

# Photocatalysis Goes Thinner Than a Hair: Carbon Nitride Thin Films as All-in-one Technology for Photocatalysis

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## Abstract

Organic  $\pi$ -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 a 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 (CVD) at different vessel walls and using them as batch and microfluidic photoreactors. This approach allows not only to fabricate technologically relevant and reusable devices, also photophysical properties of carbon nitride, such as singlet-triplet energy gap and lifetime of triplet excited states, are improved, when the material is assembled in thin films. These morphological changes are employed to maximize performance of the materials in photocatalytic reactions, in which the carbon nitride thin films show at least one orders 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.<sup>1, 2, 3, 4</sup> Recently, visible light photocatalysis has gained high momentum, not only in academic research, but also in chemical industry as a new synthetic tool,<sup>5, 6</sup> in preparation of fine chemicals and Active Pharmaceutical Ingredients (API).<sup>7, 8, 9, 10</sup>

In general, photoredox catalysis can be divided into homogeneous and heterogeneous catalysis, both effectively mediating a number of photochemical transformations.<sup>11</sup> 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,<sup>12</sup> aspect ratio between different facets of the single crystal,<sup>13</sup> just to name a few,<sup>14</sup> possess different photophysical properties and therefore demonstrate different activity.

Despite an outcome of a certain photocatalytic reaction mediated either by homogeneous or heterogeneous photocatalyst is the same, the underpinning mechanism is quite often different.<sup>15</sup> In homogeneous organic photoredox catalysis, represented, for example, by organic dyes, triplet excited states of the sensitizer with lifetime in  $\mu\text{s}$ -ms range are often engaged.<sup>16</sup> While inorganic semiconductors do not possess triplet states, organic  $\pi$ -conjugated systems fall in between inorganic semiconductors, in terms of their heterogeneous nature and processability, and molecular sensitizers, due to similarities of their local structures. Carbon nitride (CN), a polymeric semiconductor with ideal formula  $\text{C}_3\text{N}_4$ , constituted by heptazine or triazine units cross-linked via nitrogen bridges and stacked in a graphitic fashion, is one type of such materials.<sup>17</sup> It has been actively studied in organic photocatalysis.<sup>18, 19</sup> 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  $\mu\text{s}$ .<sup>20, 21</sup> In organic photocatalysis, triplet states in carbon nitrides

have been employed in energy transfer (EnT) to O<sub>2</sub> in synthesis of oxadiazoles-1,2,4<sup>20</sup> as well as sensitization of Ni(II) co-catalyst in arylation of C(sp<sup>3</sup>)-H bonds in amides.<sup>22</sup>

Semiconductor photocatalysis also offers multiple engineering solutions.<sup>23</sup> For example, coating of the photoreactor wall with semiconductor particles is appealing feature in combination with flow technology.<sup>24</sup> In this regards, Wang et al. recently reported on a fixed-bed flow system employing CN supported on glass fibers and beads.<sup>25</sup> 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 semiconductor deposited at the inner wall of the photoreactor. Very recently, our group reported a method to obtain highly homogeneous CN thin films over areas of several dozens of cm<sup>2</sup> on different substrates, regardless of their shape and surface topology by means of chemical vapor deposition (CVD).<sup>26, 27</sup> The high homogeneity and flatness allowed to apply 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, to create hydrogen,<sup>28</sup> in converting CO<sub>2</sub> into valuable products,<sup>29</sup> and synthesis of fine chemicals.<sup>30, 31, 32,33</sup> Due to exciting properties of CN, the scope of applications for this material spans beyond photocatalysis, for example, to optoelectronics,<sup>34, 35</sup> energy and membrane separation,<sup>36</sup> among others.<sup>37, 38</sup>

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 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 microfluidic reactor plate, by means of CVD. The glassware with the photocatalytically active layer is tested in 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.<sup>26, 27</sup> 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).<sup>39</sup> The CN film strongly absorbs photons with wavelength  $\leq 420$  nm as confirmed by the UV-vis absorption spectrum (Figure S1a). In the steady-state photoluminescence spectrum, the maximum is observed at 470 nm (Figure S1b).

