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Preliminary studies of photocatalytic activity of gypsum plasters containing TiO_2 co-modified with nitrogen and carbon

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The conducted studies were focused on the development of the gypsum material exhibiting self-cleaning properties. To this end, the raw gypsum was mixed with unique TiO_2-based photocatalysts, previously modified by nitrogen and/or carbon doping. The photocatalytic activity of the obtained gypsum plasters was evaluated trough the degradation of model organic compound (Reactive Red 198) under UV-vis irradiation. The impact of the photocatalysts presence on the physicochemical properties of the obtained gypsum plasters was evaluated. Furthermore, the role of non-metals presence on the photocatalytic properties of the TiO_2 was determined. It was confirmed that the addition of N,C co-modified titanium dioxide into gypsum bestows this material with self-cleaning properties. The highest dye removal rate was displayed by the gypsum plaster containing optimal amount (10 wt%) of co-modified TiO_2/N,C photocatalyst, after 20 hours of UV-vis irradiation.

Keywords: titanium dioxide, gypsum, TiO_2/N,C, self-cleaning, Reactive Red 198.

INTRODUCTION

Textile dyes and other industrial dyestuffs constitute one of the largest groups of organic compounds which represent an increasing danger to the environment[1–3]. From the environmental point of view the chemical stability of the dyes poses a problem. Recent studies have focused on the development of new methods, such as photocatalysis which, in principle, leads to the complete mineralization of the targeted pollutants[4, 5].

Among all semiconductors, the most widely used semiconductor catalyst in photoinduced processes is titanium dioxide (TiO_2)[6–9]. Photocatalytic process proceeds according to the following mechanism: photons are absorbed by TiO_2, which generates electron-hole pairs. In contact with water and oxygen, free radicals (mainly $O_2^{\bullet -}$ and $^{\bullet}OH$) are generated, which are able to oxidize organic matter to water and carbon dioxide, leaving no other residue[10, 11].

A development of photooxidation processes based on titanium dioxide has been applied in several new approaches, involving for example the preparation of photocatalytically active materials such as: paints, wallpaper, paper sheets, textiles and others[12–15]. Most recently great attention has been given to the studies of building products revealing self-cleaning properties and capability to improve outdoor or indoor air quality[16, 17]. The results presented in the literature[18, 19]describe the preparation of different verities of TiO_2-loaded coatings suitable for outdoor application. It was proven[10] that TiO_2-SiO_2 on the limestone, apart from self-cleaning properties are able to adhere firmly to the stone, and improve its robustness. However, bleaching of the selected organic dye (Methylene Blue) under visible/UV light required extensive irradiation, exceeding 1000 hours. Moreover, other authors[20] focused on the influence of photocatalysts particle size on the removal of pollutants in outdoor conditions from the surface of building materials. The films of TiO_2 nanostructured colloids synthesized by a simple hydrothermal method exhibited high self-cleaning performance, compared to P25, what was attributed to nanosize effect. Furthermore, several attempts have been made leading to successful incorporation of the photocatalyst to the bulk of the material[21–23]. The most commonly modified group of the building materials, revealing self-cleaning properties (due to addition of the photocatalyst) are cements[22, 24, 25–30]. Little attention however is given to the other group of popular building materials such as gypsum, which is a natural, environmentally friendly and fireproof material, with good acoustic performance[31]. For those reasons the gypsum-based plasters are one the most widely applied interior walls and ceilings coatings[32].

The objective of this study was to investigate whether the additive of nitrogen and carbon co-modified TiO_2 photocatalyst can improve self-cleaning properties of gypsum plasters. In view of the literature data[33–37, 25], it is believed that, the observed in pure (unmodified) TiO_2 drawbacks, regarding the high excitation energy level requirement of the TiO_2 particles[29, 40], influencing the initiation time and effectiveness of the photocatalytic process, can be overcome by doping titania with those two non-metal ions.

