation to benzaldehyde and subsequent thermal oxidation to benzoic acid.

Absorption of light by the CN thin film leads to the formation of the CN singlet excited states (S_1). Part of the singlet excited states undergoes ISC to form triplet excited states (T_1) characterized by lifetime, which are long enough to interact with O_2 via the EnT mechanism. Indeed, tr-PL data acquired for the CN thin films in oxygenated and degassed CH_3CN clearly indicate that singlet excited states are not quenched by oxygen—S_1 life time is ca. 0.6 ns regardless of the environment (Table S4). On the other hand, TAS data indicate that O_2 does quench triplet excited states as its lifetime decreases from 238 to 158 ns (Table S5). Once formed, $^1O_2$ reacts with benzyl alcohol producing benzaldehyde and presumably H_2O_2.[68] Then, benzaldehyde is converted to benzoic acid either via the thermal or photocatalytic pathway (Figure 5b).

Hence, the developed technology not only makes the Vis-BWR a convenient choice to conduct a photocatalytic reaction but is also more efficient compared to the analogous dispersion of the photocatalyst in the liquid medium.

3. CONCLUSIONS

In this work, we presented an innovative approach in visible photocatalysis exploiting CN thin films.

A common lab vial was coated employing CVD becoming a reusable reactor itself. We exploited the as-coated vials as photoreactors in the one-step oxidation of 10 alcohols, in which corresponding benzoic acids have been obtained with up to 87% yield in 24 h. Based on EPR, time-resolved emission and absorption spectroscopy, oxidation of benzyl alcohols mediated by the CN thin films involves singlet oxygen, which is sensitized via EnT from triplet excited states. Furthermore, we applied this technology also to microfluidic systems by coating the two mirror parts of a microfluidic flow reactor. The latter was successfully tested in the oxidation of five different substituted benzyl alcohols, selectively leading to benzalde-hydes with excellent yield with much shorter reaction time. We believe that the technology developed herein is a significant step forward for the improvement of photocatalysis, both at a research and industrial level, because it allows us to craft different photocatalytic tools by coating diverse objects with complex geometries, otherwise out of reach with other preparative methods. Indeed, the utilization of thin-film technology allows us to truly implement photocatalysis in automated labs, such as HTS, as no time-demanding post-separation steps of the heterogeneous photocatalysts are required, such as filtration or centrifugation. Furthermore, using CN thin films, we further overcome the typical problems occurring also in microfluidic flow reactors with heterogeneous photocatalysts, such as fouling and clogging of the reactor and/or pumping system. Exploiting CN thin films would also allow us to make more complicated tandem or cascade reaction setups, by combining different flow reactors, or graft from the surface desired functional species in a desired position, such as small molecules, polymers, and eventually enzymes. Beyond that, the presented technology can be exploited not only for photocatalysis, but furthermore for electro- and thermo-catalyses or any of their combination. Eventually, we believe that the presented technology will pave the way for new, safer, more sustainable and thereby exciting chemistry, combining the advantages of thin films and (photo-)catalysis, whereby limits are dictated by scientist imagination.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.1c02909.

Methods; material characterization; photocatalytic and photophysical studies; products characterization (PDF)

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