Modified Polymeric Carbon Nitrides for Sorption and Photodegradation of Emerging Contaminants

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Resumo/Abstract

RESUMO - A crescente presença de fármacos, pesticidas e subprodutos industriais em águas residuais exige soluções inovadoras, já que os métodos tradicionais não degradam adequadamente esses contaminantes. Este estudo aborda esse desafio empregando nitretos de carbono poliméricos (PCN) modificados, que são semicondutores responsivos à luz visível, tratado termicamente com sais de potássio (KCl/KSCN) para amplificar sua eficiência fotocatalítica. Resultados experimentais revelaram comportamentos distintos: a Rifampicina (RIF), contaminante modelo investigado, apresentou 60% de remoção em 60 minutos (atingindo 100% sob luz em 1 hora), com degradação acelerada em condições ácidas (65% em 45 minutos). Em contraste, a Tetraciclina (TC) exibiu capacidade adsortiva mínima (<30% de degradação após 2,5 horas em LED ~410 nm) independentemente do pH. O PCN otimizado demonstrou multifuncionalidade excepcional, superando o material original tanto na cinética de adsorção quanto na eficácia de fotodegradação, mantendo boa estabilidade estrutural e resistência à fotocorrosão ao longo de quatro ciclos reacionais consecutivos - um avanço crucial para aplicações ambientais escaláveis. Esta abordagem sistemática valida o potencial do PCN como solução robusta e economicamente viável para cenários de remediação de águas residuais.
Palavras-chave: nitretos de carbono, sorção, fotodegradação, contaminantes emergentes.

ABSTRACT – The increasing presence of pharmaceuticals, pesticides, and industrial byproducts in wastewater demands innovative solutions, as traditional methods fail to adequately degrade these contaminants. This study addresses this challenge by employing modified polymeric carbon nitrides (PCN), which are visible-light-responsive semiconductors, thermally treated with potassium salts (KCl/KSCN) to enhance their photocatalytic efficiency. Experimental results revealed distinct behaviors: Rifampicin (RIF), the model contaminant investigated, showed 60% removal in 60 minutes (reaching 100% under light in 1 hour), with accelerated degradation under acidic conditions (65% in 45 minutes). In contrast, Tetracycline (TC) exhibited minimal adsorptive capacity (<30% degradation after 2.5 hours under ~410 nm LED) regardless of pH. The optimized PCN demonstrated exceptional multifunctionality, outperforming the original material in both adsorption kinetics and photodegradation efficacy while maintaining strong structural stability and resistance to photocorrosion over four consecutive reaction cycles—a crucial advancement for scalable environmental applications. This systematic approach validates PCN's potential as a robust and cost-effective solution for wastewater remediation scenarios.
Keywords: carbon nitrides, sorption, photodegradation, emerging contaminants.

Introduction

The environmental impacts of new technologies often emerge gradually. While these technologies contribute to ecological challenges, they also provide essential tools for addressing them. Green chemistry focuses on developing solutions that minimize environmental harm, such as advanced water treatment methods. Conventional approaches like UV light or ozone treatment sometimes prove inadequate, creating demand for cleaner alternatives as photodegradation - one of the most environmentally benign remediation strategies (1-2).

Common wastewater treatment methods include membrane filtration, photolysis, advanced oxidation, and biological processes, each with distinct characteristics and costs. Heterogeneous photocatalysis using semiconductor catalysts offers an effective solution, degrading organic pollutants into harmless inorganic compounds under light exposure. Particularly promising are carbon nitride (CN) nanomaterials, known for their visible-light activity, stability, and earth-abundant composition (3).

Carbon nitrides (C_3N_4) are versatile carbon-nitrogen materials with crystalline, amorphous, and polymeric forms (Figure 1). These non-toxic, low-cost materials show exceptional stability and visible-light activity, making them ideal eco-friendly semiconductor catalysts (4).

