EFFECT OF EXFOLIATION CONDITIONS ON THE PHOTOCATALYTIC PROPERTIES OF GRAPHITIC CARBON NITRIDE INVESTIGATED BY ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

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Abstract

Graphitic carbon nitride (GCN) is a promising material in the field of photocatalysis. Mott-Schottky analysis and electrochemical impedance spectroscopy (EIS) were used to investigate the electronic structure of exfoliated GCN. The conduction band potential was measured by Mott-Schottky measurement. The results of Mott-Schottky measurements suggest that exfoliation can be used to modify the electronic structure of GCN and potentially improve its photocatalytic properties. Electrochemical measurement in combination with photodegradation studies provided a deeper insight into the photocatalytic mechanism of action of these materials and will allow further improvement in its photocatalytic qualities.

Keywords: Photocatalysis, electrochemistry, nanomaterials

1. INTRODUCTION

In recent years, graphitic carbon nitride (GCN) has attracted significant attention as a highly promising material in the fields of photocatalysis, energy storage, and electrocatalysis. GCN shows a distinctive electronic structure, intrinsic chemical stability, and completely metal-free composition. Structurally, GCN is a polymeric semiconductor consisting of heptazine or triazine units, with a moderate band gap of approximately 2.7 eV. This bandgap enables efficient absorption of visible light, thereby facilitating a wide range of redox reactions. Moreover, its layered structure, similar to that of graphite, provides a substantial surface area and tuneable physicochemical properties. These features predetermine GCN as an exceptionally attractive candidate for applications in sustainable energy conversion and environmental remediation, where stable, earth-abundant, and non-toxic materials are highly desirable.

Despite these advantages, pristine GCN is often constrained by several inherent limitations. The main limitations among these include low electrical conductivity, rapid recombination of photo-generated charge carriers, and a comparatively limited number of catalytically active sites. These challenges significantly limit its efficiency in practical photocatalytic processes [1]. Consequently, substantial research efforts have been devoted to strategies aimed at overcoming these drawbacks. Such approaches have included exfoliation into nanosheets, the construction of heterostructures with suitable semiconductors or co-catalysts, doping with non-metals and metals to tailor the band structure, and surface functionalisation techniques to modulate its interfacial chemistry [2].

Among these modification strategies, the exfoliation of bulk GCN into nanosheet forms has attracted particular attention. Exfoliation not only improves the accessibility of active sites but also promotes higher charge-carrier mobility, effectively reducing recombination losses. This structural refinement leads to an enhancement of the photocatalytic and electrochemical activity, rendering exfoliated GCN nanosheets particularly promising for advanced applications in energy storage and catalytic conversion processes [3].

In this paper, we focus on characterising exfoliated GCN using electrochemical impedance spectroscopy (EIS) to describe its electronic structure, charge transport, and interfacial properties. By employing this method, we aim to study the underlying charge-transfer behaviour of exfoliated GCN and electronic structure. The results obtained were further compared with the results of the photodegradation of phenol and rhodamine B.

2. EXPERIMENTAL

For the preparation of GCN, a thermal synthesis was selected. Melamine (Sigma-Aldrich, USA) was heated at 550 °C for 4 hours under an air atmosphere, and the product was labelled as bulk. The exfoliation was carried out by a thermal route, that is, heating the bulk GCN at 525 ° C for 30, 60, 90 and 120 min to achieve different stages of exfoliation, and these products were labelled exf1-4.

The specific surface area (SSA) was measured by physisorption of nitrogen in the relative pressure range of 0.05 to 0.25 in Sorptomatic 1990 (Thermo Scientific, USA)). Data were evaluated using the Brunauer-Emmett-Teller (BET) method.

Reflectance spectra were recorded on a Shimadzu UV-2600 spectrometer equipped with an integrating sphere 2600Plus (Shimadzu, Japan). Measurements were carried out at room temperature in the range of 200-900 nm.