EXPERIMENTAL

Preparation of the N and/or C modified titania photocatalysts

The commercial amorphous titania supplied by Grupa Azoty Zakłady Chemiczne „Police" S.A. (Poland) was used as a crude material for the synthesis of N and/or C modified TiO_2 photocatalysts. Before modification, basic TiO_2 was firstly rinsed with 0.6 M solution of ammonia water and then with distilled water, until pH value reached ca. 6.8. Acquired suspension was filtered and then obtained TiO_2 slurry was pre-dried for 24 hours at 90°C. Dried TiO_2 (15 g) was placed into the

central part of the tubular furnace and heated up to 100°C (5°C/min) in argon flow (100 cm^3/min, 99.999%, Messer, Poland). Successively, in the case of TiO_2/N,C photocatalyst preparation the inert gas was replaced with synthetic ammonia gas (99.85% Messer, Poland), bubbled through Dreschel bottle containing 50 cm^3 of ethanol (96.0%, POCH, Poland) with flow rate of 200 cm^3/min. The final temperature of the process (100°C) was maintained for 1.5 hours. During the preparation of the TiO_2/N or TiO_2/C photocatalysts the starting TiO_2 was exposed, respectively, only to the synthetic ammonia gas or inert gas bubbled through the alcohol. Commercial P25 photocatalyst (Evonik, Germany) and washed TiO_2 (starting TiO_2) were used as reference materials.

Preparation of gypsum plasters

Gypsum plasters were prepared by mixing different amount (1 wt%, 5 wt%, 10 wt%, 20 wt%) of starting TiO_2 or commercial P25 or co-modified TiO_2/N,C photocatalyst with pure gypsum (Dolina Nidy Sp z o.o., Poland) using porcelain mortar. The homogenous powders were blended with distilled water, including different content of additives in starting mixture. The obtained pastes were poured into silicone moulds (20 × 20 × 6 mm) and dried for 24 hours at 40°C.

Samples characterization

The surface properties of tested photocatalysts were examined by FT-IR 4200 spectrophotometer (Jasco, Japan) equipped with a diffuse reflectance accessory. The crystalline structure of the photocatalysts was characterized by X-ray powder diffraction analysis (X'Pert PRO Philips diffractometer) using Cu K_α radiation (λ = 0.154056 nm). The mean crystallites sizes of the photocatalysts were calculated according to Scherrer's formula: $D = K\lambda / (\beta\cos\theta)$, where D is the mean crystallite size (nm), λ is the wavelength of Cu K_a radiation (nm), θ is the Bragg's angle (°), and β is the calibrated width of a diffraction peak at half maximum intensity (rad). The nitrogen adsorption/desorption isotherms at 77 K were determined using of Quadrasorb SI analyzer (Quantachrome Instruments, USA). Prior to analyses, each sample was degassed at 90°C for 24 h under high vacuum. The specific surface areas (S_{BET}) of the materials were determined using multi-point analysis of adsorption isotherms applying Brunauer-Emmet-Teller (BET) equation. Carbon and nitrogen contents in TiO_2/N,C samples were measured by carbon analyser for solid materials (Analytic Jena, Germany) and ONH 836 analyser (Leco, USA), respectively.

Determination of the gypsum plasters photocatalytic activity

The photocatalytic activity of the samples was evaluated by monitoring the degradation process of Reactive Red 198 (RR198) dye (Boruta-Kolor Sp. z o.o., Poland) used as a model organic pollutant (M = 968 g/mol, λ_{max} = 516 nm, CAS number: 145017-98-7). The obtained samples were dipped into 5 cm^3 of RR198 aqueous solution (0.5 g/dm^3) for 1 hour and dried at 90°C for 24 hours. The UV-vis irradiation tests of the stained gypsum plasters were conducted for the duration of 1 to 20 hours, using 6 UV-vis lamps (20W each, Philips Cleo) with the radiation intensity of 109.7 W/m^2 and 115.2 W/m^2 for UV and vis, respectively.

The stained gypsum plasters were characterized by UV-vis/DR technique using a V-650 spectrophotometer (Jasco, Japan) equipped with an integrating sphere accessory for diffuse reflectance spectra acquisition ($BaSO_4$ was used as a reference). The dye decomposition rates (DDR) on the gypsum plasters were calculated from the equation: $DDR = (Abs_o - Abs_t) / Abs_o \times 100\%$, where DDR is the dye decomposition rate, Abs_o is the initial absorbance (λ_{max} = 516 nm) of stained gypsum plaster and Abs_t is the absorbance after definite period of irradiation.