Polymeric Carbon Nitrides (PCN) are among the oldest known polymers, first synthesized in 1834. Their simple preparation from nitrogen sources (melamine, urea, cyanamide) has made PCNs widely used for organic contaminant degradation. As visible/UV-light-active semiconductors, they're particularly valuable for environmental applications. While many studies have examined how structural modifications affect PCN's photocatalytic activity, more systematic investigations are needed, particularly focused on contaminant degradation (5-

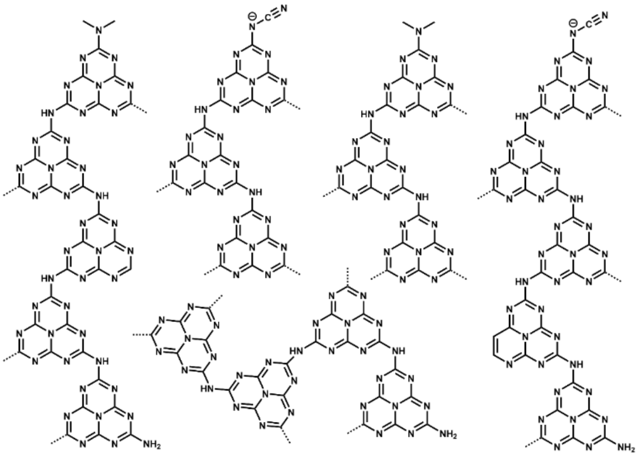

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Figure 1: Polymeric Carbon Nitrides structure. The determination of a general structure in the poorly crystalline polymeric form of carbon nitrides is still being debated in the literature.

Contaminant adsorption onto materials for water remediation represents a green technology. Photocatalysis typically works alongside adsorption mechanisms, with some contaminants being effectively removed through adsorption alone. This suggests opportunities to explore not just photocatalytic systems but also surface charge interactions (1). In this work's systems, photolysis, sorption and ROS-mediated photodegradation work together (with only sorption remaining in darkness).

One promising approach involves adding cyanamide-type groups via thiocyanate treatment, which modifies PCN's surface charge and may enhance photoactivity - though the exact mechanisms remain unclear. Surface charge influences adsorption, and PCNs can accumulate charges under irradiation, altering their surface charge balance.

Experimental

Materials Synthesis

Thermal treatment of bulk PCN with ionic salts can induce structural modifications in the polymer network. While defects (breaks in carbon nitride chains) typically reduce catalytic activity, controlled defects may enhance photocatalytic performance for wastewater treatment by decreasing electron-hole recombination.

Previous studies have functionalized cyanamide groups in CN polymers (7-8), but without examining contaminant sorption or photocatalysis. This project will use KCl and KSCN to introduce cyano groups - an established approach not yet applied for contaminant removal from aqueous media via sorption or photocatalysis.

Although KSCN treatment is known to create cyanamide groups and alter surface charge (Figure 2), we hypothesize K^+ itself may promote these groups. To test this, we compared treatments using KCl versus KSCN. These cyano groups may improve charge separation across the heptazine polymer.

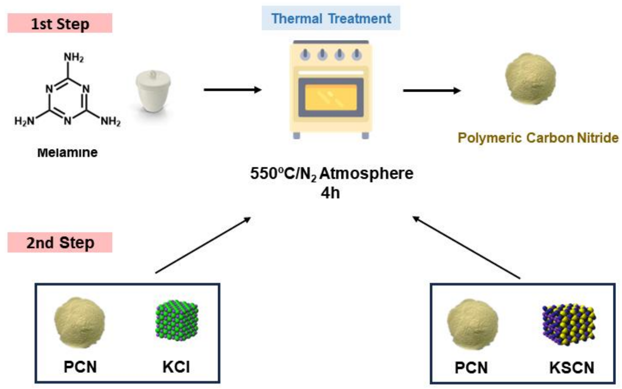

Figure 2: Synthesis of Polymeric Carbon Nitrides in a nutshell. The 2nd step is the re-treatment of the bulk synthesized PCN with potassium salts to achieve structural mods.

On the sorption and photocatalytic tests, two model contaminant molecules were used. Containing characteristic bands in the UV-Vis spectrum, these substances are the target of recent studies for their destruction, as it is known that they are commonly found in wastewater. Rifampicin (RIF) is a medicine used mainly in humans, but which also has applications in aquaculture. Tetracycline (TC) is one of the most used classes of antibiotics in the world, widely used for veterinary reasons.

The system in which the sorption and photocatalytic reaction assays took place consisted of an aliquot of the contaminant solution, irradiation by a 10W LED at 410 nm (purple light in the visible spectrum), and 10 mg of the material suspended in the vial, facilitated by magnetic stirring. The resulting reactions were measured using a Shimadzu UV-2600i spectrophotometer.