The photocatalytic activity of the synthesised materials was tested using phenol and rhodamine B (RhB) at a concentration of 10 $mg \cdot l^{-1}$. The measured mixture contained 45 mg of exfoliated GCN and 150 ml of the solution of phenol or RhB. The suspension obtained was stirred for 60 min in the dark before photocatalytic degradation. After the dark period, the suspension was irradiated with a light source (420 nm, intensity of 13.5 $mW \cdot cm^{-2}$) for 120 min. The temperature in the reaction mixtures was kept at 20 °C. 3 ml samples were taken using a syringe in regular time intervals and filtered using Chromafil GF/RC-20/25 syringe filtres (pore size 0.2–1.0 μm). The concentration of RhB was determined directly by measuring the absorbance of the filtered RhB solution at 554 nm using VIS spectroscopy. For the determination of phenol, 1 ml of filtered solution, 9 ml of distilled water, and 4 ml of 5 % solution of Na2CO3 were mixed. Subsequently, 4 ml of a diazotized solution of 4-nitroaniline was added to the previously prepared water solution of the sample and Na2CO3 and stirred. After 15 min, the absorbance of solution at 470 nm was measured.

Electrochemical impedance spectroscopy measurements were performed on a potenciostat Autolab PGSTAT302N (Metrohm, Switzerland). GCN samples were measured in the form of thin films. The preparation of the films was as follows. First, the GCN sample was dispersed in distilled water. The suspension obtained was sonicated and then dropped on the working electrode and dried in an oven at 80 °C. The electrolyte in which the measurements were carried out was 0.5 M Na2SO4. The Mott-Schottky measurements were made at 100 Hz in the potential range -1.2 to -0.5 V vs. Ag/AgCl. The Mott-Schottky plots of the bulk GCN were additionally constructed at 50, 300, and 500 Hz.

The measurement principle is based on the fact that GCN (like TiO_2) is an n-type semiconductor and that its flatband potential is nearly identical to the conduction band potential (VCB). To determine the flat-band potential, we can use the Mott-Schottky equation:

$$\frac{1}{C^2} = \frac{2}{\varepsilon\, \varepsilon_0\, e\, N\, D}\left(\mathrm{V} - \mathrm{VFB} - \frac{\mathrm{kT}}{e}\right) \qquad (1)$$

This relation allows us to determine the flatband potential (VFB), using EIS we can measure the capacitance (C) of the space-charge layer on the surface of the investigated material under an applied external potential (V). Other parameters in the equation are the semiconductor dielectric constant (ε), the vacuum dielectric constant (ε_0), the elementary charge (e), the dopant density (ND), the Boltzmann constant (k) and the temperature (T).

3. RESULTS AND DISCUSSION

The bulk GCN was successfully exfoliated as indicated by increasing the SSA values (**Table 1**). **Table 1** shows that the exf4 sample has more than 20 times higher SSA than the bulk GCN. Higher SSA can lead to improved photocatalytic properties, as a larger surface area enhances the adsorption rate, which is essential for photocatalysis [4, 5].

Table 1 Table of SSA, VFB, VCB, energy band gap and valence band potential

Material	**Specific surface ($m^2 \cdot g^{-1}$)**	**Flat-band potential (V) (vs. Ag/AgCl)**	**Conduction band potential (V) (vs. NHE)**	**Band gap (eV)**	**Valence band potential (V) (vs. NHE)**
TiO_2	46	-0.98	-0.66	3.20	2.54
Bulk	12	-1.41	-1.09	2.67	1.58
exf1	74	-1.38	-1.06	2.71	1.65
exf2	147	-1.36	-1.04	2.74	1.70
exf3	201	-1.31	-0.99	2.91	1.92
exf4	259	-1.27	-0.95	2.97	2.02

To confirm the validity of the EIS measurement, the Mott-Schottky plots of the bulk GCN were constructed for four different frequencies (**Figure 1**). The VFB resulting from extrapolated lines of the plots at different frequencies are slightly shifted from one another with deviation of approximately 5 %. This slight shift could be attributed to the particulate character of the samples and surface roughness [6].

