Photocatalytic Degradation by Graphitic Carbon Nitride - [PD]

(Anna Vanluchene)

1. Introduction

Photocatalysts are materials that use light energy to generate reactive charge carriers, namely electrons and holes, which can initiate oxidation and reduction reactions at their surface. In environmental applications, photocatalysis is often employed to degrade organic dyes or other pollutants in water, converting them into less harmful or fully mineralized products such as CO_2 and H_2O. Graphitic carbon nitride (g-C_3N_4) is particularly suitable for such applications because its band gap allows activation under visible light, which represents a significant part of the solar spectrum. [1]

A major limitation of pristine g-C_3N_4 is the fast recombination of photogenerated electrons and holes, which reduces the number of charge carriers available for photocatalytic reactions and therefore limits its activity. This drawback can be mitigated by modifying the material, for example by doping it with metal oxides. [2] Such modifications can improve charge separation, extend the lifetime of charge carriers, and enhance overall photocatalytic performance.

In this experiment, two photocatalysts based on graphitic carbon nitride will be investigated: undoped g-C_3N_4 and g-C_3N_4 doped with Fe_2O_3. Their photocatalytic activity is evaluated by comparing their ability to degrade the model dye Rhodamine B under visible light irradiation. The degradation process will be monitored using UV–Vis spectroscopy, allowing a quantitative comparison of the reaction rates and an assessment of the effect of doping on photocatalytic performance. [3]

2. Theory

2.1 Graphitic carbon nitride

Graphitic carbon nitride is a polymeric semiconductor composed of heptazine units (tri-*s*-triazine rings) linked together into a two-dimensional network (Figure 1.A). These layers stack on top of each via van der Waals interactions in a manner similar to graphite. The large number of nitrogen atoms in the structure gives g-C_3N_4 interesting electronic properties, making it suitable for visible-light photocatalysis.[4]

Due to its conjugated π-electron system, g-C_3N_4 has a defined band gap between its valence band (VB) and conduction band (CB). The band gap is about 2.7 eV, which corresponds to absorption of visible light (around 450 nm). When g-C_3N_4 absorbs light with sufficient energy, an electron is excited from the VB to the CB, leaving behind a positive hole (h^+) in the VB. This process is called photogenerated charge separation and can be described by simple equation:

$$g\text{-}C_3N_4 + h\nu \rightarrow e^- + h^+$$

The photogenerated electrons e^- and holes h^+ can further participate in reduction and oxidation reactions, respectively, at the surface of the photocatalyst (Figure 2.B).

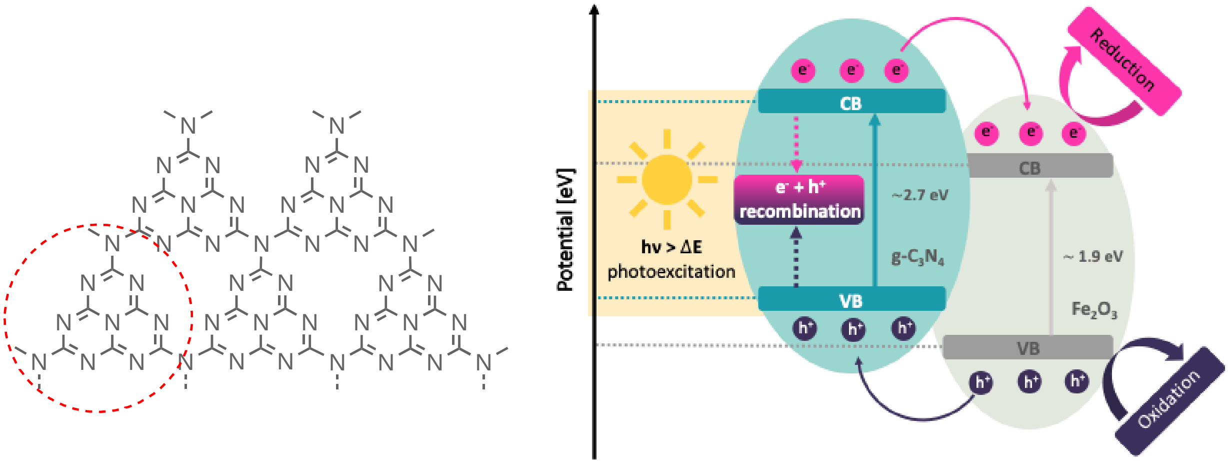

Figure 1: A) Basic structural unit of $g\text{-}C_3N_4$ and its extended network. B) Band structure of $g\text{-}C_3N_4$, electron-hole generation, recombination pathways and chargé separation improvement when Fe_2O_3 is added.

A major limitation of $g\text{-}C_3N_4$ is that the photogenerated electrons and holes can recombine very quickly. Recombination releases energy as heat or light and reduces the number of charge carriers available for photocatalysis, decreasing efficiency. In undoped $g\text{-}C_3N_4$, recombination is one of the main reasons the material often shows moderate activity. Doping improves photocatalytic activity by **creating charge-transfer pathways:** Fe_2O_3 has its own conduction and valence band positions. When combined with $g\text{-}C_3N_4$, the two semiconductors can transfer electrons or holes between each other. This enhances **charge separation**, because electrons migrate away from the holes instead of recombining. Additionally, the dopant **act as electron or hole traps:** The interface between $g\text{-}C_3N_4$ and Fe_2O_3 creates sites where charges can temporarily reside (Figure 2.A). This slows recombination and increases the lifetime of charge carriers. These factors then increase the photocatalytic activity of the material.