RESULTS AND DISCUSSION

Physicochemical properties of TiO_2 photocatalysts and gypsum plasters

The X-ray diffraction patterns measured for pure gypsum (gyp), TiO_2/N,C photocatalyst and the exemplary gypsum plaster, containing 10 wt% of the latter photocatalyst (gyp-10 wt% TiO_2/N,C) were presented in Figure 1.

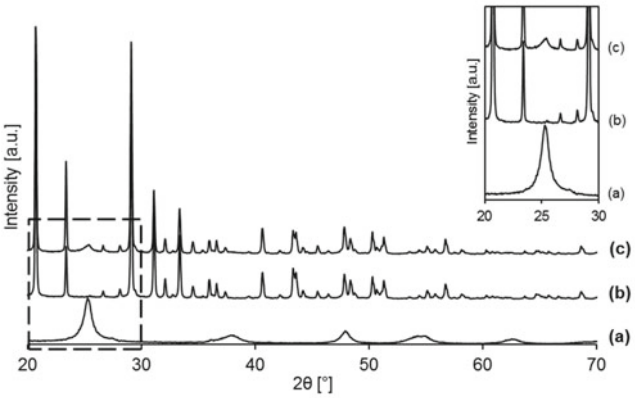

Figure 1. XRD patterns of: (a) N,C co-modified TiO_2 photocatalyst (TiO_2/N,C), (b) pure gypsum (gyp), and (c) gypsum sample loaded with 10% wt of TiO_2/N,C (gyp-10 wt% TiO_2/N,C)

The physicochemical properties of studied photocatalysts and obtained gypsum plasters were collected in Table 1 and Table 2, respectively.

The presence of the co-modified titania photocatalyst in the gypsum had no effect on the phase composition of the formed sample. The XRD pattern of gyp-10 wt% TiO_2/N,C revealed peaks characteristic for gypsum phase (calcium sulfate dihydrate $CaSO_4 \cdot 2H_2O$) and additional peak assigned to the TiO_2 anatase phase ($2\theta \approx 25.3°$). Furthermore, no significant differences of the anatase crystallites size between the starting TiO_2 and co-modified TiO_2/N,C were observed (Table 1).

S_{BET} values markedly depend on photocatalyst content in starting mixture with gypsum. The higher S_{BET} surface areas were revealed by the materials containing larger amounts of photocatalyst, added to the mixture with gypsum. It ought to be noted that the gypsum plasters loaded with 10 wt% of TiO_2/N,C photocatalyst (gyp-10 wt% TiO_2/N,C) exhibited markedly higher S_{BET} values (50 m^2/g) in comparison to gyp-P25 (28 m^2/g).

Table 1. Physicochemical properties of studied photocatalysts

Photocatalyst	Anatase crystallite size [nm]	Nitrogen content [wt%]	Carbon content [wt%]	S_{BET} [m^2/g]
P25	21.0	–	–	55
starting TiO_2	9.5	0.35	0.08	312
TiO_2/N	9.5	1.11	0.07	259
TiO_2/C	9.6	0.27	1.90	263
TiO_2/N,C	9.6	0.93	1.03	269

Table 2. BET surface areas of gypsum plaster samples

Sample	Content of photocatalyst [wt%]	S_{BET} [m^2/g]
Pure gypsum	0	23
gyp-P25	10	28
gyp-stTiO_2	10	41
gyp-TiO_2/N	10	41
gyp-TiO_2/C	10	41
gyp-TiO_2/N,C		
	5	20
	10	50
	20	78

Figure 2 displays the FT-IR/DRS spectra of unmodified TiO_2 (starting TiO_2) and TiO_2/N,C photocatalyst.