Results and Discussion

Materials Characterization

X-Ray Diffraction (XRD), Diffuse Reflectance Spectroscopy (DRS) and Fourier Transformed Infrared Spectroscopy (FT-IR) were employed for material characterization. XRD analysis revealed two distinct peaks at ~27° and ~13.0° for the pristine material (PCN). These peaks correspond to the (002) plane (associated with interlayer stacking of aromatic systems in C_3N_4) and the (100) plane (related to in-plane structural packing), respectively. For the thermally treated materials, a small but pronounced peak appears around 8°.

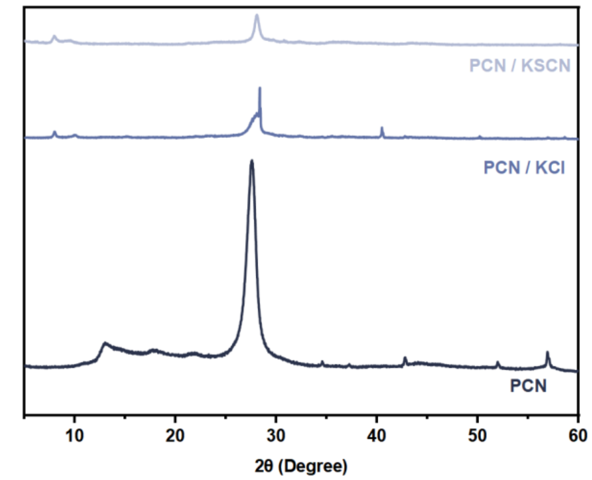

Figure 3: XRD patterns of the matrix material (PCN) and the obtained ones (PCN/KCl; PCN/KSCN).

Polymeric carbon nitrides have an action spectrum that begins at the end of the visible spectrum and extends into the ultraviolet (Figure 4). For this reason, tests conducted with LEDs in this spectral range are more suitable for carbon nitrides, as their photocatalytic properties manifest in this interval.

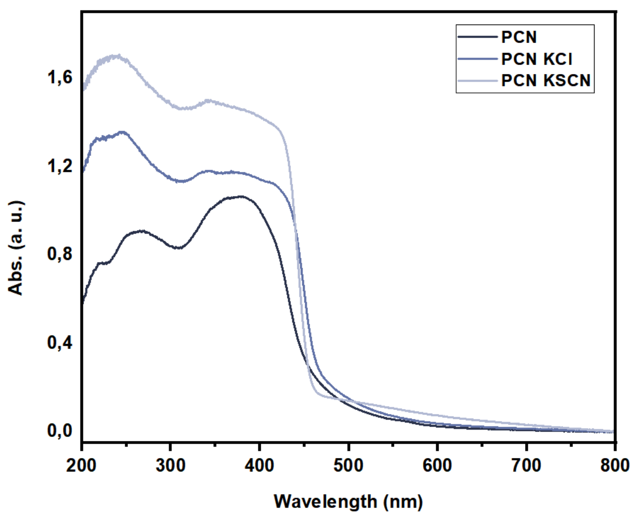

Figure 4: Diffuse Reflectance Spectroscopy for PCN and subsequent materials. The materials do not differ significantly from each other in their action spectrum.

An FT-IR measurement was taken for the first samples that underwent thermal treatment with the potassium salts, as well as for the original material (PCN). Stretching corresponding to cyanamide groups appears in the spectrum (~2220 cm−1) (Figure 5). At first glance, the PCN structure appears to have been incorporated with the desired groups.

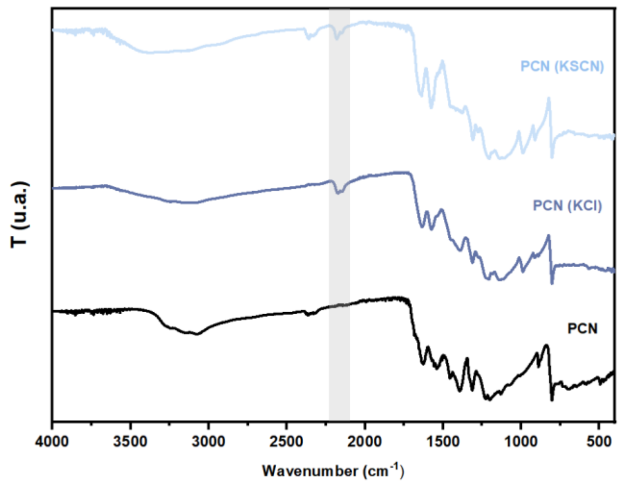

Figure 5: FT-IR spectra of the first synthesized materials, demonstrating the presence of cyanamide groups after thermal treatment with potassium salts.