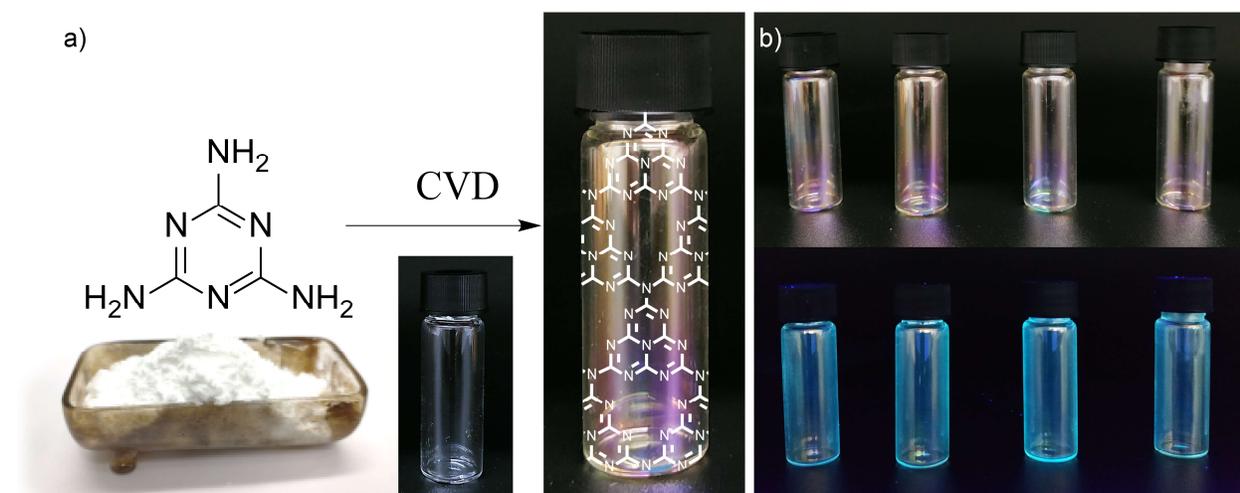


Figure 1 – Fabrication of Vis-BWR and their appearance. a) Schematic representation of the CVD process of vial coating with CN, showing the ideal heptazine structure. b) Vis-BWR under visible and 365 nm light.

A CN film with a thickness of about 170 nm was obtained as evidenced by atomic force microscopy (AFM) (Figure 2a). CN coating in the Vis-BWR is homogeneous and flat, while surface roughness is  $< 1$  nm over the field of view  $5 \times 5 \mu\text{m}^2$ , as confirmed by AFM (Figure S2) and scanning electron microscopy (SEM, Figure 2b). Despite fluorescence 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 2c-e).<sup>40</sup> At the nanoscale, the film reveals the presence of a layered structure, where each shade of grey represent a stack of graphitic layers (Figure 2f). Graphitic-like structure was further confirmed by X-ray diffraction, where we identified the  $\pi$ - $\pi$  stacking peak at  $27.4^\circ$  (Figure S4). Based on interlayer distance of 0.33 nm and film thickness of 170 nm, we estimate average number of

layers in the CN film to be ca. 500. Electron energy loss spectroscopy (EELS) reveals the presence of carbon (as a peak at 287 eV) and nitrogen (400 eV), which are integrated in strongly  $sp^2$ -conjugated structure as confirmed by pronounced  $\pi^*$  peak (Figure 2g). The surface of the CN film is free of oxygen contaminations as concluded from the absence of a peak at ca. 532 eV (Figure 2g), which is in good agreement with previous results.<sup>26</sup> 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, flasks, into a Vis-BWR, according to the reaction requirements.