2.1 Degradation of Rhodamine B

Rhodamine B (RhB) is a common model dye used in photocatalytic studies because it is brightly colored, has a strong absorption peak in the visible range, and its concentration can be easily monitored by UV–Vis spectroscopy. During photocatalysis, RhB is gradually oxidized and broken down by reactive oxygen species (ROS) such as $\bullet OH$ and $\bullet O_2^-$, which are generated on the surface of the illuminated photocatalyst. Over time, the dye first loses its chromophore (the group responsible for its colour), and with continued oxidation it is eventually mineralized into CO_2, H_2O, NO_3^-, and other small inorganic ions. As the dye degrades, its pink color fades. A decrease in absorbance at the maximum wavelength (λ_max ≈ 554 nm) directly indicates a decrease in RhB concentration.

A decrease in RhB concentration over time reflects the progress of the photocatalytic degradation. If the catalyst concentration and light intensity remain constant, the degradation of Rhodamine B typically follows pseudo–first-order kinetics. This means that the reaction rate depends only on the dye concentration, because all other conditions are constant or present in large excess.

The reaction rate is described by the differential rate law:

$$r = -\frac{dc}{dt} = kc$$

Separating variables and integrating from the initial concentration C_0 (at $t = 0$) to the concentration C_t at time t:

$$\int_{C_0}^{C_t} \frac{1}{c} dc = -\int_{t=0}^{t} kdt$$

$$-\ln\left(\frac{C_t}{C_0}\right) = kt$$

Since absorbance is proportional to concentration (Lambert-Beer law), you can substitute absorbance values into the equation:

$$-\ln\left(\frac{A_t}{A_0}\right) = kt$$

Plotting $-\ln(A_t/A_0)$ versus time gives a straight line whose slope is the **rate constant $\boldsymbol{k}$**. A higher value of k indicates a more active photocatalyst.

3. Aim of the Experiments

The aim of this experiment is to compare the photocatalytic activity of two carbon nitride–based catalysts using the photodegradation of a model dye. A reaction mixture containing Rhodamine B and the photocatalyst will be prepared and irradiated under controlled visible-light conditions. Samples will be collected at regular time intervals over the course of the experiment.

Each collected sample will be centrifuged to remove the photocatalyst particles and subsequently analysed by UV–Vis spectroscopy. By monitoring the decrease in absorbance of Rhodamine B as a function of time, the apparent pseudo–first-order reaction rate constant will be determined. The photocatalytic performance of undoped and Fe_2O_3-doped g-C_3N_4 will then be compared based on the obtained rate constants

4. Material

3.1 Chemicals

- Photocatalyst: g-C_3N_4 and g-C_3N_4 doped by Fe_2O_3 (provided by assistant)

- Stock solution of Rhodamine B (with concentration around 70 µM)
- Distilled water

3.2 Equipment and Materials

- Glass quartz cuvette with magnetic stirrer
- LED light source with heatsink and fan
- Disposable plastic cuvettes for UV-Vis measurement
- 2 mL microtubes (Eppendorf tubes) 2 mL
- Automatic pipettes

5. Machine: UV-Vis spectrophotometer

In this experiment, a UV–Vis spectrophotometer will be used. It works on the principle of measuring how much ultraviolet and visible light is absorbed by a sample as the light passes through it. The decrease in light intensity at specific wavelengths corresponds to the concentration of the absorbing compound.

6. Plan of Work

The setup for the kinetic measurements consisted of a 2 cm quartz cuvette equipped with a magnetic stir bar, placed on a magnetic stirrer, and illuminated by a 100 W LED lamp positioned 10 cm from the cuvette.

6.1 Photocatalytic Reaction Procedure

First, prepare the reaction mixture by adding **25 mg of g-C_3N_4 photocatalyst to 25 mL of an aqueous Rhodamine B (RhB) stock solution** with a known concentration (approximately 70 µM; the exact value will be provided by the assistant**). Before adding the catalyst**, withdraw 500 µl aliquot of the RhB solution to later evaluate its absorbance. Sonicate the suspension for 10 minutes to ensure uniform dispersion of the catalyst and to allow adsorption–desorption equilibrium of RhB on the catalyst surface thereby minimizing the influence of initial adsorption on the evaluation of the reaction rate constant.

After sonication, withdraw a **500 µL aliquot** and label it as the sample corresponding to **t = 0 min**. Place a magnetic stir bar into a quartz cuvette, transfer the reaction mixture into the cuvette, and position the cuvette on a magnetic stirrer. Set the stirring speed to 1200 rpm to maintain a homogeneous suspension during the experiment.