Sorption and Photocatalytic Tests

In primary tests, pristine PCN was tested against Tetracycline (TC). In addition, materials treated with potassium salts were also tested (Figure 6). At first glance, the subsequently treated materials had briefly better activity, which can be related to defects caused in the structure of the material, changing not only its surface charge, but also its charge recombination properties.

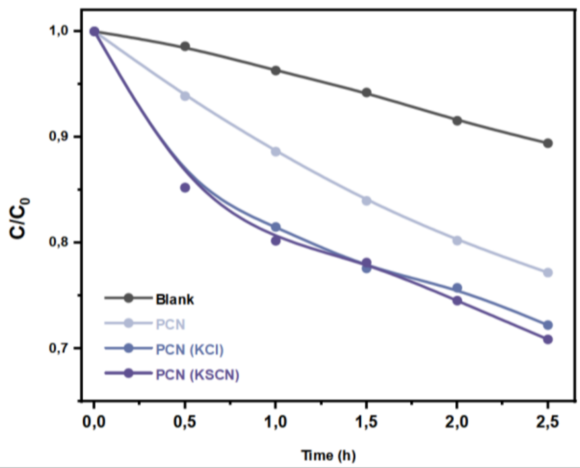

Figure 6: Photocatalytic degradation efficiency of TC. Modified PCN's were slightly better than the primary material.

The sorption capacity of a material towards a contaminant will depend on its electronic affinity, that is, its surface charge and how it interacts with the pollutants in neutral, basic, or acidic medium. In Figure 7, the materials synthesized from PCN show an advantage in the sorption of the substrate. It can be conjectured that the surface charge of the original material was modified after treatment with potassium salts.

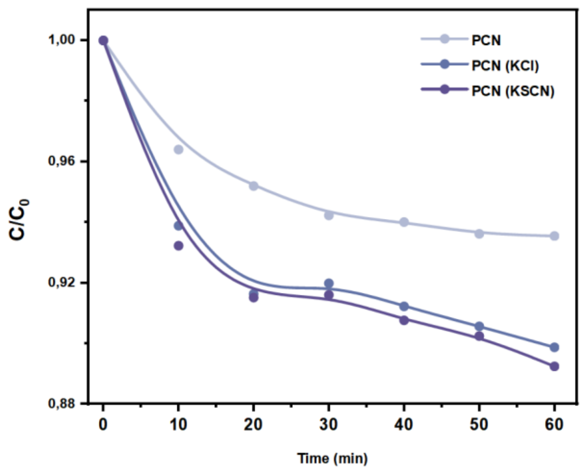

Figure 7: Sorption efficiency of TC relative to modified PCN's (pH ~7).

In the Rifampicin (RIF) tests, the contaminant demonstrated good reactivity. For materials other than PCN, sorption was slightly enhanced due to improved catalyst-substrate charge interactions from surface cyanamide groups (Figure 8). The reaction medium reached equilibrium after approximately 50 minutes of testing, with no further sorption observed. Upon LED activation (Figure 9), within 45 minutes of irradiation, PCN degraded slightly over 80% of the remaining solution material - underperforming compared to modified PCNs which achieved near-complete substrate removal (≈100%) within the same timeframe, reaching full degradation at 60 minutes.

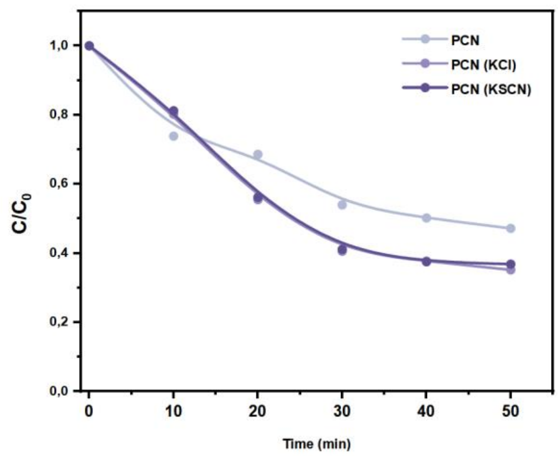

Figure 8: Rifampicin's sorption into the carbon nitrides.