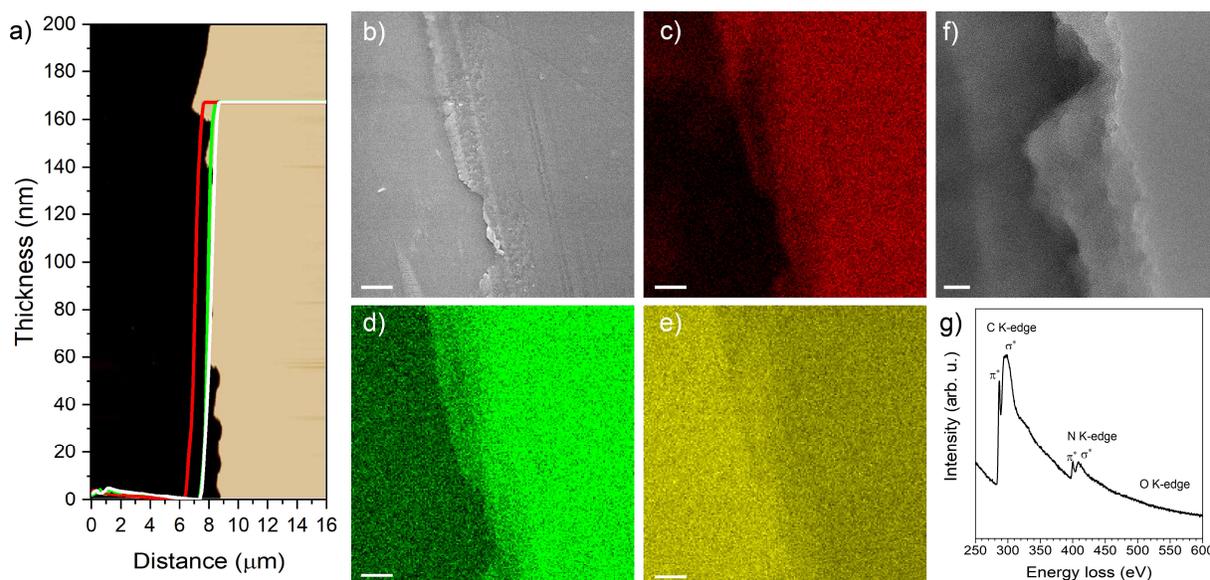


Figure 2 – CN film characterization. a) AFM step-height analysis of the CN thin film deposited on the 4 ml vial (background is the original image obtained from the AFM, superimposed with the graph). b) SEM image of a scratched area of the coated vial; c-e) SEM-EDX mapping of carbon (in red), nitrogen (in green) and silicon (in yellow); scale bar 2  $\mu\text{m}$ . f) TEM image of the CN thin film (scale bar 20 nm) and g) EELS core loss spectrum.

CVD allows growing CN thin films, while at the same time the technique does not alter substantially positions of HOMO and LUMO,<sup>26</sup> which in combination with numerous earlier reports using suspended CN particulate, enables us to consider such films as very promising candidates for using them as photocatalyst in net oxidative reactions under visible light. Taking into account innovative approach used in this work, we have chosen oxidation of benzyl alcohols to benzoic acid as a benchmark reaction to compare 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 towards dissolution of oxygen and high chemical stability against reactive oxygen species, such as superoxide radicals and

singlet oxygen.<sup>41</sup> Thorough optimization of reaction conditions is given in the Supporting Information (Table S1). Control experiments confirmed that the reaction is purely photocatalytic. Thus, 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 potential driving force (entry 14). Reaction did not proceed in dark either (entry 15). Under optimized conditions benzoic acid was obtained in 87% yield along with quantitative conversion of benzyl alcohol under illumination with 400 nm LED for 24 hours.<sup>42</sup> 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 formation of benzaldehyde in our case as well (entries 1-12).<sup>43</sup>

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 group 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.<sup>44</sup>

