

TESTING OF THE SELF-CLEANING PERFORMANCE OF THE SURFACES MODIFIED WITH g-C₃N₄

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Abstract

Self-cleaning properties of the surfaces of the building materials represent a significant benefit that reduces the operational costs connected to maintenance of the building structures. In principle, the self-cleaning phenomenon can be achieved by three effects: i) hydrophobic, ii) photocatalytic, and iii) a combination of hydrophobic and photocatalytic effects. In our work, we focused on the evaluation of the self-cleaning performance of blocks of pastes made of white cement achieved by the photocatalytic effect. The photocatalyst g-C₃N₄ was applied on the surface of hardened cement pastes and self-cleaning performance of such treated surfaces were evaluated using UNI 11259 'Determination of the photocatalytic activity of hydraulic binders - Rodamina test method, and ČSN ISO 27448 Fine ceramics (advanced ceramics, advanced technical ceramics) — Test method for self-cleaning performance of semiconducting photocatalytic materials — Measurement of water contact angle'. Although the principles of both methods differ, the results obtained using both methods indicate that surfaces covered with g-C₃N₄ exhibit significant self-cleaning performance. In addition, the method based on the measurement of the changes in water contact angle confirmed the suitability of method based on RhB degradation for testing of light-yellowish g-C₃N₄ modified surfaces.

Keywords: g-C₃N₄, photocatalysis, self-cleaning surfaces, nanomaterials

1. INTRODUCTION

Photocatalysis is a promising method for degrading harmful substances, especially in water and air. There are several comprehensive articles addressing this issue, such as [1, 2]. The basic principle of photocatalysis is based on the adsorption of radiation of suitable energy (wavelength) by a photocatalyst, which generates an electron (e⁻) / hole (h⁺) pair. The resulting free charge carriers on the surface of the photocatalysts can directly contribute to the degradation of the harmful substances, but they are mainly involved in the formation of reactive oxygen species (ROS), including superoxide radicals (•O₂⁻), singlet oxygen (¹O₂), hydrogen peroxide (H₂O₂), and hydroxyl radicals (•OH) [3]. During the process of photodegradation ROS participate in chemical reactions with the molecular structures of pollutants, resulting in the generation of carbon dioxide, water, and, based on the specific contaminant, a variety of smaller organic compounds.

The application of photocatalysts in building materials is currently concentrated on three principal areas: self-cleaning, self-disinfecting, and air purification. By applying photocatalysts to the surface of building materials, all three of these benefits can be provided to these surfaces. The most used photocatalyst is TiO₂ in anatase form, with a band gap energy of 3.2 eV [4], and thus can be activated by UV light of wavelengths around 380 nm and shorter. Application of TiO₂ for the preparation of self-cleaning surfaces in the building industry was reported by several authors, for example, [5, 6]. Recently, graphitic carbon nitride (g-C₃N₄) was proven as a promising photocatalyst for the preparation of self-cleaning surfaces, as reported, for example, by Sčučka et

al. [7]. The advantage of g-C₃N₄ over TiO₂ is its narrower band gap, reaching an energy of 2.7 eV [8], which predetermines this photocatalyst for applications in the VIS light spectra.

There are several approaches for evaluation of self-cleaning performance; the most often reported is the one based on UV-assisted discoloration of Rhodamine B (RhB) applied on the surface of building materials based on white concrete. This procedure is described by the standard UNI 11259:2008, (UNI 11259:2008 Determination of the photocatalytic activity of hydraulic binders - Rodamina test method. UNI, Milan, 2008). The changes in the value of coordinates a* in CIE L*a*b* colour space after 4 and 26 h of irradiation is used to indicate whether the surface shows the self-cleaning performance. Although this method is widely used for the characterization of non-white surfaces, the interpretation of the results could bring difficulties, and the utilization of the other methods is preferable. The method based on measuring the light-induced changes in the contact angle of a water drop applied on the tested surface modified with oleic acid is one of the candidates described by the ISO standard (ISO 27448:2009 Fine ceramics (advanced ceramics, advanced technical ceramics) — Test method for self-cleaning performance of semiconducting photocatalytic materials — Measurement of water contact angle).

In our research, we focus on evaluating the suitability of the RhB method defined by UNI 11259:2008 for characterizing the self-cleaning performance of white cement surfaces modified with a light-yellowish exfoliated g-C₃N₄ photocatalyst. The results of RhB tests are compared with the results obtained from the tests described by ISO 27448:2009 standard, based on measurement of water contact angle. The irradiation of the tested surfaces proceeds under simulated daylight, and constant temperature and humidity in a climate chamber.

