

# Carbon dots/TiO<sub>2</sub> hybrids for photocatalytic degradation of drugs in the aquatic environment

Daniela Kujawa<sup>a</sup>, Marzena Fandzloch<sup>a</sup>, Oleksii Bezkrovnyi<sup>a</sup>, Anna Grzegórska<sup>b</sup>, Anna Zelińska-Jurek<sup>b</sup>, Paweł Głuchowski<sup>a</sup>

<sup>a</sup> Institute of Low Temperature and Structural Research, Polish Academy of Sciences, Okólna 2, Wrocław, 50-422, Poland

<sup>b</sup> Department of Process Engineering and Chemical Technology, Faculty of Chemistry, Gdańsk University of Technology, G. Narutowicza 11/12, Gdańsk, 80-233, Poland

## INTRODUCTION & AIM

In this work, the aim was to enhance the photocatalytic activity of anatase TiO<sub>2</sub> in carbamazepine degradation by incorporating carbon dots (CDs) into its pores. This was achieved by impregnating two types of TiO<sub>2</sub> with two types of CDs. TiO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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 & DISCUSSION

### STRUCTURE & MORPHOLOGY

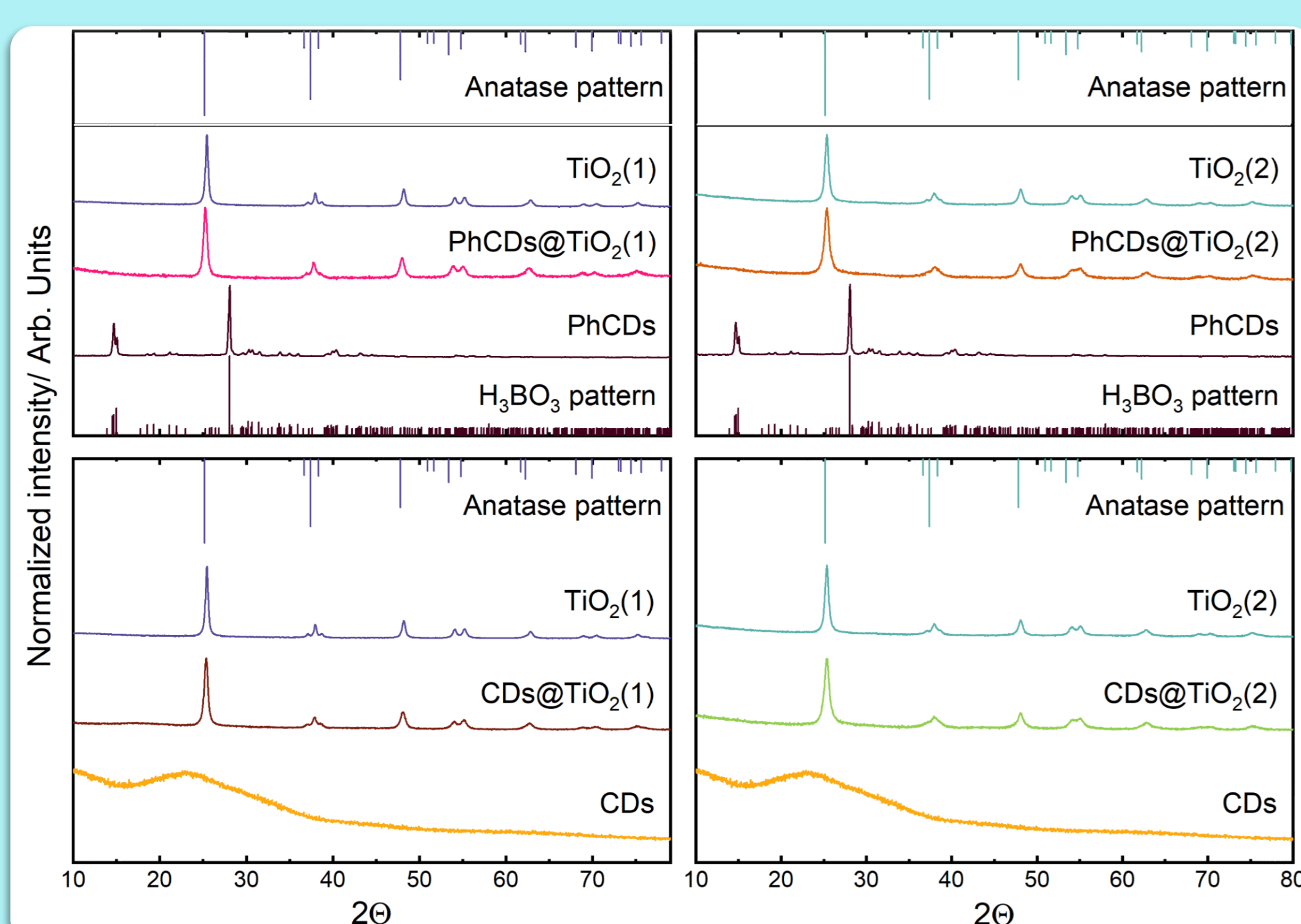


Figure 1. XRD diffractogram for raw TiO<sub>2</sub>, CDs and hybrid materials.