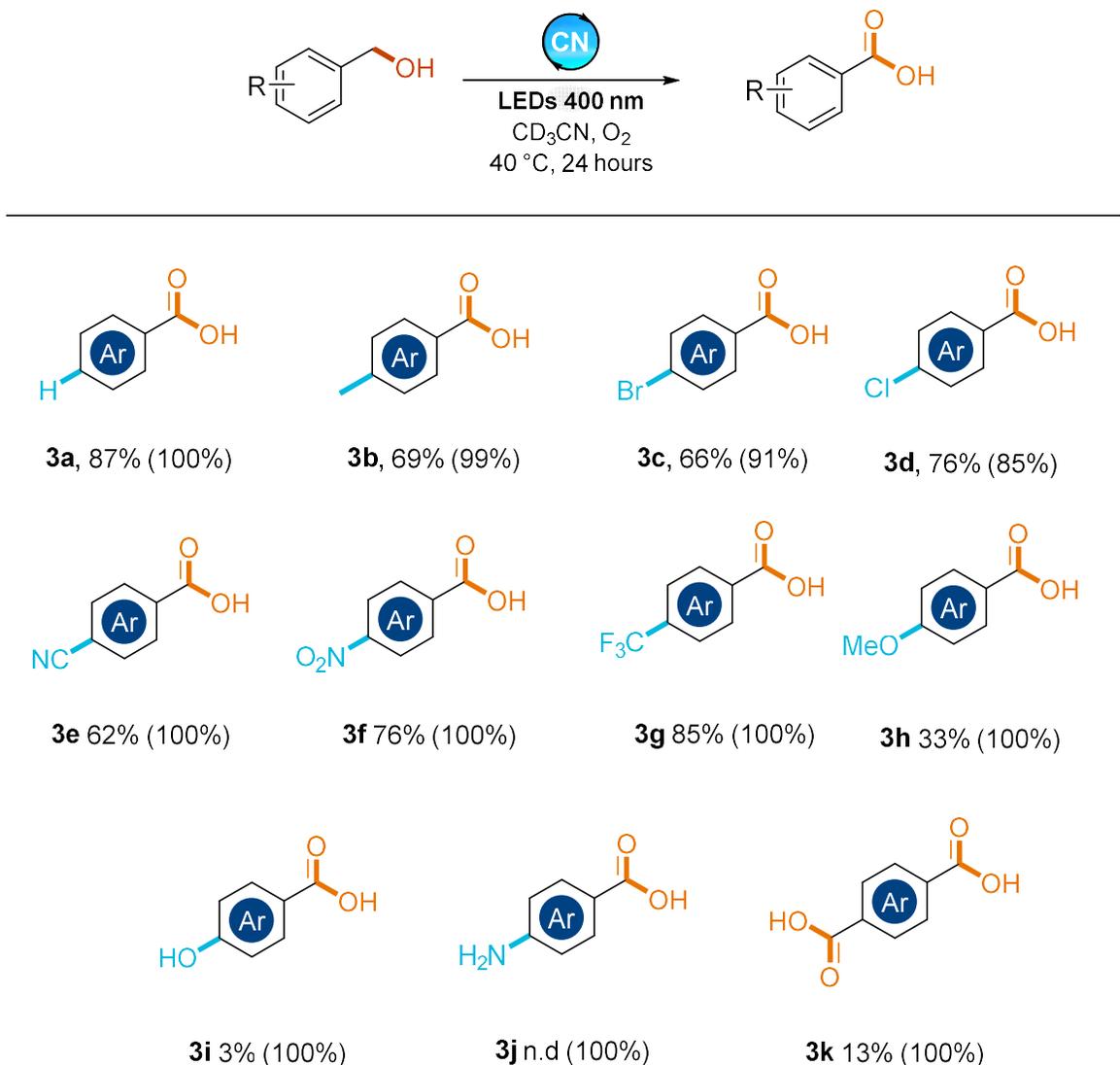


Figure 3 – Scope of benzyl alcohols. Reaction conditions: alcohol (0.01 mmol),  $CD_3CN$  (3 mL),  $O_2$  (1 bar), reaction was conducted in 4 mL Vis-BWR. See experimental procedure for details in ESI. Yields and conversions (in parentheses) have been determined using 1,3,5-trimethoxybenzene as internal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

Conventional CVD method allows fabricating several vials at once with high reproducibility, which makes the technology highly relevant to the needs of high-throughput photocatalysis (Figure 4a).<sup>45</sup> In addition, Vis-BWR coated with CN thin film are stable and can be reused many times, here proven only for three catalytic cycles (Figure 4b).

As suggested by electron microscopy and AFM, CN films deposited at the glass surface are dense and non-porous (Figure 2). Therefore, the surface area of the sensitizer is defined by geometric area of the coating that is in contact with the reaction mixture in the photocatalytic experiments. To evaluate performance of the CN films and compare it with other photocatalysts, we calculated a number of benzyl alcohol molecules converted by a surface

area unit and expressed in  $\text{mmol m}^{-2}$  for several standard photoredox catalysts under the same conditions (Table S2, Figure S6). For the Vis-BWR reactor, such parameter is  $9.5 \text{ mmol m}^{-2}$ , for suspended photocatalyst particulate it is ca.  $10^{-2} \text{ mmol m}^{-2}$  and for common homogeneous Ir and Ru complexes is ca.  $10^{-6} \text{ mmol m}^{-2}$ . Such difference point to substantially faster reaction kinetics in case of using the semiconductor thin film created under controlled conditions of the CVD. Furthermore, higher selectivity was achieved in case of Vis-BWR (Figure S6b). Explanation for such a remarkable enhancement of the activity is given below taking into account results of time-resolved spectroscopic characterization of the CN thin films.