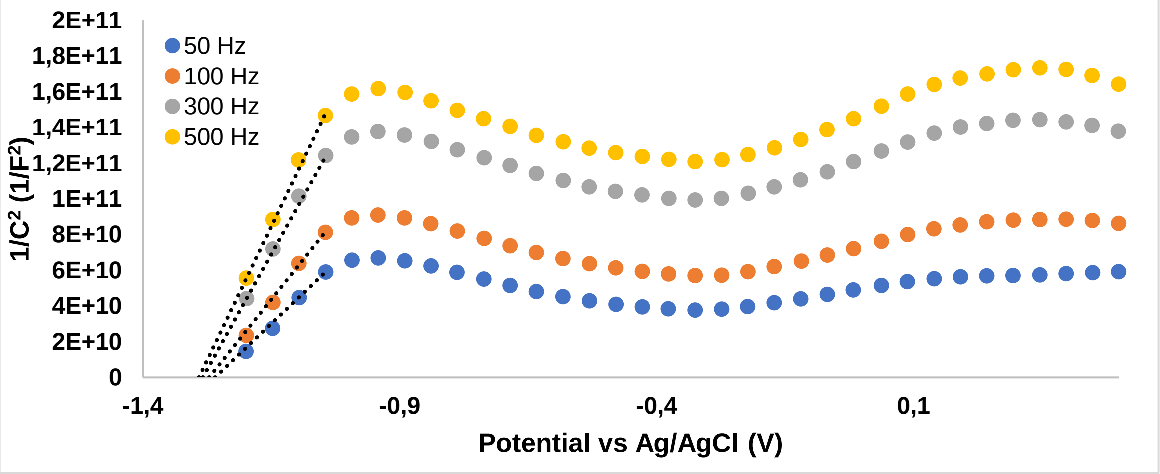

Figure 1 Mott-Schottky plots of bulk GCN at frequencies 50, 100, 300 and 500 Hz

The VFB of commercial TiO_2 was -0.66 V vs. NHE, which is consistent with the literature [7, 8]. The VFB of the bulk GCN was -1.09 V vs NHE, and the GCN in progressing stages of exfoliation exhibited a gradual shift of VFB towards less negative potentials. This trend is visualised in **Figure 2**, which shows the Mott-Schottky plots of all the samples compared to each other.

The dopant density of the material is inversely proportional to the slope of the extrapolated lines of the Mott-Schottky plots (**Figure 2**) and the dielectric constant of the material. Dopant stands for impurities, or defects in the crystalline structure that act as an electron donor. The slope of the lines constructed from Mott-Schottky plots of the bulk GCN is approximately 3 times higher than that of TiO2. Since the dielectric constant of GCN at 100 Hz is 7 and TiO_2 is 80 – 90 [9], meaning 12 times lower, we can presume that the dopant density of synthesised GCN is at least 4 times higher than that of TiO_2.

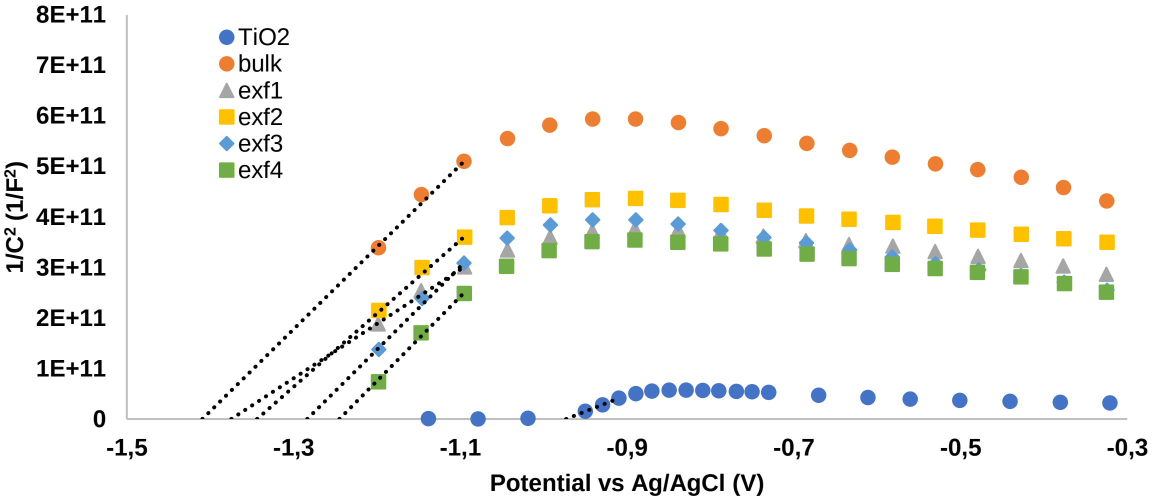

Figure 2 Mott-Schottky plots of TiO_2, bulk, exf1, exf2, exf3 and exf4 samples at 100 Hz