2. EXPERIMENTAL

2.1 Sample preparation

Bulk g-C₃N₄ was prepared by thermal polycondensation of melamine precursor. In a typical procedure, 10 grams of melamine was put to ceramic crucible, which was covered with a ceramic lid and calcined for 4h at 550 °C in a muffle furnace. After the calcination step, the sample was let to cool down slowly in a furnace. The resulting bulk g-C₃N₄ was labelled as Bulk-gCN.

The exfoliation of g-CN was carried out thermally at 550 °C. In this process, approximately 0.25 g of g-CN was placed on the bottom of a ceramic dish to form a thin layer. The prepared sample was heated at 550 °C for 30 and 45 minutes and the sample was designated TEX30 and TEX45, respectively.

The samples of hardened cement pastes were prepared by mixing white cement (150 g) and tap water, the water to solid ratio was 0.4. After the homogenization of cement and water the resulting paste was introduced to the mold with cavities of dimensions 100 × 50 × 10 mm and further stored in the hydration box (25 °C, 99 %RH) for 24 h. After this period, the samples were unmolded and again stored in hydration box for next 7 days. After this period the samples were taken out and stored in laboratory conditions.

For the coating of hardened cement pastes the suspensions of TEX30 and TEX45 in demineralized water with a concentration of 4 g·dm⁻³ were prepared. The suspensions were mixed in an ultrasonic homogenizer Omni Sonic Ruptor 400 for 15 minutes. The prepared suspensions were applied to the surface of the tested white cement block samples by spraying in two layers.

2.2 Sample characterization

Carbon, hydrogen and nitrogen content of prepared samples was determined on instrument LECO 828 (LECO, USA). Typically, around 100 mg of sample was loaded in tin foil. In a next step the tin foil with sample was gently squeezed and such prepared sample was loaded to an autosampler. The burning of the sample

occurred at 950 °C and the released CO₂ and H₂O are detected using IR cells, while N₂ using thermal conductivity detector.

X-ray diffraction (XRD) analysis was performed using MiniFlex600 theta/2theta diffractometer (Rigaku, Japan) equipped with Co tube ($\lambda = 1,78897 \text{ \AA}$) and a 1D silicon strip D/teX Ultra250 detector. The powder sample was pressed in a rotational holder, the patterns were recorded in the range 10 – 80 °2Theta with step 0.02 °, and scan speed 3 °·min⁻¹. The obtained data were visualised using SW Origin 2020b.

UV-VIS DRS spectra were registered using Shimadzu UV-2600 UV-VIS spectrometer equipped with integrating sphere 2600Plus (Shimadzu Ltd). Powder samples were placed inside a dedicated holder with quartz window and the spectra were recorded at room temperature in the range 200-800nm. Barium sulphate powder was used for base line registration. Tauc's plots [12] were used to evaluate indirect band gap energies.

Specific surface area of the samples was obtained with the method based on physisorption of nitrogen using an instrument Sorptomatic 1990 (Thermo Scientific, USA). The data of adsorbed volume of nitrogen was registered in the range of 0.05 – 0.25 of relative pressure, and further evaluated using Brunauer–Emmett–Teller (BET) method.

The self-cleaning tests were carried out using a method based on ISO 27448:2009 and UNI 11259:2008 standards.

The procedure described by ISO 27448:2009 standard evaluates the ability of photocatalytic materials to decompose organic contaminants based on changes in water contact angle. Contact angles were measured with a contact angle meter (OCA 11, DataPhysics Instruments) using 5 μl droplets at room temperature. A layer of a fatty substance (typically oleic acid) was applied to the sample surface and then exposed to a defined light irradiation under controlled conditions. The effectiveness of the self-cleaning performance was assessed by monitoring changes in the water contact angle during exposure. In our procedure, oleic acid was applied to the samples, which were then placed in a climate chamber (ICH110L, Memmert, Germany) for 24 hours at 20 °C and 60% relative humidity without irradiation. After this period, the daylight source inside the climate chamber was switched on, and the relative humidity was increased to 70%. Contact angle measurements were taken at the start of the test and after 4 and 26 hours of irradiation. The decrease in contact angle at each irradiation time was determined relative to the initial (pre-irradiation) value and expressed for θ_4 for 4 and θ_{26} for 26 hours.

