Enhancement of carbamazepine photodegradation using hybrid of phosphorescent carbon dots coupled with highly porous TiO_2 photocatalyst

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Introduction

In this work, the aim was to enhance the photocatalytic activity of anatase TiO_2 in carbamazepine degradation by incorporating carbon dots (CDs) into its pores. This was achieved by impregnating two types of TiO_2 with two types of CDs. TiO_2 was obtained in two different ways, which allowed obtaining anatase phase materials, but differing in size, shape, porosity and therefore possessing different properties. Two types of carbon dots were used to show the influence of their different spectroscopic properties on the photocatalytic activity. Luminescent CDs were added to shift the absorption edge of TiO_2 to enable the hybrid to be used in a wider range of light (including the visible range). Phosphorescent CDs also shift the absorption range, but additionally, due to the longer emission decay (slower carrier recombination), they allow to increase the photocatalytic activity of the hybrid. It was assumed that the presence of CDs in the TiO_2 pores would increase the absorption of light in the visible range, improve the energy transfer in the semiconductor, and due to the use of phosphorescent dots, the carrier recombination process would be slowed down. All the above changes would result in an increase in photocatalytic activity.

Results

Structure and morphology

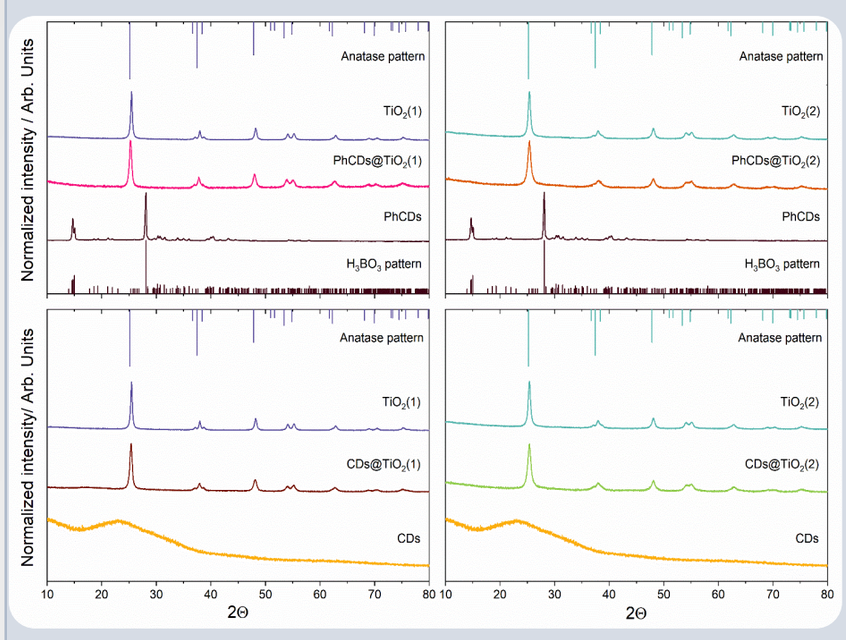

Figure 1. XRD diffractogram for raw TiO_2, CDs and hybrid materials.

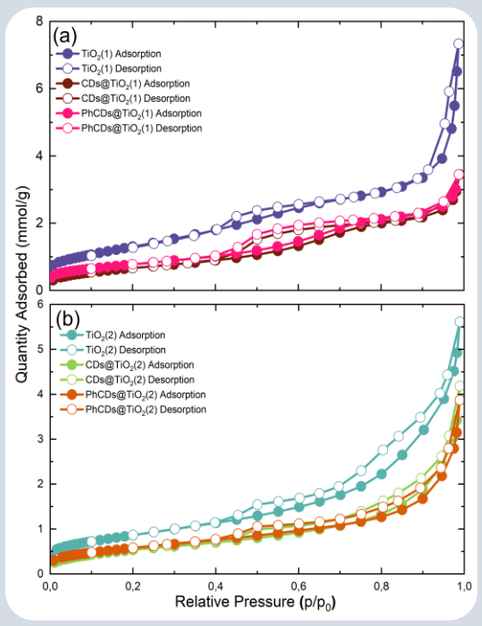

Figure 2. N_2 adsorption-desorption isotherms (77 K)