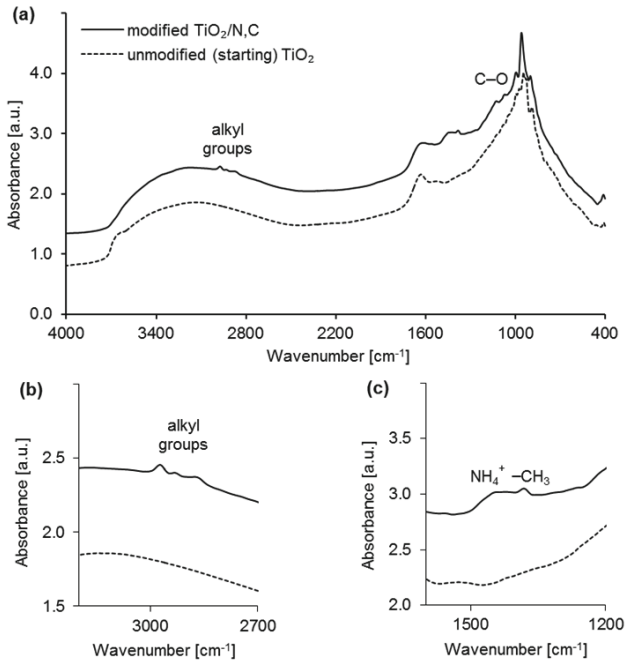

Figure 2. FT-IR/DRS spectra of the unmodified and the N,C co-modified TiO_2 photocatalysts

Figure 2. FT-IR/DRS spectra of the unmodified and the N,C co-modified TiO_2 photocatalysts.

It was noted that both tested photocatalysts showed a very broad absorption band in the range of 3800–2600 cm^{-1}, characteristic for the O–H stretching mode of interacting hydroxyl groups and the symmetric and asymmetric O–H stretching modes of molecular water coordinated to Ti^{4+} ions[41]. The weak band at 3674 cm^{-1} possible to observe in starting TiO_2 was assigned to stretching mode of different types of free hydroxyl groups[42]. The narrow band at 1640 cm^{-1} and strong band at 970–930 cm^{-1} were attributed to the molecular water bending mode and phonon modes, respectively[43, 44]. Heat treatment of starting TiO_2 sample at 100°C causes to total disappearance of band found at 3674 cm^{-1} due to the changes in content of surface –OH groups[45]. Moreover, modification of starting titania with ethanol leads to appearance of new species: alkyl groups[37, 46] at 3000–2800 cm^{-1} (Fig. 2b) and $–CH_3$ group[46] at 1360 cm^{-1} (Fig. 2c). A weak bands at 1107 cm^{-1} and 1058 cm^{-1} were assigned to stretching mode of C–O group. The ammonium groups NH_4^+ (band at 1440 cm^{-1})[47, 48] were only present in the co-modified sample (Figure 2c). Moreover, in comparison to the unmodified TiO_2 (starting TiO_2) the content of the non-metals dopants in the co-modified TiO_2/N,C photocatalyst was significantly higher (Table 1). The presence of nitrogen in the starting sample may be explained as a resultant of the preparation procedure (initial rinsing with ammonia water) applied for this material, in order to remove the residues of sulphuric acid (crude TiO_2 obtained by the sulphate technology).

Photocatalytic activity of gypsum plasters

Figure 3 illustrates the influence of the type of the photocatalyst added to the gypsum material and its impact on the self-cleaning properties of the prepared gypsum plasters.

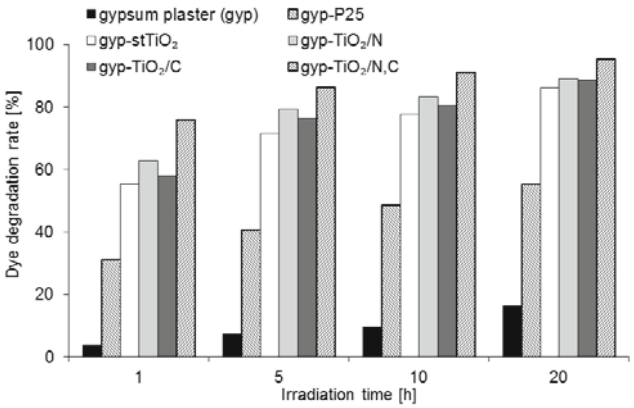

Figure 3. Photocatalytic degradation rate of RR198 dye on gypsum plasters, containing 10 wt% of different photocatalysts, determined during UV-vis irradiation tests