The band gap of the bulk GCN was 2.67 eV and gradually increased with the level of exfoliation to 2.97 eV in the most exfoliated sample (**Table 1**).

Photocatalytic degradation of pollutants involves oxidation by reactive oxygen species such as superoxide and hydroxyl radicals. Photogenerated electrons (e^-) and holes (h^+) on the surface of the photocatalyst react with water, oxygen, or hydroxyl molecules to produce such reactive species. This reaction occurs when the edges of the conduction or valence band of the photocatalytic material are more negative or positive than the redox potential of the generation of reactive species [10].

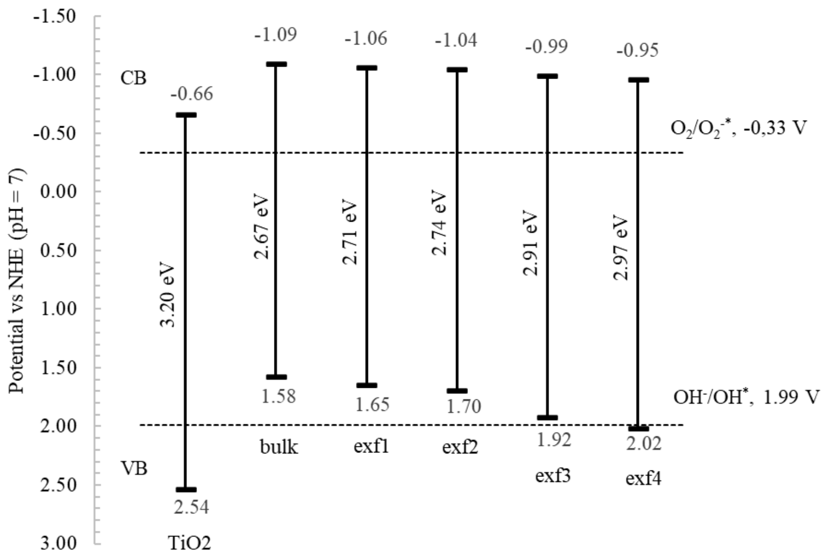

Figure 3 Diagram of conduction and valence band potentials and band gap energies of TiO_2, bulk, exf1, exf2, exf3 and exf4 samples

As evidenced in **Figure 3**, the shift of the VCB and a wider band gap in the exfoliated samples resulted in the potential of the valence band of the exf4 sample reaching the potential of the generation of hydroxyl radicals and thus allowing another mechanism of pollutant degradation. The overlap is very small, and the generation of hydroxyl radicals needs to be confirmed by another method. However, this demonstrates the potential of exfoliation to manipulate the energy structure of GCN to achieve a specific photocatalytic effect.

The most efficient material tested for the photocatalytic degradation of both phenol and RhB was exf3 as can be seen in **Figures 4 and 5**. These figures also clearly demonstrate that there is an optimal degree of exfoliation of the material to achieve the highest photocatalytic performance. Comparing the data in both figures, it is clearly observable, that the photodegradation of RhB was more efficient compared to phenol. After 120 minutes of irradiation, the extent of RhB degradation reached 98.6 % in the case of sample exf3, whereas only 64.2 % of phenol degradation was reached over the same sample.