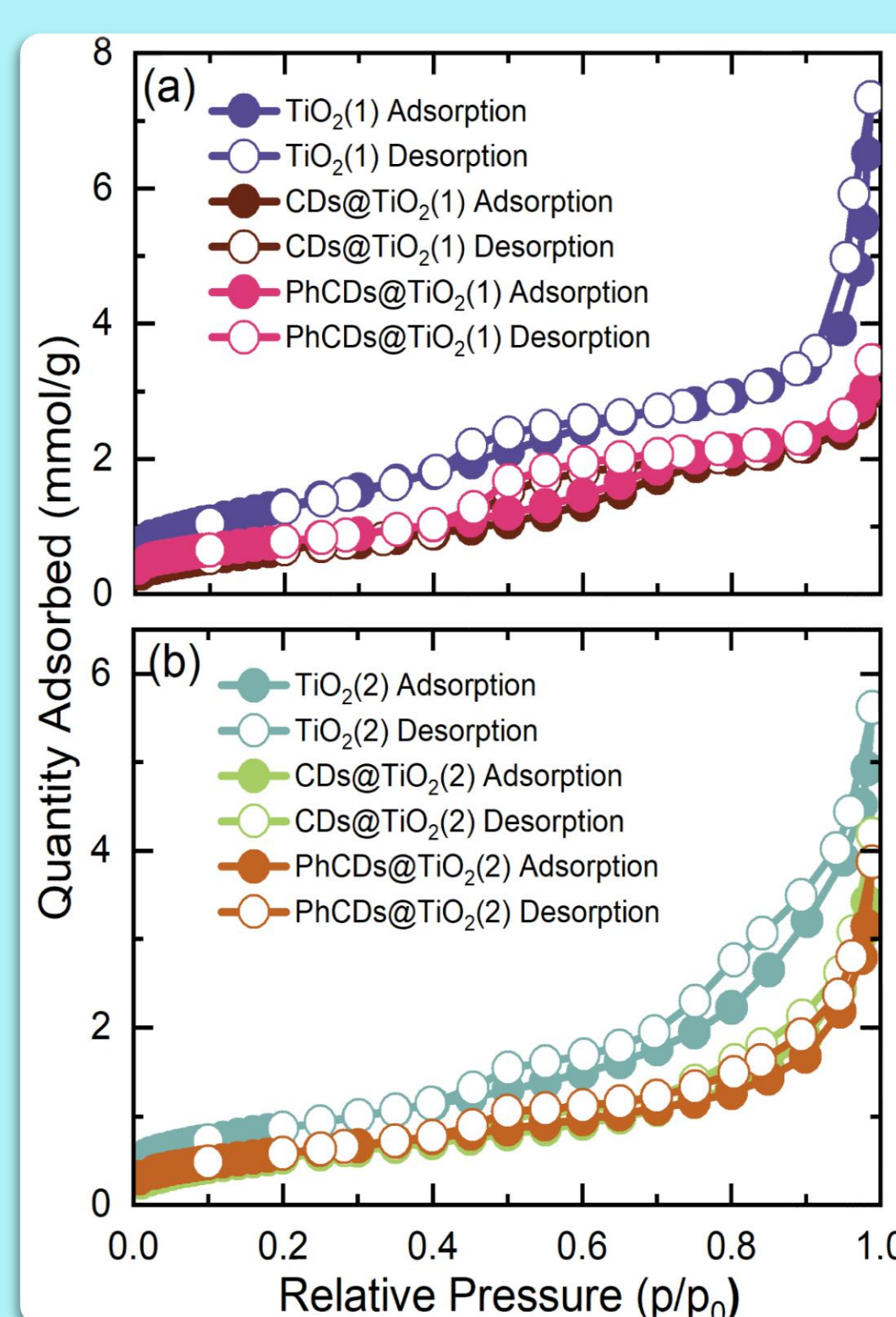


Figure 2. N<sub>2</sub> adsorption-desorption isotherms (77 K)