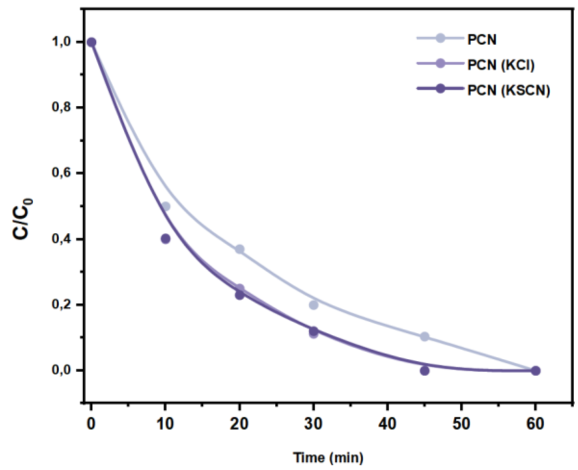

Figure 9: Material's photocatalytic performance towards RIF.

In acidic medium, rifampicin exhibits slightly enhanced sorption compared to neutral pH (Figure 10). This behavior stems from molecular deprotonation under these conditions, combined with the carbon nitride surface acquiring a more negative charge at low pH (9). With increased sorbed molecules, the photocatalytic process becomes more optimized, resulting in complete substrate degradation after approximately 45 minutes of irradiation (Figure 10, left).

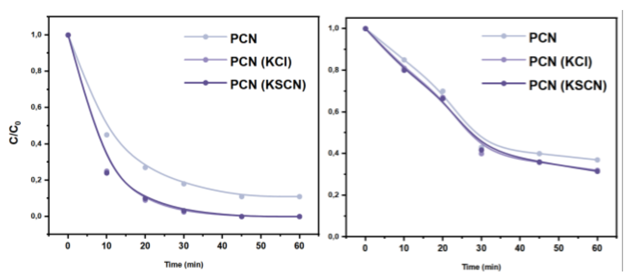

Figure 10: Material's photocatalytic performance towards RIF on acidic pH (3). After the lights came on (left) and dark sorption (right).

FT-IR analyses were performed after the reaction during material reuse to verify whether the cyano groups were still present in the CN's (Figures 11 and 12). The characteristic stretching vibrations corresponding to these defects persisted in the materials, demonstrating the groups' resistance to reaction conditions in both neutral and acidic pH media.

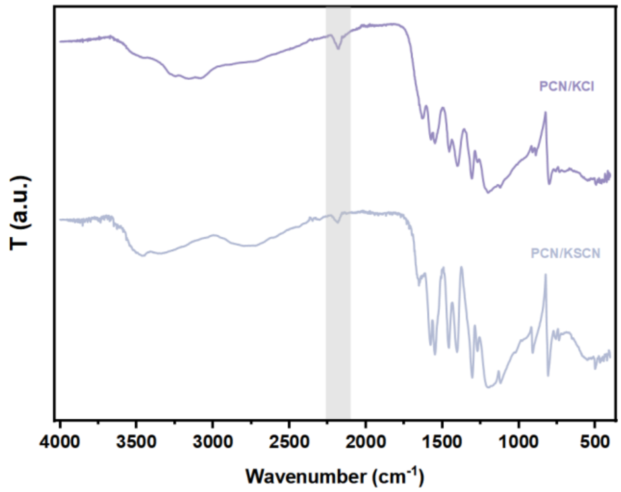

Figure 11: FT-IR measurements after photoreactions (pH 3).

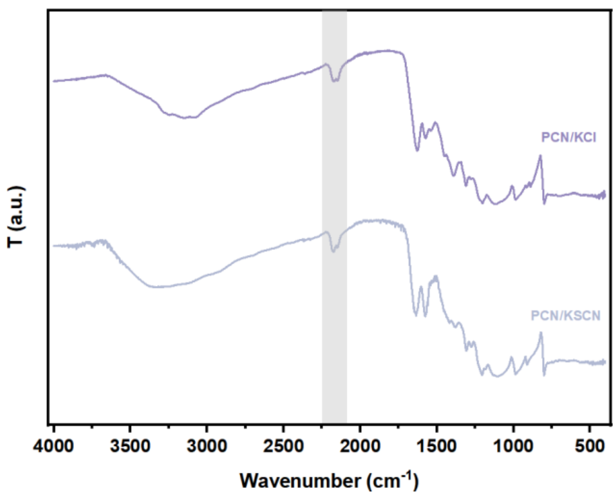

Figure 12: FT-IR measurements after photoreactions (neutral pH).

