

Photocatalytic and Antistain Properties of Ceramic Tiles Functionalized with Tungsten-Doped TiO₂

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Tiles functionalized with W-doped TiO₂ film has been prepared and tested in the discoloration of aqueous solution of methylene blue (MB) used as model pollutants, in presence of UV light.

The influence of tungsten and its loading on tiles surface were evaluated.

Photocatalytic tests, performed at controlled temperature and atmospheric pressure, have shown that the increase in the tungsten loading strongly influences the photocatalytic activity; higher content of tungsten induces an increase of the discoloration rate. Moreover, the addition of tungsten modifies the structure of titania determining a remarkably photocatalytic activity.

1. Introduction

Since it was found that irradiation of TiO₂ with UV-light induced redox active electron-hole pairs, TiO₂ photocatalysis has been extensively used to purify water (Vaiano et al., 2014), air (Murcia et al., 2013) to degrade organic and inorganic contaminants (Gaya and Abdullah, 2008) and to inactivate microorganisms (Barudin et al., 2013). The properties of TiO₂, such as thermal and chemical stability, high photocatalytic activity, low-toxicity, and low cost make TiO₂ one of the most intensely investigated photocatalyst which may be utilized for the environmentally compatible treatment (Segota et al., 2011).

The low quantum efficiency of titania is one of the major problems limiting its practical use (Rauf et al., 2011). In addition, titania has a relatively high band gap value of 3.2 eV, which means that it can be activated only with UV light. However for the practical applications it would be desirable to extend the band gap excitations towards the visible region, and to confer prolonged lifetime of photogenerated charge carriers. Doping of titanium dioxide with transition metal ions, such as tungsten, provides a relatively well-studied and convenient way of solving both problems described above. Doped titanium dioxide showed significantly higher photocatalytic efficiencies (Farahani et al., 2011).

For air stream and wastewater purification the photocatalyst can be fixed on a substrate, e.g. tiles to promote oxidation reactions. The immobilization method is more convenient for practical use. Recently it was shown that it was possible to obtain the complete removal of NO_x from air stream without deactivation of the TiO₂ film deposited on ceramic tiles (Sannino et al., 2013). Moreover TiO₂ on tile surface has induced the total methylene blue (MB) discoloration after many hours of irradiation. With the aim to enhance discoloration rate W-doped TiO₂ film on ceramic tiles has been prepared and tested in the decolorization of aqueous solution of MB in presence of UV light.

2. Experimental

2.1 Preparation of sol-gel TiO₂ films

TiO₂ films were deposited on porous ceramic tiles with dimensions 97 mm X 87 mm X 12 mm. The tiles were carefully cleaned prior to the process of deposition. The substrates were ultrasonically cleaned in acetone for 10 min and dried in oven at 120 °C for 30 min.

For the preparation of solution (TiO₂ sol), the following components were used:

- Titanium (IV) isopropoxide, TIP (Ti(C₃H₇O)₄, Sigma Aldrich) as a titanium precursor;
- Ethanol, (C₂H₅OH, Fluka Analytical) as a solvent;

- Glacial acetic acid (CH_3COOH , Aldrich Chemistry) as a catalyst;
- Acetylacetone ($\text{CH}_3(\text{CO})\text{CH}_2(\text{CO})\text{CH}_3$, Sigma Aldrich) as a chelating agent;
- Bidistilled water for gelation;
- Polyethylene glycol, PEG ($\text{HO}(\text{C}_2\text{H}_4\text{O})_n\text{H}$, $M_r = 5,000\text{--}7,000$, Aldrich Chemistry) as an organic additive (dispersant and binder);
- Ammonium (para)tungstate hydrate, $(\text{NH}_4)_{10}\text{H}_2(\text{W}_2\text{O}_7)_6 \cdot x\text{H}_2\text{O}$, Sigma Aldrich) as a doping agent;
- Nitric acid (HNO_3 , Sigma Aldrich) as an acidifier.