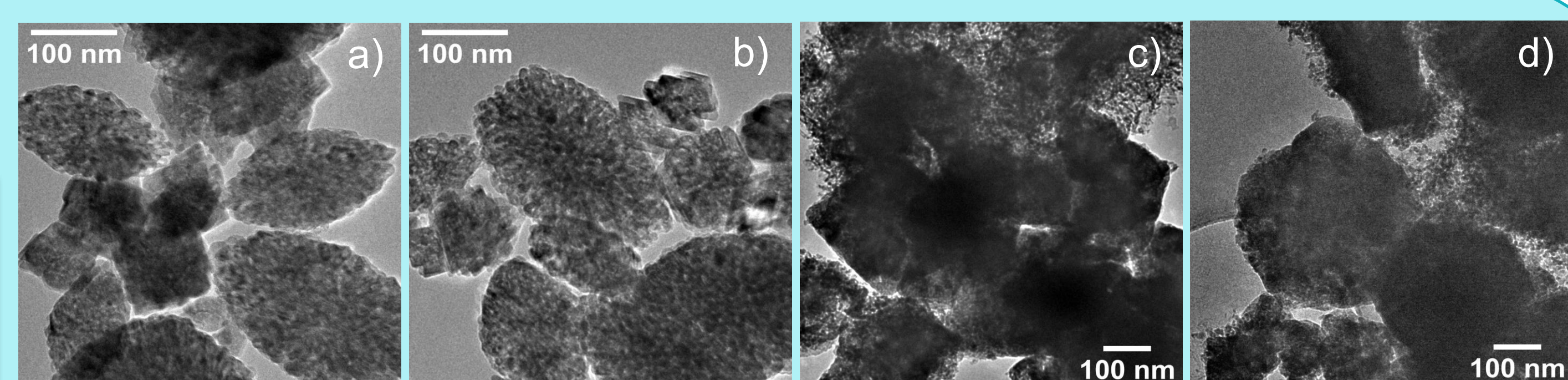


Figure 3. TEM images of (a) CDs@TiO<sub>2</sub>(1), (b) PhCDs@TiO<sub>2</sub>(1), (c) CDs@TiO<sub>2</sub>(2), (d) PhCDs@TiO<sub>2</sub>(2).

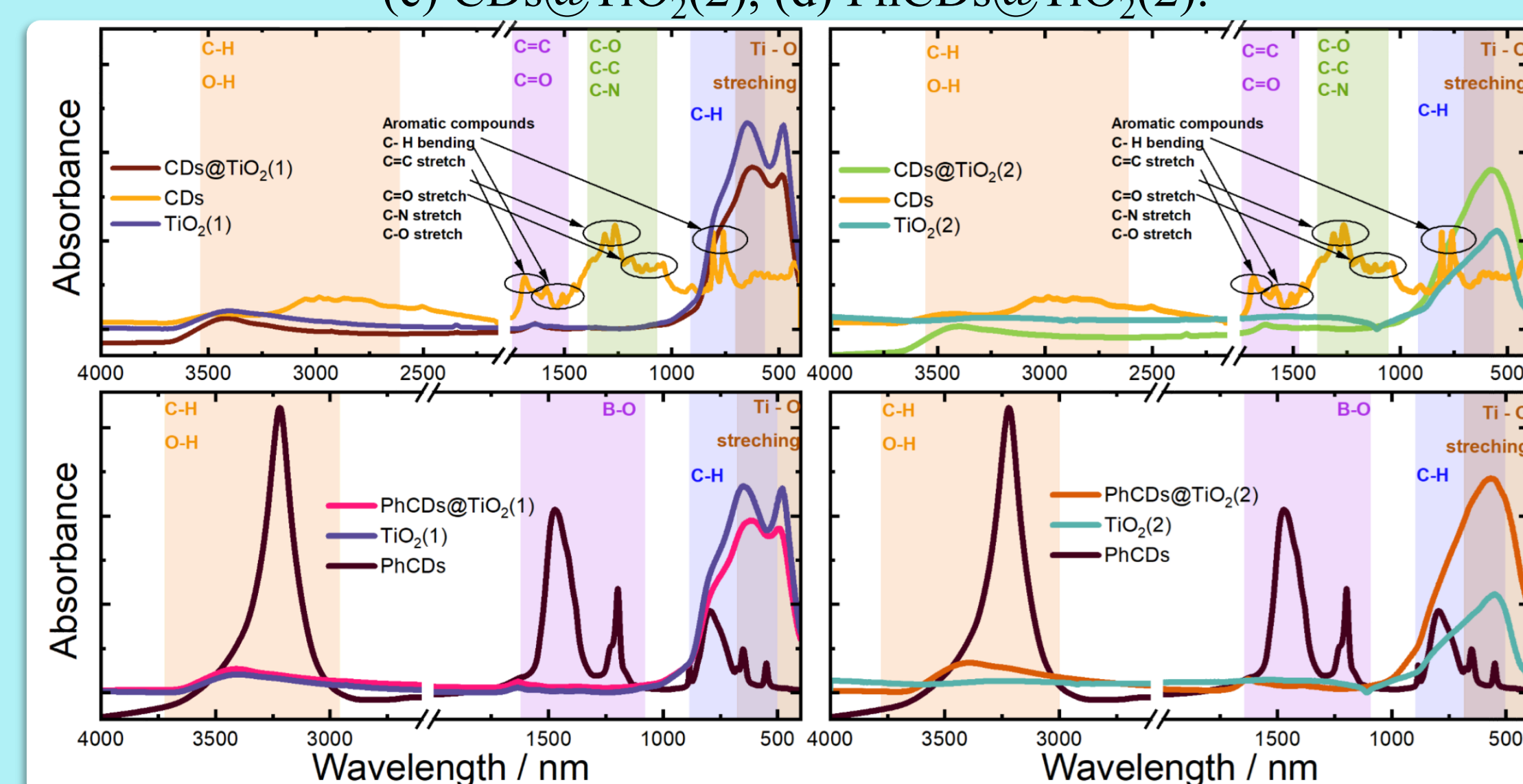


Figure 4. IR spectra of CDs, TiO<sub>2</sub>, and hybrid materials.