Immobilization of the CN films at glass surface simplifies work up procedure and more importantly eliminates the necessity of photocatalysts 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.<sup>46</sup> Here, two mirror parts of a microfluidic reactor (channel diameter  $250 \mu\text{m}$ ) 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 in oxidation of benzyl alcohol under illumination with  $400 \text{ nm}$ . In this setting, the main product is benzaldehyde (Figure 4d). Therefore, depending on the reactor configuration, one can select which type of product to synthesize. The optimization of the reaction conditions led to linear dependence of the yield versus the residence time, implying that the reaction follows zero-order kinetics with the respect of benzyl alcohol (Figure 4e). Apparently, the reaction depends on  $\text{O}_2$  concentration, which may explain formation of benzaldehyde as the main product. Applying recirculation of the reaction mixture, the yield of benzaldehyde reached 96% after 93 minutes (Figure 4d,e).

To gain insight 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 4f). The capillary was charged with the solution of 2,2,6,6-tetramethylpiperidine in  $\text{O}_2$  saturated solution of MeCN followed by irradiation with  $415 \text{ nm}$

in the cavity of the EPR spectrometer. Appearance of TEMPO signal indicates that in this set of experiments, CN films sensitize singlet oxygen ( $^1\text{O}_2$ ) (Figure 4g, see ESI for further details).