Solution was prepared by dissolving titanium isopropoxide in ethanol. A magnetic stirrer was used to continuously mix the liquid. Then, acetylacetone and glacial acetic acid were slowly added. The resulting solution was stirred for 10 min and after that it was sonicated for 10 min. In a different flask, 4 g of polyethylene glycol (PEG), 0.62 g of ammonium tungstate and 0.5 mL of nitric acid were added to bi-distilled water under continuous stirring. The achieved solution was mixed with the first solution and stirred vigorously. The obtained clear solution was sonicated for 10 min. Tiles were impregnated with the TiO_2 sol by dispersing it carefully on tiles surface. In particular a known volume of solution was dispersed on the tile to impregnate the entire surface (tile W1-1). The molar ratios of components used to prepare titania coating solutions are shown in Table 1. In the case of tile functionalized with undoped TiO_2 (tile T), only ammonium tungstate was not added in the preparation. All coated substrates were dried at $120\text{ }^\circ\text{C}$ for 60 min and then calcinated at $550\text{ }^\circ\text{C}$ for 2 h. For the tile W1-2 the process (impregnation – calcination) was replicated two times.

Table 1: Composition of coating solution and molar ratios.

Component	TIP	$\text{C}_2\text{H}_5\text{OH}$	$\text{CH}_3(\text{CO})\text{CH}_2(\text{CO})\text{CH}_3$	CH_3COOH	H_2O	PEG	$(\text{NH}_4)_{10}\text{H}_2(\text{W}_2\text{O}_7)_6 \cdot x\text{H}_2\text{O}$
Molar Ratio	1	40	1.3	0.9	20	0.0008	0.06

2.2 Characterizations of samples

Samples were characterized with different techniques.

Spectra were recorded with a Perkin Elmer spectrometer Lambda 35. Equivalent band gap determinations were obtained from Kubelka-Munk theory (Ciambelli et al., 2007) by plotting $[F(R_\infty) \cdot h\nu]^2$ vs $h\nu$ and calculating the x intercept of a line through $0.5 < F(R_\infty) < 0.8$.

Laser Raman spectra were obtained at room temperature with a Dispersive MicroRaman (Invia, Renishaw), equipped with 514 nm diode-laser, in the range $100\text{--}1,200\text{ cm}^{-1}$ Raman shift.

X-Ray fluorescence spectroscopy (XRF) was performed using a ThermoFischer ARL QUANT'X EDXRF spectrometer equipped with a rhodium standard tube as the source of radiation and with Si-Li drifted crystal detector.

2.3 Photocatalytic tests

As model pollutants, dyes are commonly used, because their concentration can be easily monitored using a spectrophotometer. Among them, methylene blue (MB) has been widely studied due to its highly coloured nature and good chemical stability. The method which employs MB dissolved in water in the presence of TiO_2 as thin film has been considered as a standard test for photocatalytic surfaces by the ISO (ISO 10678-2010) (International-Organization-for-Standardization, 2010).

Since the substrates exhibit the tendency to adsorb the dye molecules, pre-adsorption of the surface was performed, using an aqueous solution of MB with a concentration equal to 10 ppm. 200 mL of the dye adsorption solution were placed into a glass beaker and the dye was adsorbed in the dark for 24 h. If the remaining concentration of the dye in this solution was larger than that of the solution used in the photocatalytic test, the adsorption was considered to be complete. Otherwise, the procedure was repeated for another 12 h using a fresh adsorption solution. The tests were then performed using a solution of 5 ppm. After the adsorption process of the dye was complete, tiles were placed in a plate reactor (0.20 L in volume) realized in stainless steel with a pyrex window (90 mm X 90 mm). This window was illuminated by four UV lamps (Philips, nominal power 32 W) with emission spectrum centred at 365 nm. The photoreactor is provided of temperature controlling system, consisting of a thermal exchanger within the metal body and a cooling system. Liquid samples were analysed in continuous for the first time by spectrophotometric measurement. In particular, a special assembly with a flow cuvette and an external pump for the recirculation of liquid was realized, permitting to determine the change of MB concentration, measured with a Perkin Elmer UV-Vis spectrophotometer at $\lambda = 663\text{ nm}$. A standard calibration curve was obtained for different MB concentration and allowed to convert absorbance to concentration (mg/L) units. In order to assess the photocatalytic efficiency of the TiO_2 coated samples, measurements were also performed on non-coated ceramic tile.