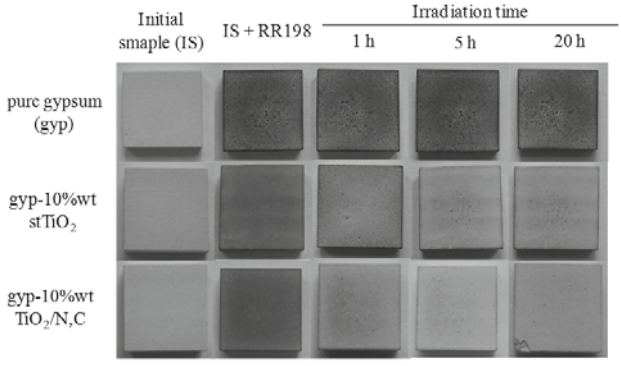

Figure 4. The photographs of studied exemplary gypsum plasters stained with RR198 dye, taken after 1, 5 and 20 hours of UV-vis irradiation

Additionally, the selected photographs of the gypsum samples illustrating gradual dye degradation, after consecutive hours of irradiation, were presented in Figure 4.

It ought to be noted that the pure gypsum plaster (gyp sample) displayed negligible self-cleaning properties. Nevertheless, with the increase of the irradiation time, a negligible increase of the dye removal rate was recognized.

In case of the other examined samples, it can be clearly seen that the addition of the respective photocatalyst into the gypsum had a significant impact on degradation rate of the pollutant. Furthermore, according to the data presented in Figure 5, after 20 h of UV-vis exposition, the dye decomposition rate of the gypsum plasters,

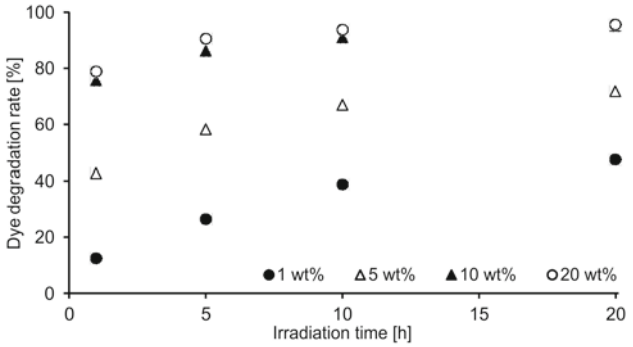

Figure 5. The effect of the TiO2/N,C photocatalyst loading (in %wt) in the gypsum samples on the RR198 dye degradation rate under UV-vis irradiation

containing 10 wt% or 20 wt% of the N,C co-modified photocatalyst reached very similar values (ca. 95% and 96%, respectively).

The increase of photocatalyst dose in gypsum plasters up to 20 wt% did not caused the expected increase of the dye removal rate. This effect can be connected with the increasing rate of the electron–hole recombination, leading to a partial deactivation of the active sites. The similar interference effect was also described in literature[17, 49, 50]. Namely, insufficient quantity of the species, acting as carrier traps, could have been preadsorbed on the photocatalyst surface. The species acting as the carrier trap (e.g. oxygen) must be preadsorbed on the photocatalyst surface before the arrival of the activating photon. Otherwise, the amount of generated charge carriers is too high in comparison to amount of preadsorbed carrier traps, what results in higher rate of charge carriers recombination.

This might explain why the increase of the photocatalyst loading in the gypsum mass sample above 10 wt% only slightly effected the decomposition rate of the dye. In view of this fact, from economic point of view the TiO_2/N,C contents in gypsum plaster should not exceed 10 wt%. Moreover, the results of the irradiation tests confirmed that the gypsum plaster loaded with 10 wt% of N,C co-modified titania (gyp-10 wt% TiO_2/N,C) displayed significantly higher photocatalytic activity than the reference gyp-P25 sample, leading to almost complete (over 95%) removal of the RR198 dye form the material, after 20 hours of UV-vis exposition (Fig. 3). Furthermore, it is worth pointing out that after similar irradiation time the gypsum plasters, loading with starting TiO_2 (gyp-stTiO_2) revealed lower degradation rate of the dye, reaching approximately 86%.