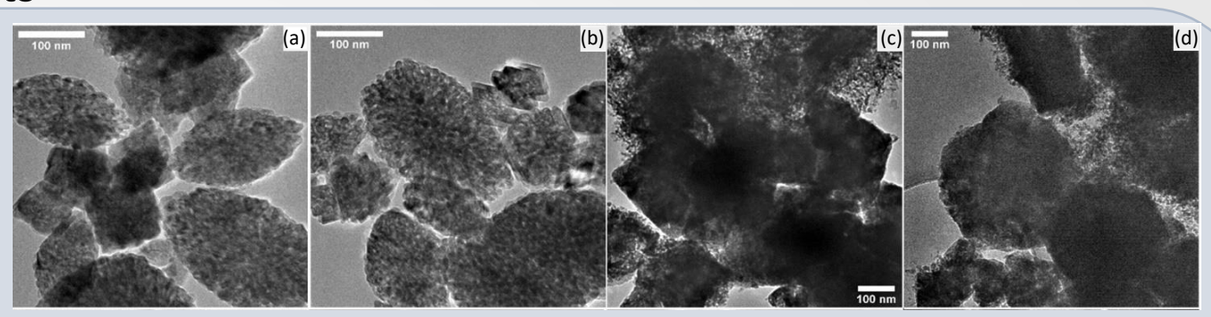

Figure 3. TEM images of (a) CDs@TiO_2(1), (b) PhCDs@TiO_2(1), (c) CDs@TiO_2(2), (d) PhCDs@TiO_2(2).

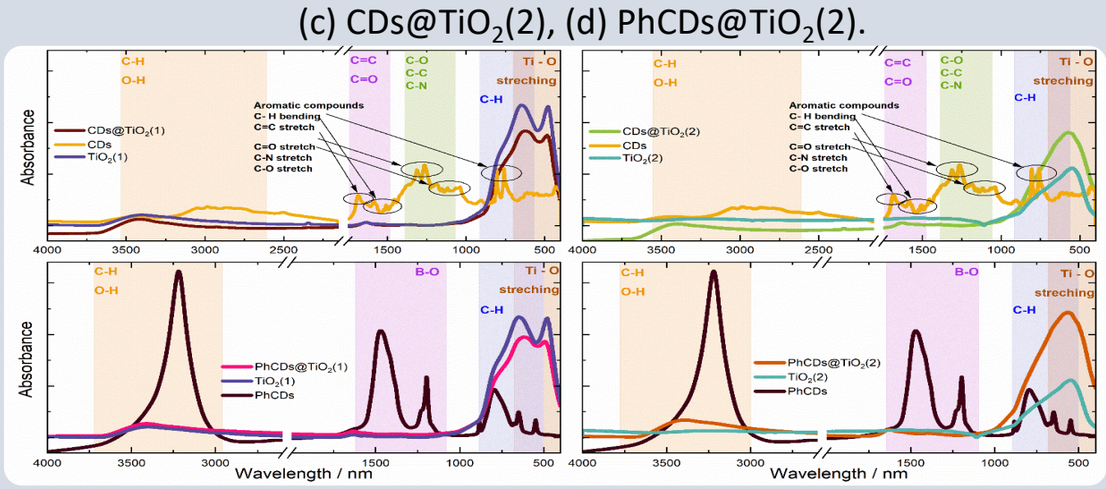

Figure 4. IR spectra of CDs, TiO_2, and hybrid materials.