### SPECTROSCOPIC PROPERTIES

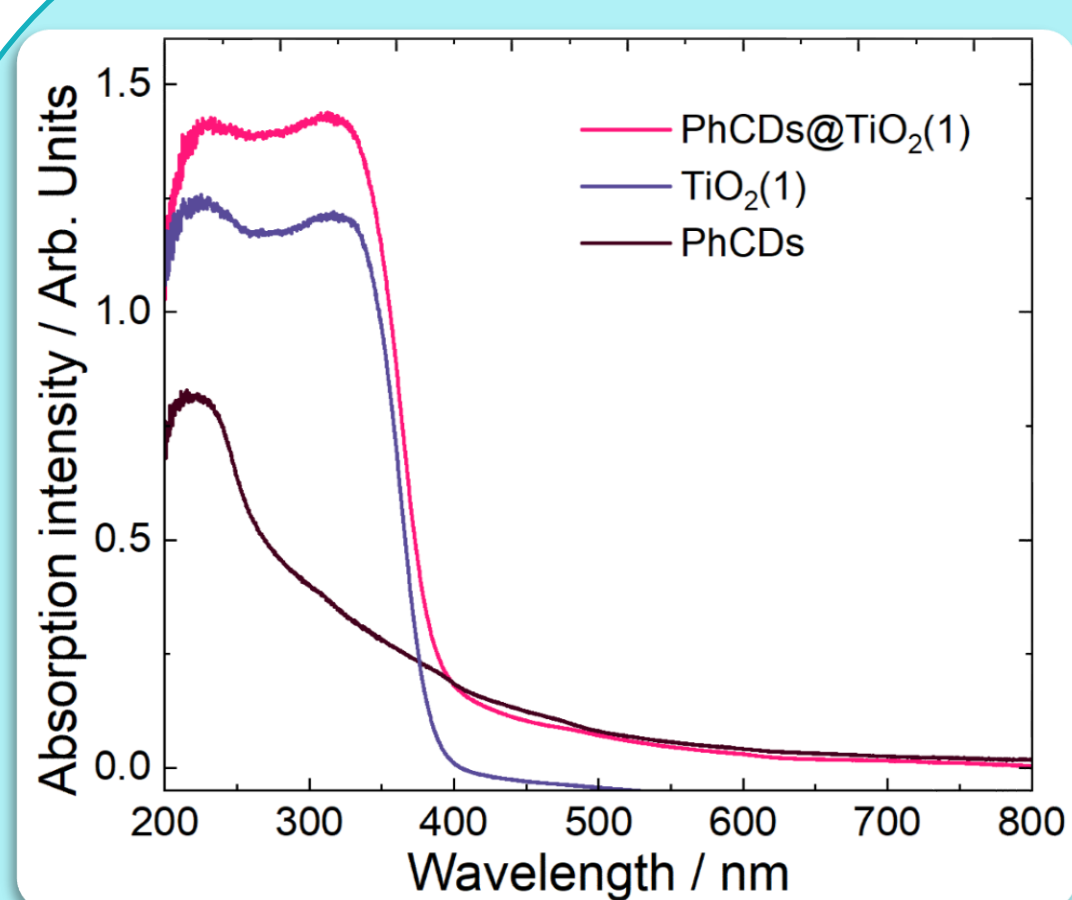


Figure 5. Absorption spectrum of PhCDs, TiO<sub>2</sub>(1) hybrid material