The self-cleaning test according to UNI 11259:2008 standard method is based on the discoloration of RhB applied on the surface of the tested samples. Our procedure included application of RhB solution with a concentration of 50 g·dm⁻³ on the sample surfaces using a lab sprayer. After the RhB application, the samples were conditioned in a dark in climate chambre ICH110L (Mettler, Germany) for 24 h at a temperature of 20 °C and a relative humidity of 60 %. After a 24h dark period, the relative humidity inside the chamber was raised to 70%, and the illumination with a daylight source inside the chamber was started. The colorimetric coordinates $L^*a^*b^*$ of the samples were measured after 4 and 26h of irradiation using a MiniScan EZ 4500S spectrophotometer (HunterLab, VA, USA). The relative changes in coordinate a^* at a given time of irradiation in comparison with this value measured before the irradiation were calculated and expressed as R_4 and R_{26} .

3. RESULTS AND DISCUSSION

Carbon, nitrogen, and hydrogen content were determined using elemental analysis, and the results are compared for both samples in **Table 1**. As evident in **Table 1**, the sum of these elemental contents does not reach 100 wt.% and for both samples, around 5 wt.% is missing, and this content corresponds to oxygen, which was not determined. Carbon content decreased in the case of samples TEX30 and TEX45, while hydrogen and nitrogen contents increased in these samples. The C/N ratio calculated for Bulk-gCN reached 0.59, indicating a non-fully polymerized gCN structure, which typically has a ratio of 0.64. The decrease in C/N ratio observed for samples TEX30 and TEX45 (see **Table 1**) is in good agreement with the results observed

by the other authors [9], indicating that the carbon of the tri-s-triazine building blocks was attacked and burned out during the thermal exfoliation process.

Table 1 Specific surface area and band gap energy of the prepared samples

Samples	C (wt.%)	H (wt.%)	N (wt.%)	C/N	SSA (m ² ·g ⁻¹)	E _g (eV)
Bulk-gCN	35.3	1.82	59.5	0.59	10	2.67
TEX30	34.3	2.07	60.5	0.57	140	2.82
TEX45	32.8	2.08	60.9	0.54	184	2.87

The structure of the samples was studied using the XRD method, and the registered diffraction patterns are shown in **Figure 1a**. The strong diffraction peak centered at approximately 32°2θ (CoKα) corresponds to the (002) plane and is characteristic of the interlayer stacking of aromatic systems, while the low intensity diffraction peak centered at around 15°2θ (CoKα) belonging to the (100) planes corresponds to the interplanar separation [10]. The character of the three diffraction patterns is closely similar and indicates that the character of g-C₃N₄ remained unchanged after exfoliation. A slight shift of the maxima of the TEX30 and TEX45 (002) diffraction peaks towards higher angles is related to a denser packing of g-C₃N₄ layers.

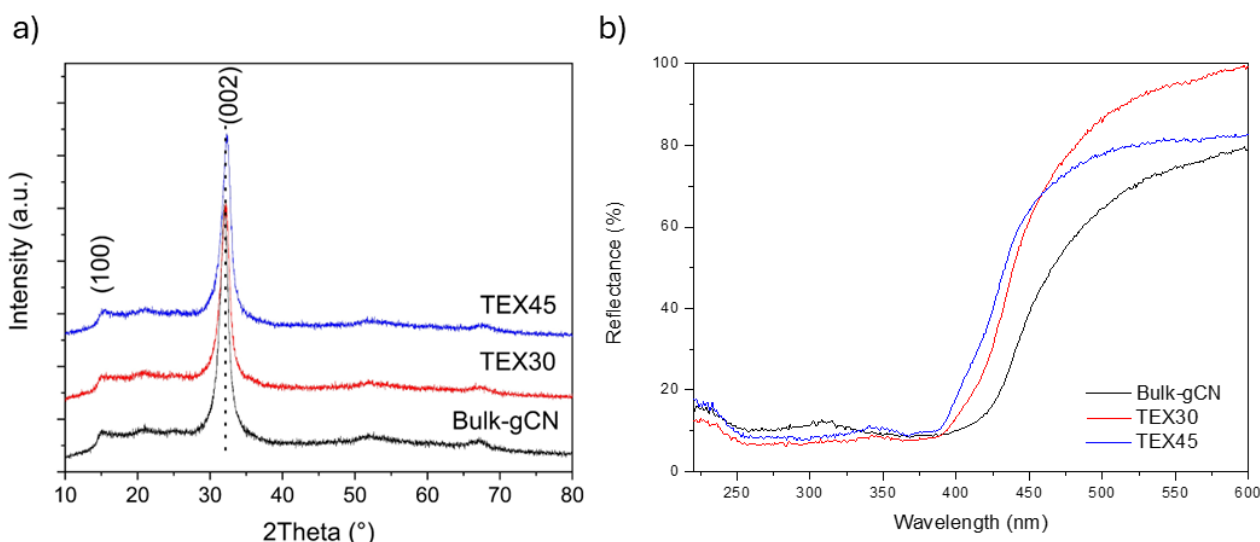


Figure 1 a) X-ray diffraction patterns, and **b)** UV-VIS DRS spectra of bulk-g-CN, TEX30 and TEX45 samples