Spectroscopic properties

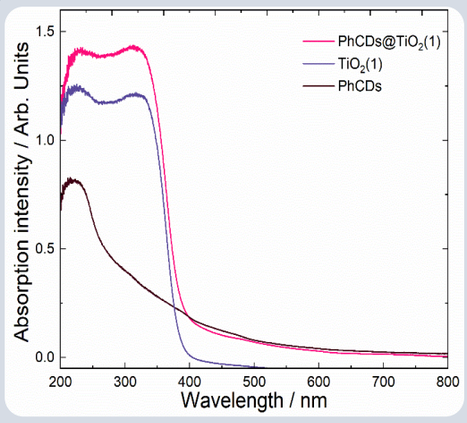

Figure 5. Absorption spectrum of PhCDs, TiO_2(1) hybrid material

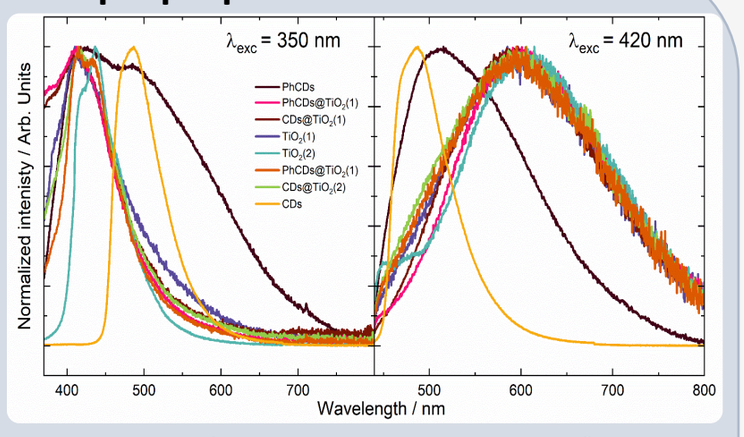

Figure 6. The emission spectrum of CDs, TiO_2, and hybrid materials under excitation wavelength 350, 420 nm.

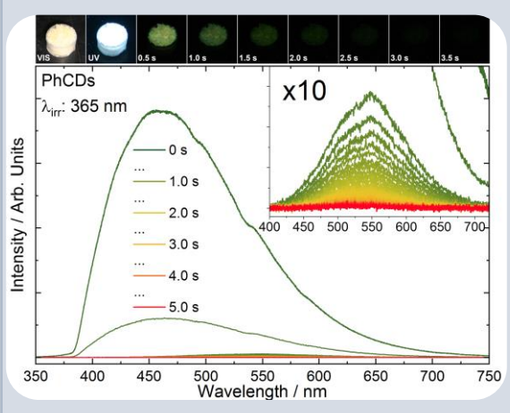

Figure 7. PhCDs luminescence spectrum in the function of time

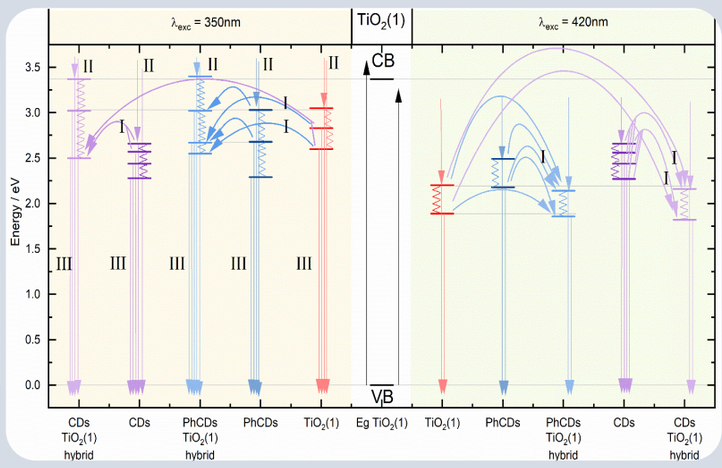

Figure 8. Mechanism of energy transfer in TiO_2(1), PhCDs, CDs, and hybrid materials