3. Results and discussion

3.1 Catalysts characterization

The reflectance measurements of undoped and W-doped TiO_2 in powder form synthesized by drying and calcination at 550°C of sol-gel, are reported in Figure 1. The experimental data show that the absorption properties of W-doped titania shifted from UV to visible region, determining a decrease of band-gap values from 3.2 eV (the typical band-gap of undoped TiO_2) to about 3.0 eV. This change in band-gap is attributed to the presence of tungsten in the crystal structure phase. In Figure 2 it is reported the comparison between XRF results of raw tile, tile T, tile W1-1 and tile W1-2. The surface concentration of titanium and tungsten in the functionalized samples (Figure 2) increases by increasing the number of preparation steps, reaching the value of about 11.5 % and 0.26 % for titanium and tungsten respectively (tile W1-2). Moreover the decrease of silicon and calcium concentration indicated that TiO_2 is built up as thin film on the tile surface. The result obtained with UV-vis analysis is confirmed by the Raman spectra of the tiles (Figure 3). In the range $100 - 900\text{ cm}^{-1}$ (Figure 3a) functionalized tiles display bands at 144, 396, 514 and 637 cm^{-1} and a weak shoulder at 195 cm^{-1} , due to the Raman-active fundamental modes of titania in anatase phase (Ciambelli et al., 2008). In the range $700 - 1,100\text{ cm}^{-1}$ (Figure 3b), samples T and W1-1 show signals at 970 and $1,020\text{ cm}^{-1}$ due to the chemical composition of raw tile. These bands disappeared in the case of tile W1-2, indicating that a double step of the preparation process is able to induce the formation of a W-doped TiO_2 layer that covers the entire surface of the support. Moreover, for the same tile, the band at about 800 cm^{-1} is due to the structure of TiO_2 in anatase phase.

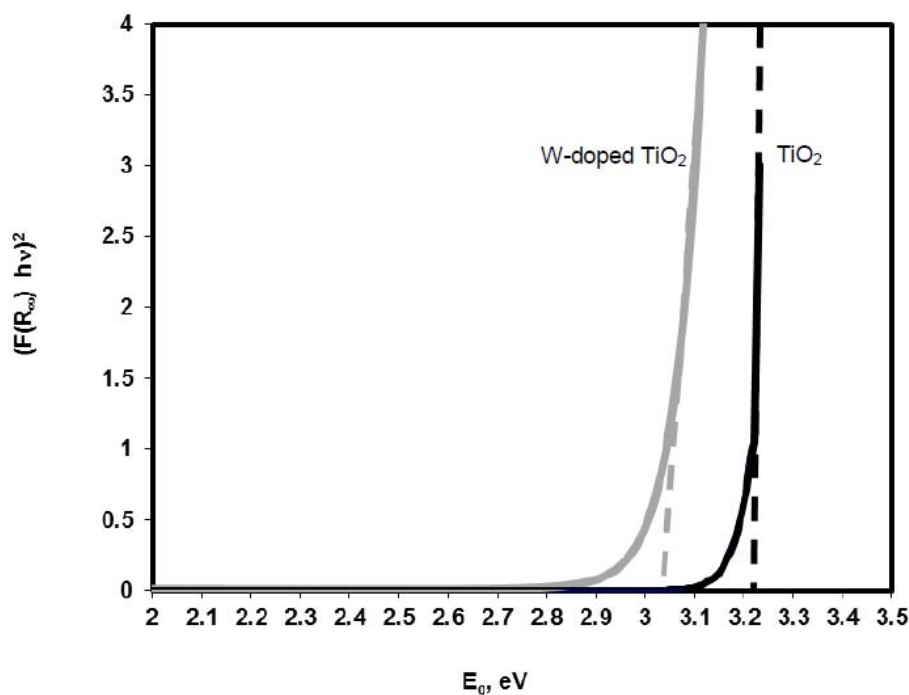


Figure 1: UV-Vis DRS spectra for TiO_2 and W-doped TiO_2 as powders

3.2 Photocatalytic activity tests

Discoloration of MB as a model reaction was studied to investigate the photocatalytic activities of tiles under UV irradiation. The changes in the concentration of MB recorded in continuously mode are shown in Figure 4.

Control experiment carried out on raw tile showed that MB concentration decreases very slowly throughout all the irradiation time, reaching a final value of about 4.6 ppm. During photolysis test, MB is almost stable and its concentration decreased only of about 3 % after 48 h of irradiation.