The observed tendencies of gypsum plasters discoloration were connected with physicochemical properties of the studied photocatalysts, present in the prepared gypsum plasters. The advantageous self-cleaning properties of the gyp-TiO_2/N,C and gyp-stTiO_2 materials were most likely related with the relatively high S_{BET} values (Table 1) of the added photocatalysts. According to the literature[51, 52] the preadsorption of the pollutant on the photocatalyst surface has an important meaning during occurring photocatalytic reactions because the photocatalytic process, takes place rather on the photocatalyst surface than in the bulk solution. In view of this fact the acquirement of the highest possible surface area of the photocatalyst is a desired factor, which positively influence the overall photodegradation process of the contaminant. One should notice however that despite higher S_{BET} value of the photocatalyst added to the gyp-stTiO_2 sample, this material revealed clearly lower RR198 decomposition rate (ca. 86%), then the gyp-TiO_2/N,C sample (over 95%). It is believed that this effect is related with the presence of the non-metal dopants (N, C) in the photocatalyst (Table 1). It is postulated in literature[53, 54] that the modification of TiO_2 with carbon and/or nitrogen causes the occurrence of defects in TiO_2 lattice. The lattice impurities can inhibit recombination of the photoinduced electrons and holes, leading to the increased quantum efficiency. Moreover, the presence of both dopants in the TiO_2 may further enhance the photoactivity of the photocatalyst due to the occurrence of the synergic influence of both non-metals. This effect is connected with partial replacement of oxygen atoms on the TiO_2 surface with nitrogen, whereas the carbon atoms formed a mixed layer of deposited carbon and C–O band species on the surface of the TiO_2 particles[55]. It was repeatedly indicated that modification of pure TiO_2 with nitrogen and/or carbon enhances photocatalytic activity of TiO_2-based materials[56, 57]. In our case the simultaneous modification of TiO_2 with both carbon and nitrogen dopants was also justified. As presented in Figure 3, the gypsum plasters containing TiO_2/C or TiO_2/N photocatalysts displayed higher dye removal rates in comparison to the gyp-stTiO_2 and gyp-P25 materials. It should be noted that the gypsum plasters containing TiO_2/C or TiO_2/N photocatalysts exhibited noticeably lower photocatalytic activity during RR198 dye degradation, than the samples loading with TiO_2/N,C additive. However, the presented results do not indicate the occurrence of the synergistic effect between the nitrogen and carbon dopants, present in the modified TiO_2 photocatalyst. Besides, this fact, the highest photocatalytic activity of the gyp-10 wt% TiO_2/N,C can be explained by the formation of new energy levels in semiconductor particle. The mentioned phenomena might cause suppression of the recombination of photogenerated electron-hole pairs[58–60]. It is worth pointing out that the new energy levels may be also created in the case of separate nitrogen or carbon TiO_2 doping. However, in comparison to TiO_2/N,C materials, the faster recombination of electron-hole pair is more likely to occur in N or C single modification.

CONCLUSION

In this work the primarily result of self-cleaning properties of the TiO_2-containing gypsum plaster were verified, trough the degradation of Reactive Red 198 dye under UV-vis light. It was confirmed that the dye degradation rate dependent on the quantitative and qualitative composition of the materials. The best self--cleaning properties were displayed by the gypsum plaster containing optimal amount (10 wt%) of co-modified TiO_2/N,C photocatalyst, after 20 hours of UV-vis irradiation. The role of the non-metal (N, C) presence in the TiO_2 lattice on the dye removal rate was discussed. It was confirmed that the gypsum plasters containing TiO_2/C or TiO_2/N photocatalysts exhibited noticeably lower photocatalytic activity than the samples loading with TiO_2/N,C additive. However, the presented results do not indicate the occurrence of the synergistic effect between the nitrogen and carbon dopants, present in the modified TiO_2 photocatalysts.

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