Photocatalytic activity

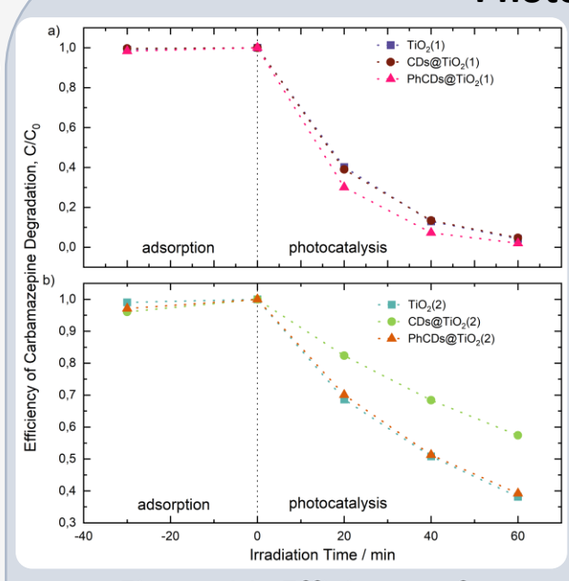

Figure 11. Efficiency of carbamazepine degradation

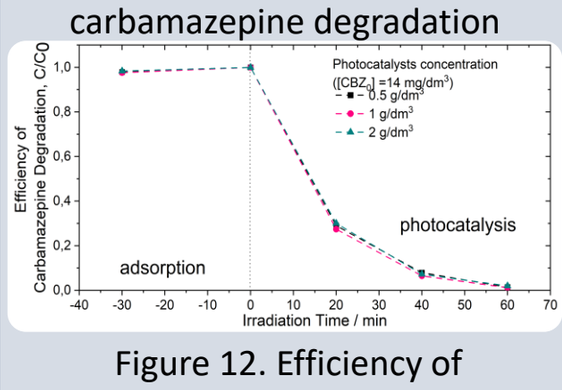

Figure 12. Efficiency of carbamazepine degradation at various dosages of PhCDs@TiO_2(1)

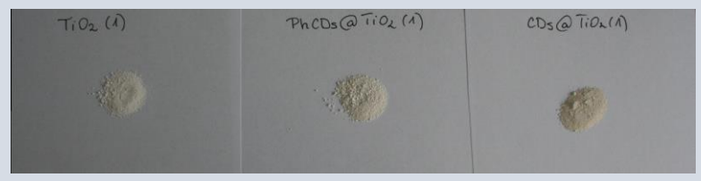

Figure 13. Image of TiO_2(1) and hybrid materials.

Table 1. Photocatalytic activity of the prepared samples

Sample name	Carbamazepine degradation efficiency (%)	Degradation rate constant $k \cdot 10^{-2}$ (min^{-1})	Degree of reduction TOC (%)
TiO_2(1)	95.8	5.31	50.7
CDs@TiO_2(1)	95.3	5.11	2.4
PhCDs@TiO_2(1)	98.0	6.59	60.2
TiO_2(2)	61.8	1.60	0
CDs@TiO_2(2)	42.6	0.93	0
PhCDs@TiO_2(2)	60.8	1.56	0

Table 2. Photocatalytic activity of the PhCDs@TiO_2(1) photocatalyst applied at various dosages

Photocatalyst dosage	Degradation rate constant $k \cdot 10^{-2}$ (min^{-1})	Efficiency of TOC reduction (%)
0.5 g/dm³	7.01	63.1
1 g/dm³	7.33	61.9
2 g/dm³	6.59	60.2

Conclusions

- **Four hybrids were created consisting of two types of TiO_2 and two types of carbon dots. Structural tests showed no changes in the structure of TiO_2 after the addition of carbon dots, which was confirmed by SEM, TEM and BET analysis. In Raman and IR spectroscopy, no significant differences were observed between the hybrid materials and pure titanium oxide due to the small number of CDs.**
- **Absorption measurements showed that adding CDs to TiO_2(1) causes the absorption edge to shift towards visible light. Analysing the emission spectra of the raw and hybrid materials allowed for understanding the mechanism of luminescence in hybrid materials.**
- **Photocatalytic activity tests show that in the case of TiO_2(1), the addition of phosphorescent dots improved the photocatalytic process. The optimal photocatalyst concentration was determined as 1 g/dm³. The addition of CDs to this type of titanium oxide did not cause major differences in this process. In the case of TiO_2(2), the addition of both types of carbon dots resulted in a reduction in the efficiency of this process.**
- **To summarize, the thesis regarding the improvement of the photocatalysis process by adding phosphorescent carbon dots to titanium oxide has been confirmed. It has been proven that to improve this process, it is important to create a material that can hold electrons in the excited state. This will slow down the recombination of electron-hole pairs, which has a significant impact on the photocatalysis process.**