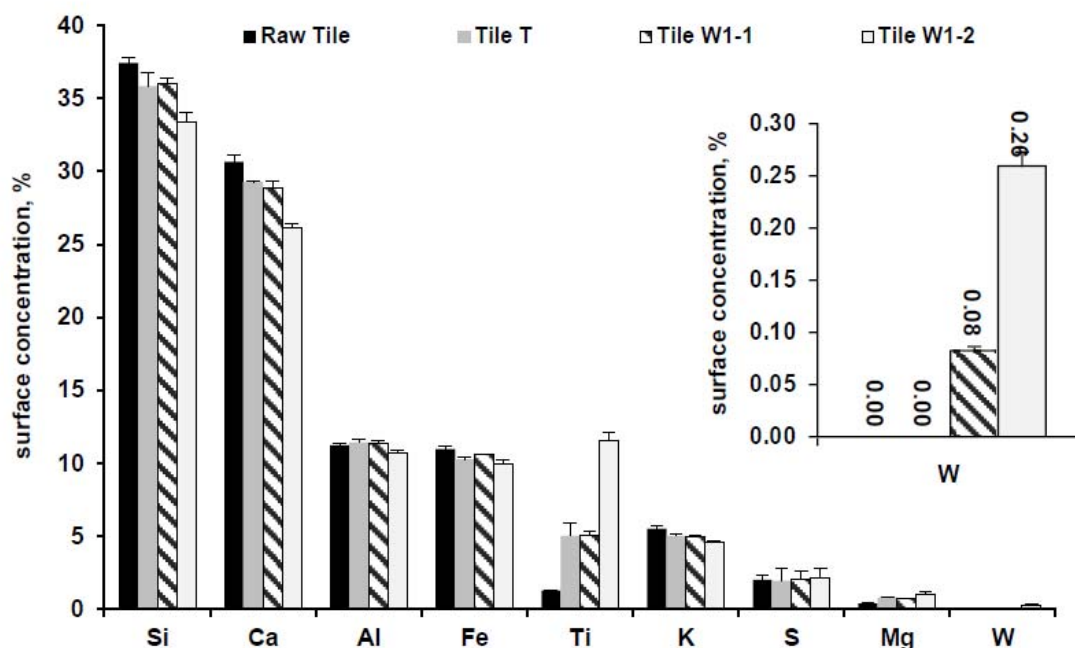


Figure 2: XRF analysis of surface for raw tile and functionalized tiles

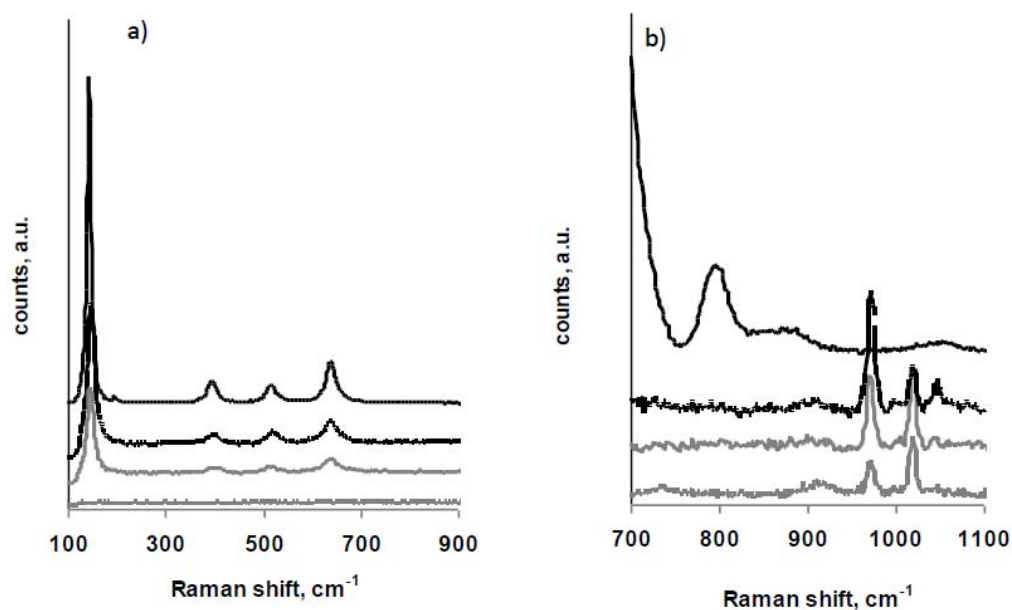


Figure 3: Raman spectra of functionalized and raw tile: (a) in the range $100 - 900 \text{ cm}^{-1}$, (b) in the range $700 - 1,100 \text{ cm}^{-1}$