Before switching on the LED light source, put on the approved **dark safety goggles**. Switch on the LED lamp only when wearing protective eyewear. Position the 100 W **LED light source at a distance of exactly 10 cm from the quartz cuvette**. Make sure the cuvette is always placed in the same orientation to ensure reproducible irradiation conditions. Once everything is in position, switch on the LED lamp to start the photocatalytic reaction and the cooling fan attached to the heat sink at the LED lamp.

During irradiation, **withdraw 500 µL samples every 4 minutes** over a total reaction time of 40 minutes. Transfer each sample into a labelled microcentrifuge tube for further processing.

When the reaction with the first catalyst is finished, repeat the entire procedure using the second photocatalyst, g-C_3N_4 doped with Fe_2O_3. After completing the experiment, switch off the LED light source and the cooling fan. Thoroughly and carefully wash quartz cuvette used during the experiment with ethanol and distilled water and allow them to dry.

6.2 Sample Processing

Centrifuge all collected samples for **15 minutes at 3000 rpm** in a microcentrifuge to remove the photocatalyst particles. After centrifugation, carefully transfer **400 µL of the clear supernatant** into a spectrophotometric cuvette and **dilute it to a total volume of 3 mL** with distilled water. Make sure that no catalyst particles are transferred, as suspended photocatalyst would interfere with the UV–Vis absorbance measurements.

Measure the absorbance **of each prepared sample** using a **UV–Vis** spectrophotometer at the characteristic absorption maximum of Rhodamine B. Determine the RhB concentration from the calibration curve. Using the obtained concentration–time data, calculate the apparent **pseudo–first-order reaction rate constant *k*** for each experiment and compare the photocatalytic activity of the doped and undoped g-C_3N_4 photocatalysts.

7. Data processing and protocol

For each collected sample, record the absorbance at the characteristic absorption wavelength of Rhodamine B, i.e. at 554 nm. Prepare an overview table containing the following information: sample number, reaction time (time at which the sample was taken), absorbance, calculated RhB concentration, and the normalized concentration ratio c_t/c_0, where c_t is the concentration at time t and c_0 is the initial concentration of the reaction mixture of RhB and the photocatalyst. In addition, evaluate the extent of Rhodamine B adsorption on the photocatalyst by comparing the absorbance of the pure RhB solution (measured before catalyst addition) with the absorbance of the suspension after the dark equilibration step (defined as c_0). The difference between these values reflects the amount of dye adsorbed on the catalyst surface during the dark phase.

Create a graph showing the decrease of Rhodamine B concentration as a function of reaction time to visualize the photocatalytic degradation process.

Subsequently, linearize the data by plotting $-\ln(c_t/c_0)$ versus reaction time. Perform a linear fit of the data points. The slope of the fitted line corresponds to the apparent pseudo–first-order reaction rate constant k. Determine the value of k for both photocatalysts and compare their photocatalytic activities.

In the protocol, evaluate how well the experimental data follow pseudo–first-order kinetics. Discuss the quality of the linear fit, for example by commenting on the linearity of the data points and the correlation coefficient. Deviations from linear behaviour, especially at short or long reaction times, should be identified and briefly discussed. Furthermore, discuss possible sources of experimental inaccuracy. These may include incomplete removal of catalyst particles before UV–Vis measurement, fluctuations in light intensity, inaccuracies in sampling time or volume, deviations from ideal mixing, or errors associated with dilution and absorbance measurements.

Finally, compare the photocatalytic performance of the two catalysts. Comment on the differences in the obtained reaction rate constants and discuss possible reasons for the observed behaviour.

8. Safety instructions

Always **wear protective laboratory dark goggles** when working with the LED light source. Never look directly into the LED. Switch on the LED lamp only when wearing approved dark safety goggles. Ensure that the cooling fan is operating during irradiation. After completing the experiment, switch off the LED lamp and the fan before handling or cleaning the equipment.

9. Control questions

1. What is photochemistry and where is it applied?
2. How does a semiconductor photocatalyst work?
3. Why are photocatalysts doped and how does doping affect their electronic structure?
4. How can the efficiency of different photocatalysts be evaluated and how may their performances differ?
5. What safety precautions must be followed during this experiment?

10. Literature

1. Liu, J., Wang, H., & Antonietti, M. (2016). Graphitic carbon nitride “reloaded”: emerging applications beyond (photo) catalysis. *Chemical Society Reviews*, *45*(8), 2308-2326.
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4. Sudhaik, A., Raizada, P., Shandilya, P., Jeong, D. Y., Lim, J. H., & Singh, P. (2018). Review on fabrication of graphitic carbon nitride based efficient nanocomposites for photodegradation of aqueous phase organic pollutants. *Journal of Industrial and Engineering Chemistry*, *67*, 28-51

11. List of Symbols

Symbol	**Description**	**Unit**
e^-	electron	–
h^+	hole	–
h	Planck constant	J·s

ν	frequency of light	s^{-1} (Hz)
CB	conduction band	–
VB	valence band	–
r	reaction rate	$mol \cdot L^{-1} \cdot s^{-1}$
c	concentration	$mol \cdot L^{-1}$
t	time	s
k	reaction rate constant	s^{-1}
A	absorbance	–