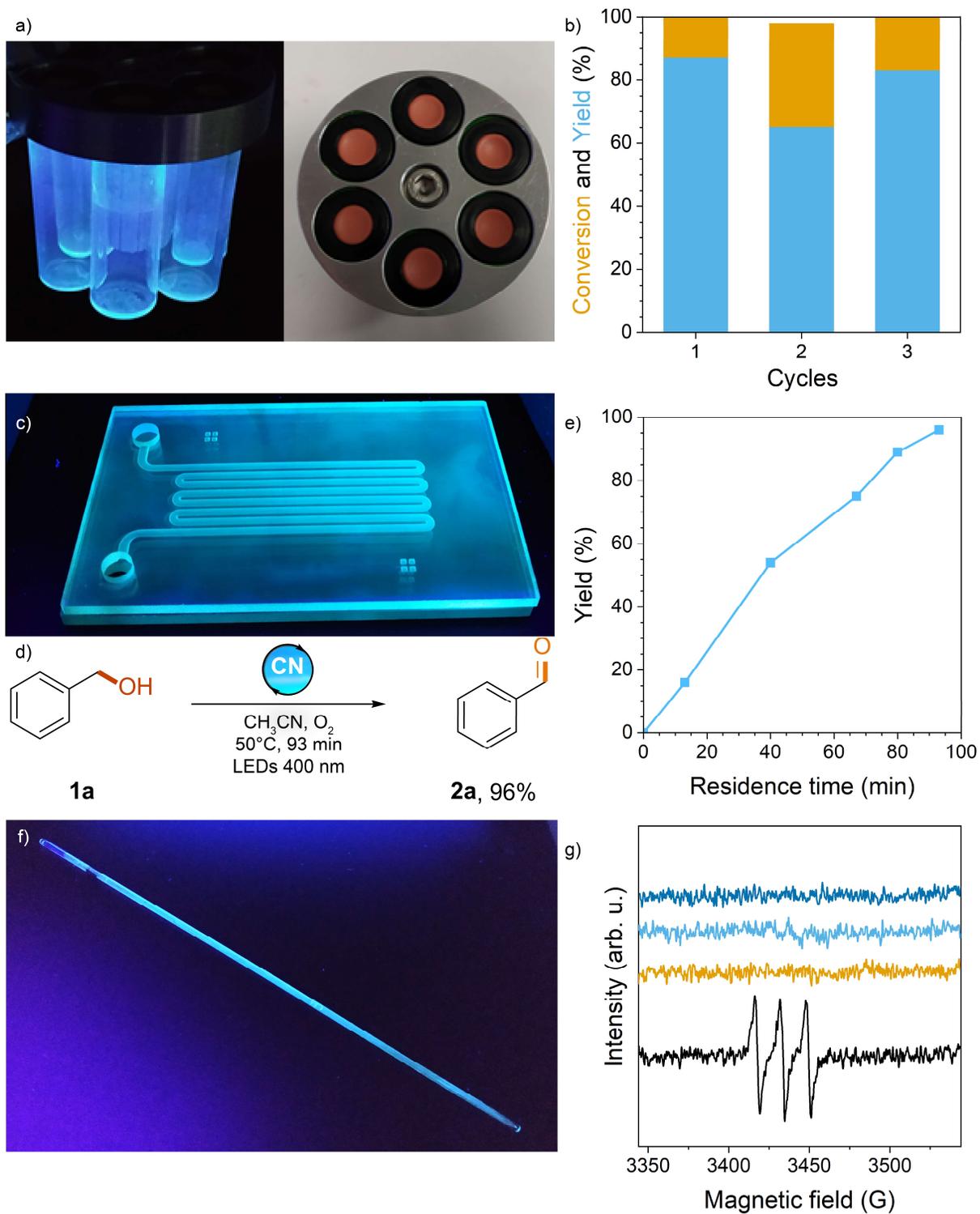


Figure 4 – Application of the CN thin film in photocatalysis. a) Vis-BWR for high-throughput screening. b) Recyclability of Vis-BWR. c) Half cell of Vis-FWR coated with CN film under 365 nm light. d) Scheme of the reaction in flow. e) Yield optimization. f) Coated capillary. g) TEMPO generation and detection via in-situ EPR.

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 (TC-SPC) 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  $\frac{1}{2}$  and a lifetime of  $\sim 0.6$  ns (Figure S7, Table S3). Such behavior is common for polymer systems that present defects and traps, in good agreement with the recorded relatively low internal quantum efficiency (IQE) of 0.6% (Figure S1b).<sup>47</sup> According to the TAS data acquired under  $N_2$  (Figure S8), excitation of the CN film leads to the appearance of a broad band in the observed wavelength range (500–750) nm ascribed to excited states absorption (ESA).<sup>48</sup> Such behavior of the CN thin films is significantly different from the dispersion of CN in liquid phase reported earlier.<sup>49,20</sup> Therein, a negative photoinduced  $\Delta OD$  signal in the visible range was attributed to ground state bleaching (GSB) of the CN, whereas we observe a positive  $\Delta OD$  signal from the CN thin films, indicating a transient photoinduced absorption.<sup>49</sup> 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 micro-second time scale suggests that the process is characterized by two lifetimes (Figure S9). The faster process is described by the same parameters ( $\beta = \frac{1}{2}$ ,  $\tau = 0.6$  ns) as tr-PL, which suggest that the singlet excited states ( $S_1$ ) of the CN possess broad absorption in the visible range (Table S4). We assume the depopulation of  $S_1$  in the CN film proceeds via three pathways: i) radiative relaxation, ii) singlet-triplet ISC, and iii) non-radiative recombination. Taking into account extremely low fluorescence quantum yield,  $< 0.6\%$  (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  $T_1$  are converted back into  $S_1$ , such as triplet-triplet annihilation (TTA, which would exhibit a density-dependent rate) explains the intensity dependence of TA recombination rate in nano- to micro-second time scale (Figure S10) and the longer time constants obtained, when the CN film was in degassed acetonitrile (Table S5).<sup>21</sup> 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.<sup>50</sup> Absence of noticeable peak

shift in the TAS indicate 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)<sup>49</sup> 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  $\Delta E_{ST}$ , which facilitates singlet-triplet ISC. Until now, CN materials prepared by condensation of the precursors in bulk have been reported to have  $\Delta E_{ST}$  of 0.156-0.248 eV.<sup>20</sup> Furthermore, absence of voids in the structure of the CN thin film is also beneficial to suppress non-radiative recombination of triplet excited states (vibrational relaxation) by decreasing free volume in the crystal lattice.<sup>51</sup> These differences strongly point that a strict control over reaction conditions 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 spectroscopic study with experimental data and propose the following mechanism of benzyl alcohols oxidation by the CN thin films (Figure 5a). 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 undergo ISC to form triplet excited states ( $T_1$ ) characterized by lifetime, which are long enough to interact with  $O_2$  via 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 S3). On the other hand, TAS data indicate that  $O_2$  does quenches triplet excited states as their lifetime decreases from 238 ns to 158 ns (Table S4). Once formed,  $^1O_2$  reacts with benzyl alcohol producing benzaldehyde and presumably  $H_2O_2$ .<sup>54</sup> Then, benzaldehyde is converted to benzoic acid either via thermal or photocatalytic pathway (Figure 5b).