As it can be seen for the tile functionalized with undoped titania (tile T) MB concentration decreases progressively, reaching a discoloration of about 63 % in 48 h of irradiation. At fixed irradiation time, with the same titanium loading (5 %), the presence of W-doped TiO_2 thin film (tile W1-1) showed a higher discoloration rate. By increasing W loading (tile W1-2), the photocatalytic activity is strongly enhanced, reaching the almost complete disappearance of MB within 48 h.

4. Conclusions

In this work W-doped TiO₂ was deposited on ceramic tile by coating method and photocatalytic properties were analyzed in presence of UV light.

The characterization results of functionalized tiles showed that the coating method is able to induce the formation of W-doped TiO₂ on the tile surface.

Photocatalytic tests on MB removal in liquid solution, performed at controlled temperature and atmospheric pressure, have shown that the increase in the tungsten loading strongly influences the photocatalytic activity; higher content of tungsten induces an increase of the discoloration rate.

Moreover, the addition of tungsten modifies the structure of titania determining a remarkably photocatalytic activity. In particular, the comparison of the tiles with the same titania load shows that the presence of tungsten allows to reach a MB discoloration after 48 h of about 80 %, higher than that one obtained without the doping agent (about 40 %).

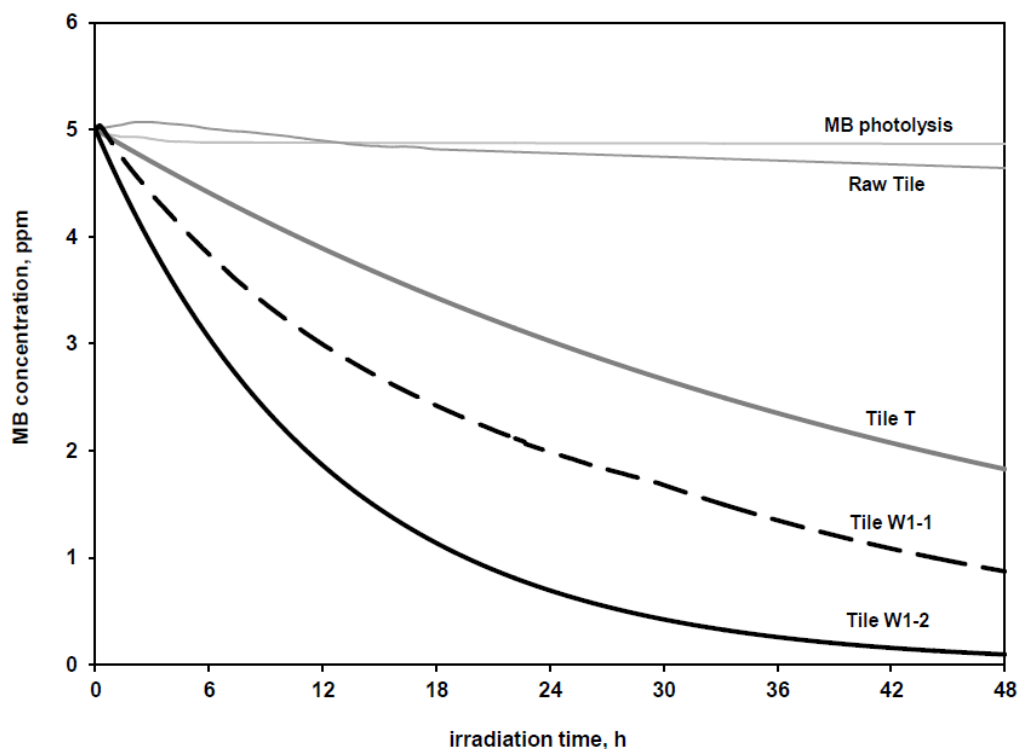


Figure 4: MB discoloration as a function of UV irradiation time

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