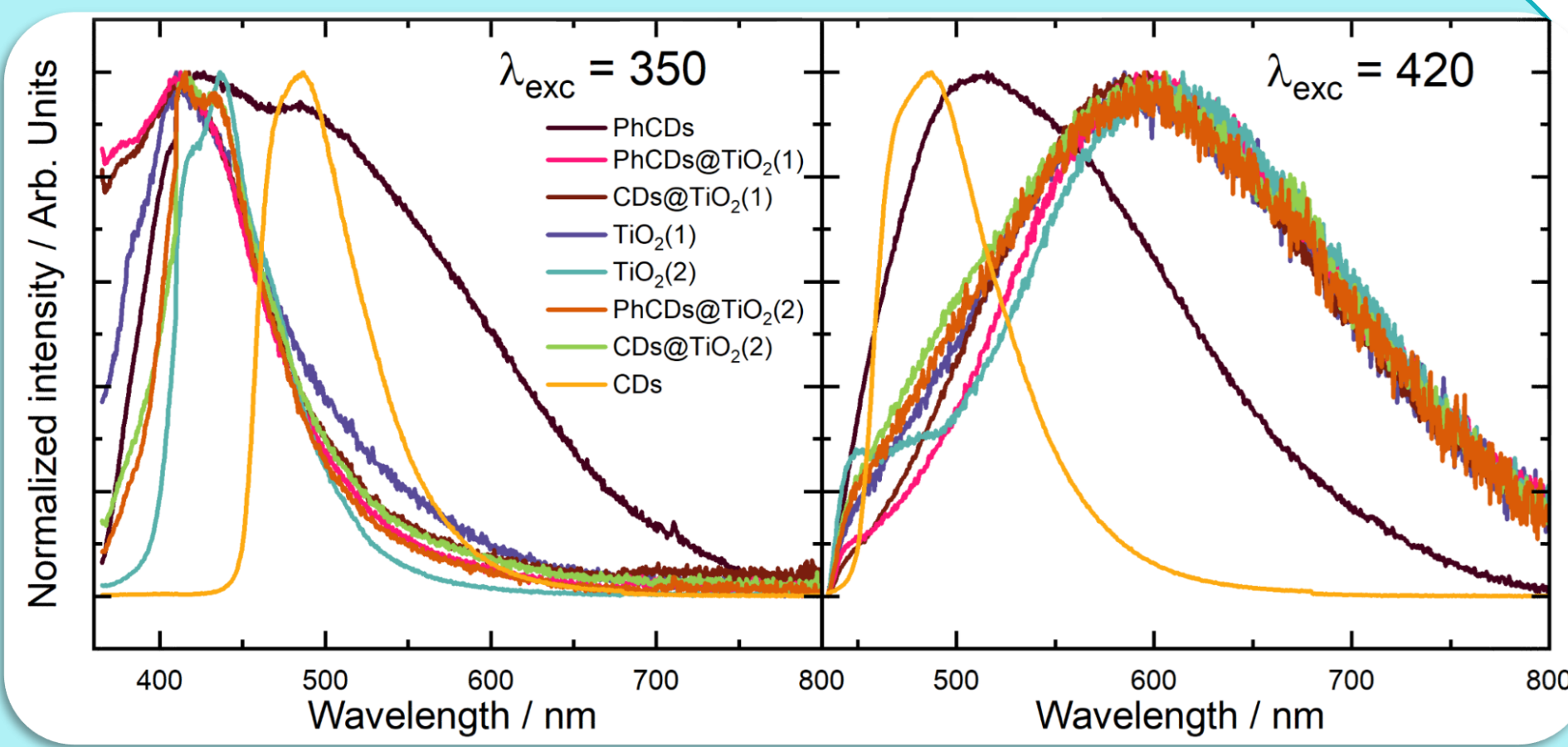


Figure 6. The emission spectrum of CDs, TiO<sub>2</sub>, and hybrid materials.