For systematic catalyst application, stability across reaction cycles is crucial. Reusability tests of the modified materials were conducted to evaluate their stability under the applied reaction system. After each cycle, the materials were recovered from the reactors, washed, centrifuged, and dried. The materials were analyzed over 4 reaction cycles (Figure 13), showing only minimal activity loss while maintaining contaminant removal efficiency above 80% through the third reuse cycle.

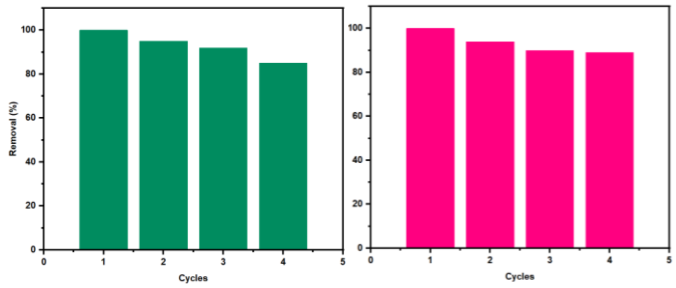

Figure 13: Recycles and overral stability of PCN/KSCN (left) and PCN/KCl (right) for the RIF reactions (neutral pH).

Conclusions

The synthesis of the polymeric carbon nitride (PCN) photomaterial was successfully carried out. Seeking better sorption conditions to explore the effect of cyano groups on the material's surface, the original material was submitted to thermal treatment with potassium salts. The presence of such groups was confirmed through FT-IR analyses.

The synthesized materials were tested against two contaminants, Rifampicin and Tetracycline. For the first one, after 60 minutes of reaction, about 60% of the substrate was removed from the medium, reaching 100% removal after 1 hour of reaction in the presence of light. When the pH of the reaction medium is increased, there is a slight worsening in both the adsorption and photodegradation activity of RIF. However, when the medium is acidic, the contaminant sorbs more quickly, with about 65% removal in 45 minutes of reaction, and 100% degradation for the same amount of time in the presence of light.

For TC, neither the starting material nor the modified ones showed sufficient sorption effect, and remained neutral for the same purpose at different pHs. In the presence of light, this pollutant reached about 30% removal after 2.5 hours of reaction. Since the modified materials showed superior activity, both in sorption and photodegradation compared to the original PCN, in addition to good stability and resistance to photocorrosion after 4 reaction cycles, there are potential opportunities for continued exploration of carbon nitrides applied to photocatalysis and environmental chemistry.

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References

1. F. Silva, I. F. Teixeira, R. D. F. Rios, G. M. do Nascimento, I. Binatti, H. F. V. Victória, K. Krambrock, L. A. Cury, A. P. C. Teixeira and H. O. Stumpf, Journal of Hazardous Materials, **2021**, 401, 123713.

2. S. Li, S. Shan, S. Chen, H. Li, Z. Li, Y. Liang, J. Fei, L. Xie and J. Li, Journal of Environmental Chemical Engineering, **2021**, 9, 105967.

3. Z. Zeng, F. Ye, S. Deng, D. Fang, X. Wang, Y. Bai and H. Xiao, Chemical Engineering Journal, **2022**, 444, 136561.

4. G. F. S. R. Rocha, M. A. R. da Silva, A. Rogolino, G. A. A. Diab, L. F. G. Noleto, M. Antonietti and I. F. Teixeira, Chemical Society Reviews, **2023**, 52, 4878-4932.

5. T. Huo, G. Ba, Q. Deng, F. Yu, G. Wang, H. Li and W. Hou, Applied Catalysis B: Environmental, **2021**, 287, 119995.

6. M. Wu, X. He, B. Jing, T. Wang, C. Wang, Y. Qin, Z. Ao, S. Wang and T. An, Journal of Hazardous Materials, **2020**, 384, 121323.

7. V. W.-h. Lau, I. Moudrakovski, T. Botari, S. Weinberger, M. B. Mesch, V. Duppel, J. Senker, V. Blum and B. V. Lotsch, Nature Communications, **2016**, 7, 12165.

8. H. Ma, Y. Jia, G. Zhu, F. Zhang, S. Rhee, B. Lee and C. Liu, Applied Surface Science, **2020**, 507, 144885.

9. F. M. Colombari, M. A. R. da Silva, M. S. Homsi, B. R. L. de Souza, M. Araujo, J. L. Francisco, G. T. S. T. da Silva, I. F. Silva, A. F. de Moura and I. F. Teixeira, Faraday Discussions, **2021**, 227, 306-320.