Figure 1b) shows the registered reflectance spectra of Bulk-gCN, TEX30, and TEX45, respectively. Although both spectra show similar runs, the blue shift of the descending part of the reflectance curve, noticeable in the range of 400- 550 nm observed for TEX30 and TEX45, is a result of the exfoliation process, which caused the origination of 2D gCN nanosheets. The band gap energy values (E_g) obtained using a Tauc's approach (**Table 1**) confirmed the blue shift in the case of the TEX30 and TEX45 samples.

Exfoliated samples of TEX30 and TEX45 were used to coat the surface of white cement samples, and **Figure 2a** shows photograph of white cement samples treated with sample TEX45 and in agreement with UNI 11259:2008 standard stained with RhB. **Figure 2b** and **Figure 2c** show the surface of this sample in different time periods of irradiation. The left side of the sample was protected against the irradiation with aluminium foil, and the **Figure 1b and 1c** clearly document the stability of RhB in position under the foil, contrary to the right side, which evidences the progressive discoloration of the irradiated surface.



Figure 2 White cement block with TEX45 photocatalyst and RhB at **a)** 0, **b)** 4, and **c)** 26 hours of irradiation

The quantitative expression of changes in coordinate a^* is depicted by the values R4 and R26 listed in **Table 2**. Higher relative changes in a^* value after 4 and 26h of irradiation were reached for the cement block coated with TEX45, indicating this sample as a better photocatalyst for self-cleaning surfaces.

Table 2 Self-cleaning test results according to UNI 11259:2008 and ISO 24448:2009

Samples	UNI 11259:2008		ISO 24448:2009	
	R4 (%)	R26 (%)	Change θ_4 (%)	Change θ_{26} (%)
Substrate	2	6	-6	-2
TEX30	44	68	44	68
TEX45	53	76	53	76

The light induced change in the contact angle of a water drop on the surface of hardened cement paste, modified with TEX45 and then coated with oleic acid, is visible before and after 24 hours of irradiation by comparing **Figure 3a** and **Figure 3b**.

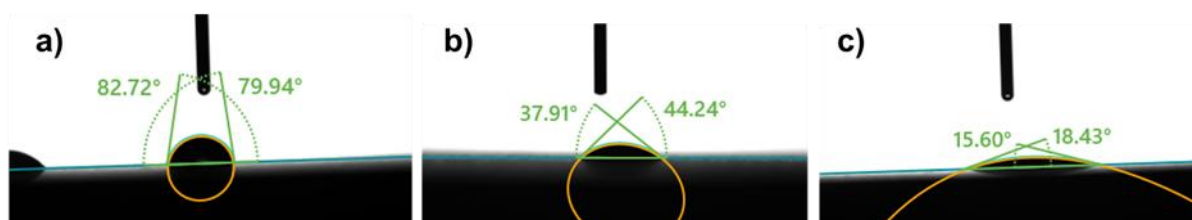


Figure 3 Contact angle of sample TEX45 **a)** before irradiation, **b)** after 4 hours and **c)** after 26 hours of irradiation

The percentage reduction in contact angles after irradiation for 4 and 26 hours for both samples is listed in **Table 2** as θ_4 and θ_{26} . In the case of the substrate (sample without TEX layer), the contact angle increased; this fact is evidenced by the negative values of θ_4 and θ_{26} in **Table 2**. On the other hand, the expected decrease in hydrophobic behaviour of the surface coated with oleic acid due to its photodegradation over the TEX30 and TEX40 photocatalyst is clearly evidenced by the positive values in **Table 2**.

Although both methods used for evaluation of self-cleaning performance are based on measurement of totally different parameters, i.e. R4 and R26 vs θ_4 and θ_{26} , **Table 2** shows identical quantitative differences in these parameters.

4. CONCLUSION

Exfoliated graphitic carbon nitride represents a very promising photocatalyst for modifying surfaces to achieve self-cleaning performance. Its light-yellow coloration could negatively affect the results of the tests defined by UNI 11259:2008 based on the degradation of RhB, which is dedicated to white surface. The test described by

ISO 24448:2009 is more robust since it is not affected by the surface colour. Close similarity in the results obtained by both methods confirmed the usability of RhB test for testing of the surfaces modified with g-C₃N₄.

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DATA AVAILABILITY

The data presented in this study are available in ZENODO at [10.5281/zenodo.17340501](https://zenodo.org/doi/10.5281/zenodo.17340501)

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