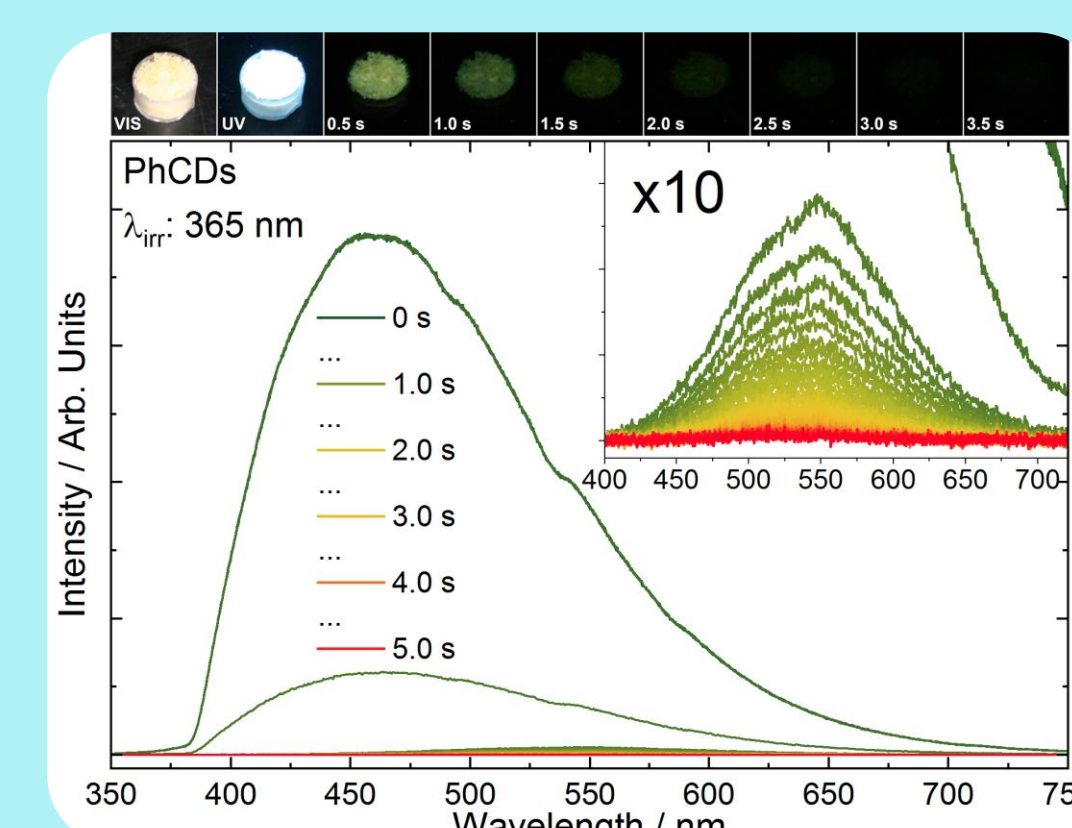


Figure 7. PhCDs luminescence spectrum in the function of time

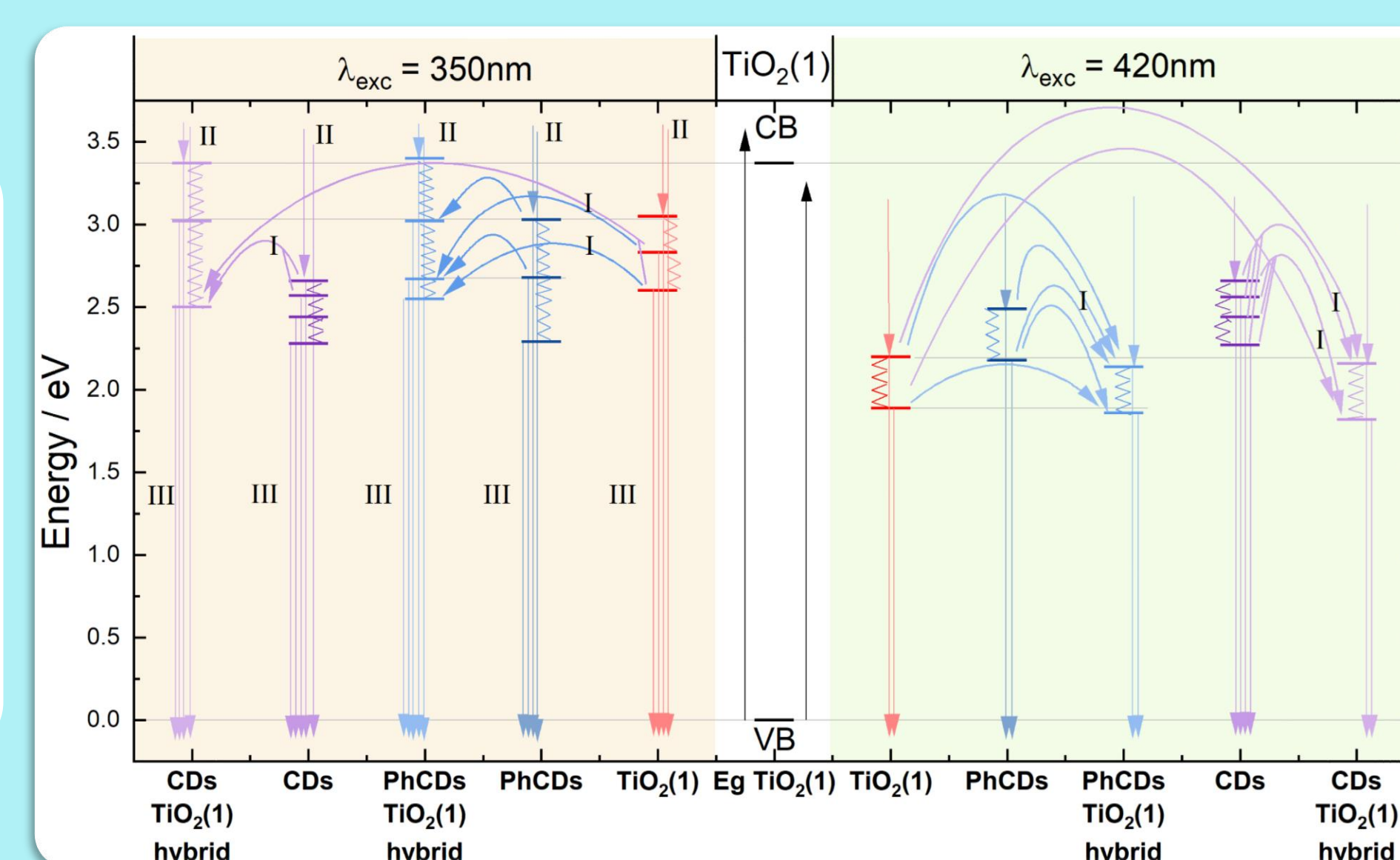


Figure 8. Mechanism of energy transfer in TiO<sub>2</sub>(1), PhCDs, CDs, and hybrid materials