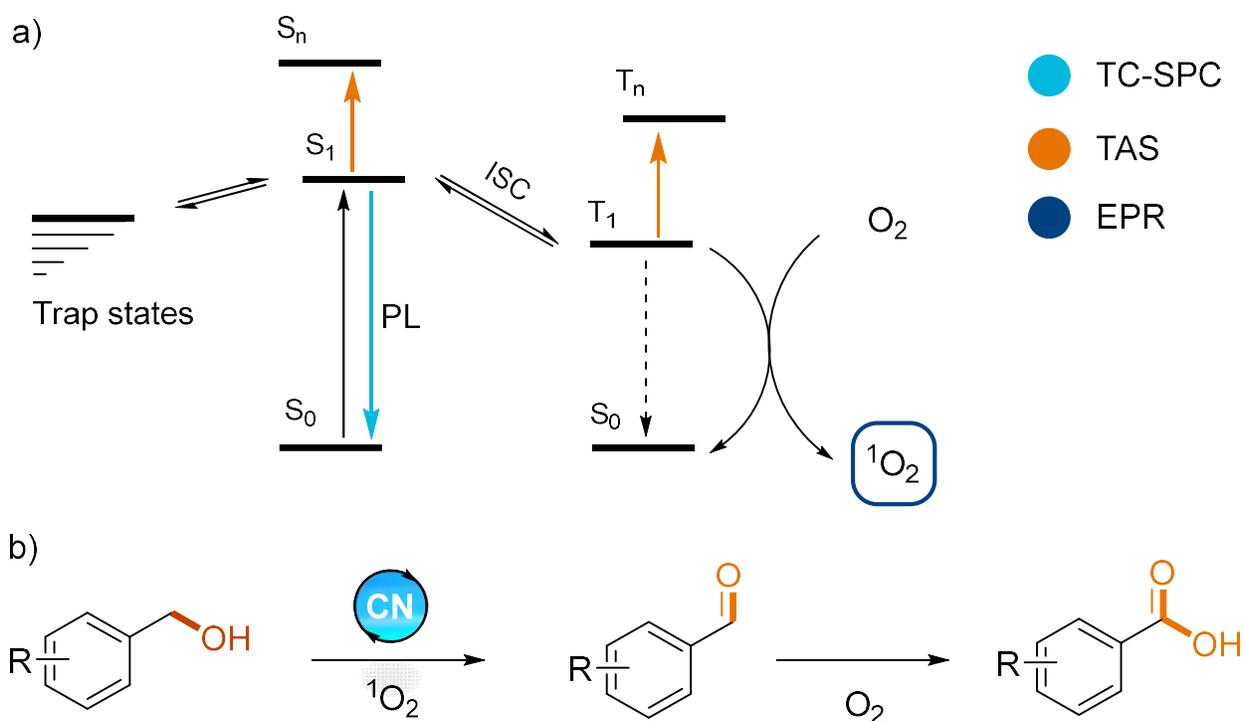


Figure 5 – Mechanism of benzyl alcohol oxidation using thin CN films. a) Proposed photophysical mechanism. b) Photocatalytic mechanism of benzyl alcohol oxidation to benzaldehyde and subsequent thermal oxidation to benzoic acid.

Hence, the developed technology not only makes the Vis-BWR a convenient choice to conduct a photocatalytic reaction, it is also more efficient compared to the analogous dispersion of photocatalyst in 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 ten alcohols, in which corresponding benzoic acids have been obtained with up to 87% yield in 24 hours. 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 energy transfer 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 for the oxidation of benzyl alcohol, leading to benzaldehyde with the yield linearly increasing up to 96% in ca. 90 minutes. We believe that the technology

developed herein is a significant step forward for the improvement of photocatalysis, both at a research and industrial level. Indeed, the utilization of thin film technology allows 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 photocatalyst, such as fouling and clogging of the reactor and/or pumping system. Exploiting CN thin films would also allow 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 in electro- and thermo- catalysis, 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 scientists imagination.

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