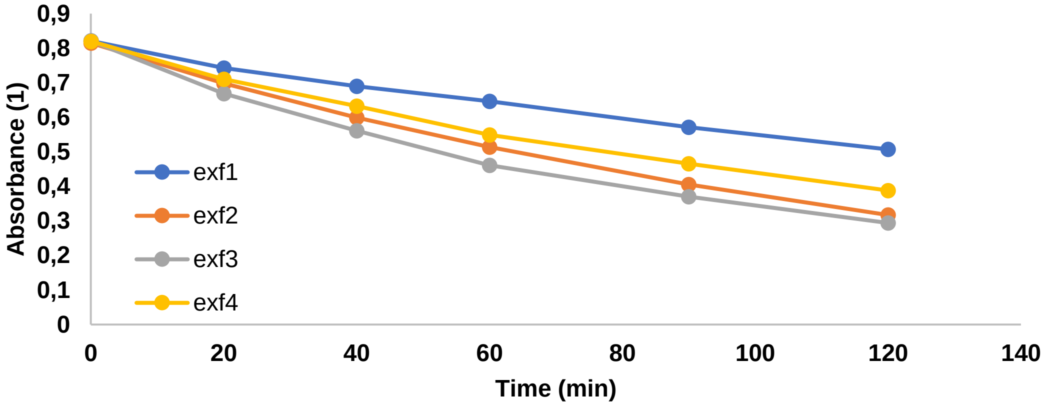

Figure 4 Plot of photodegradation of phenol over time

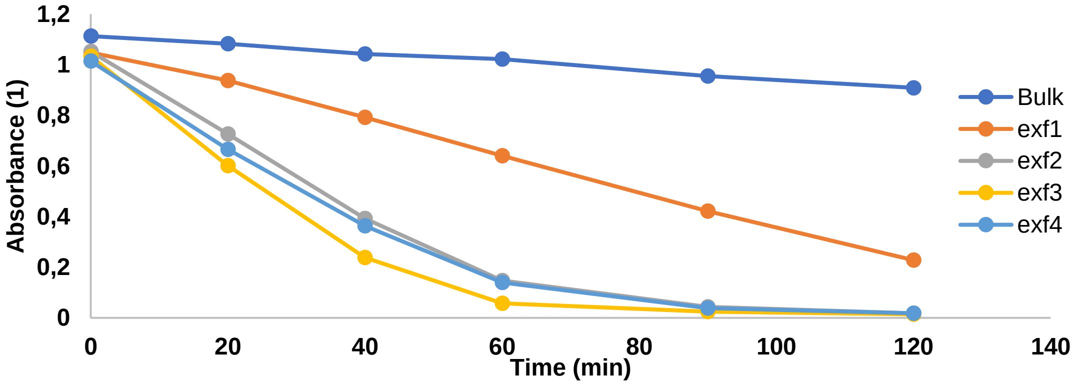

Figure 5 Plot of photodegradation of rhodamine B over time

With an increasing degree of exfoliation, the specific surface area increases, which is closely associated with an enhancement of photocatalytic efficiency. Therefore, sample exf4 would be expected to exhibit the highest activity. However, photodegradation measurements indicate that sample exf3 is the most effective. This discrepancy can be explained by Mott–Schottky and reflectance measurements, which revealed that exfoliation also leads to an increase in the band gap energy. Consequently, the material requires more energy for excitation and therefore for initiating photodegradation processes, which in turn reduces photocatalytic efficiency [11]. These two opposing effects reach an optimum in sample exf3, which achieved the highest degradation efficiency for both RhB and phenol.

4. CONCLUSION

Exfoliated graphitic carbon nitride with high specific surface area was prepared. It was proved that the extent of the exfoliation affects the conduction band potential and band gap energy. It was found that exfoliation leads to the shift of the conduction band potential to more positive values and increases the energy of the band gap as well. The electronic structure of GCN can be altered through exfoliation to improve its photocatalytic properties. Photodegradation measurements revealed that the exf3 sample had the highest degradation activity. A combination of electrochemical probing, surface area measurement, and photodegradation studies was used, and the obtained data were used for discussion of the relation between the degree of GCN exfoliation and its photodegradation activity. Other methods such as the scavenger test or photocurrent measurement can be substantially used in future studies to support the deeper discussion of the effect of GCN exfoliation on the RhB and phenol photodegradation mechanism.

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DATA AVAILABILITY

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