### PHOTOCATALYTIC ACTIVITY

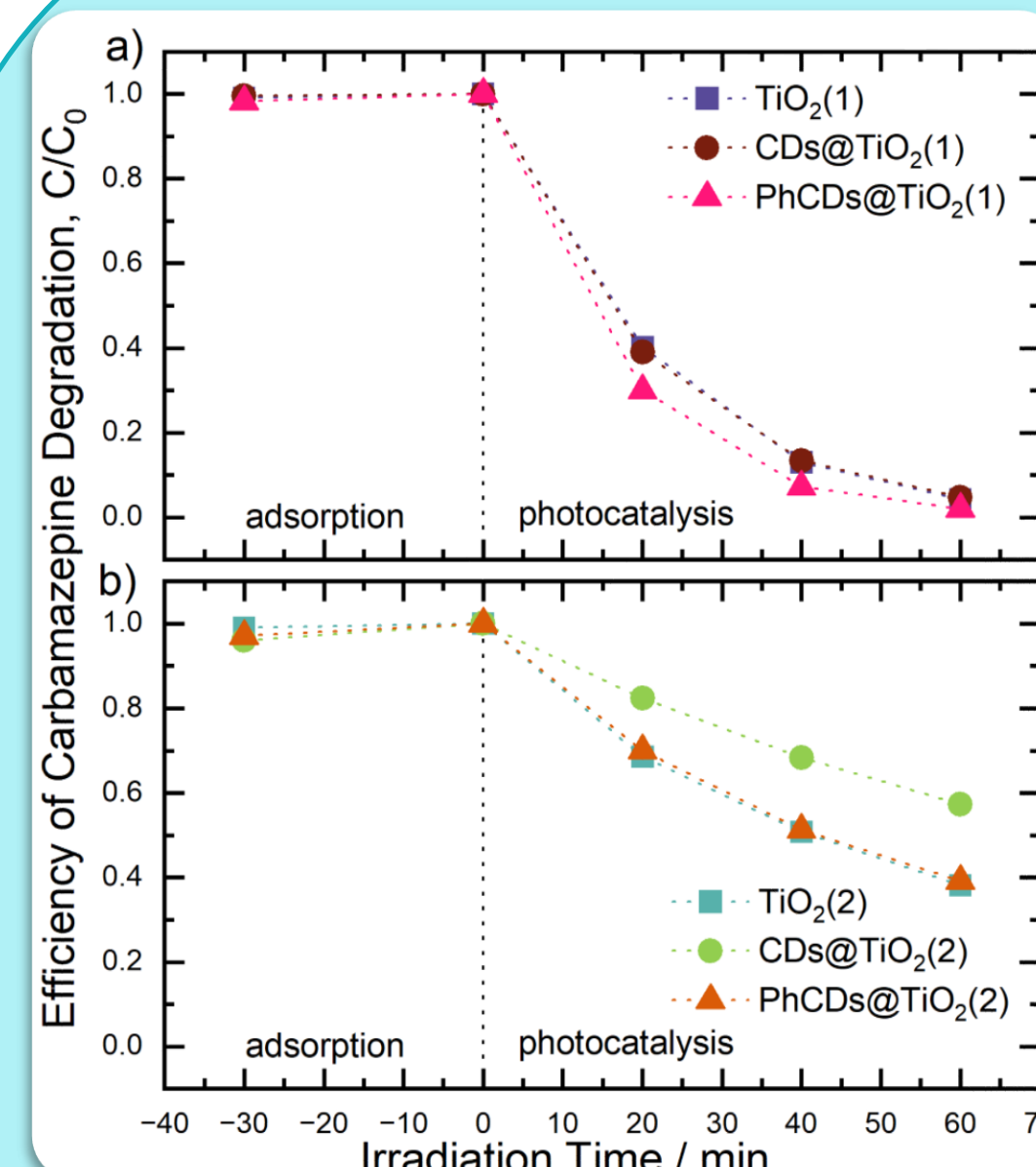


Figure 11. Efficiency of carbamazepine degradation

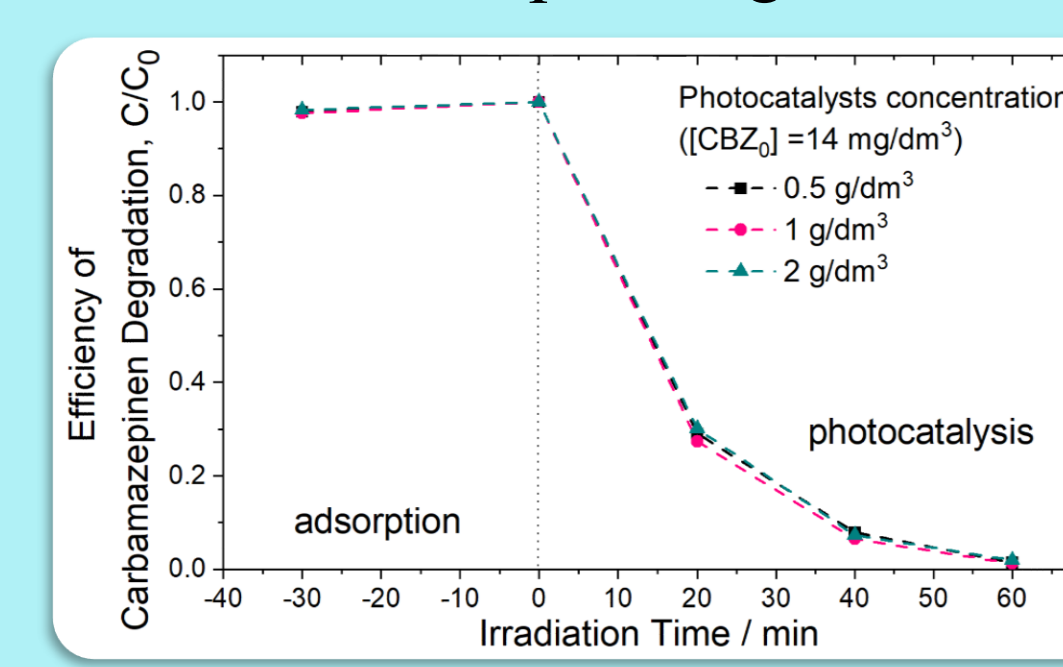


Figure 12. Efficiency of carbamazepine degradation at various dosages of PhCDs@TiO<sub>2</sub>(1)

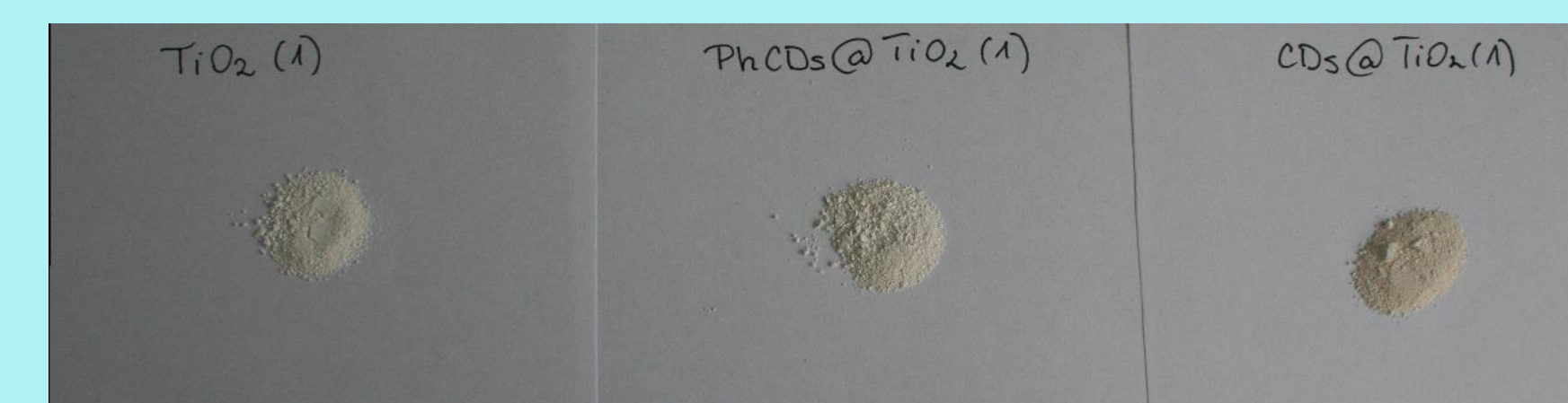


Figure 13. Image of TiO<sub>2</sub>(1) and hybrid materials.

Table 1. Photocatalytic activity of the prepared samples

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

Table 2. Photocatalytic activity of the PhCDs@TiO<sub>2</sub>(1) photocatalyst applied at various dosages

Photocatalyst dosage	Degradation rate constant $k \cdot 10^{-2}$ (min <sup>-1</sup> )	Efficiency of TOC reduction (%)
0.5 g/dm <sup>3</sup>	7.01	63.1
1 g/dm <sup>3</sup>	7.33	61.9
2 g/dm <sup>3</sup>	6.59	60.2

## CONCLUSIONS

- Four hybrid materials were prepared using two types of TiO<sub>2</sub> and two types of CDs. Structural analysis showed that the addition of CDs did not alter the TiO<sub>2</sub> structure. Absorption studies indicated a shift of the absorption edge toward visible light for TiO<sub>2</sub>(1) after PhCDs modification, and emission spectra analysis helped explain the luminescence mechanism in the hybrids.
- Photocatalytic tests revealed that phosphorescent CDs improved the activity of TiO<sub>2</sub>(1), with an optimal catalyst concentration of 1 g/dm<sup>3</sup>. In contrast, adding CDs did not cause major differences in this process. In the case of TiO<sub>2</sub>(2), the addition of both types of carbon dots resulted in a reduction in the efficiency of this process.
- Overall, the results confirm that phosphorescent carbon dots can enhance photocatalysis by stabilizing electrons in the excited state, thereby slowing electron-hole recombination.