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TiO2/Ag2O immobilized on cellulose paper: A new floating system for enhanced photocatalytic and antibacterial activities

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Dear Editor of Environmental Research,

We are enclosing herewith a manuscript entitled "TiO_2/Ag_2O immobilized on cellulose paper: A new floating system for enhanced photocatalytic and antibacterial activities" to be considered for its publication in Environmental Research special issue "Photocatalysis Frontiers (ISFP 2020): Environmental, Energy, and Process Mechanism".

In this work we report a facile and effective strategy to incorporate TiO_2-Ag_2O on cellulose paper and the influence of the amount of Ag_2O to obtain a novel floating photocatalytic material, which can be adapted to several environmental applications and is active in the abatement of aniline in water under simulated sunlight illumination at room temperature. Considering the lacking literature on the photocatalytic degradation of such carcinogenic compound by TiO_2/Ag_2O under sunlight, we think that the article contains innovative results and fits well with the scope of the special issue and is of great interest for Environmental Research readers.

All of the authors have read and approved the paper and it has not been published previously nor is it being considered by any other peer-reviewed journal, and this study does not involve human subjects.

Kindly consider the manuscript for publication in your journal. Thanks in advance for the collaboration.

Yours sincerely,

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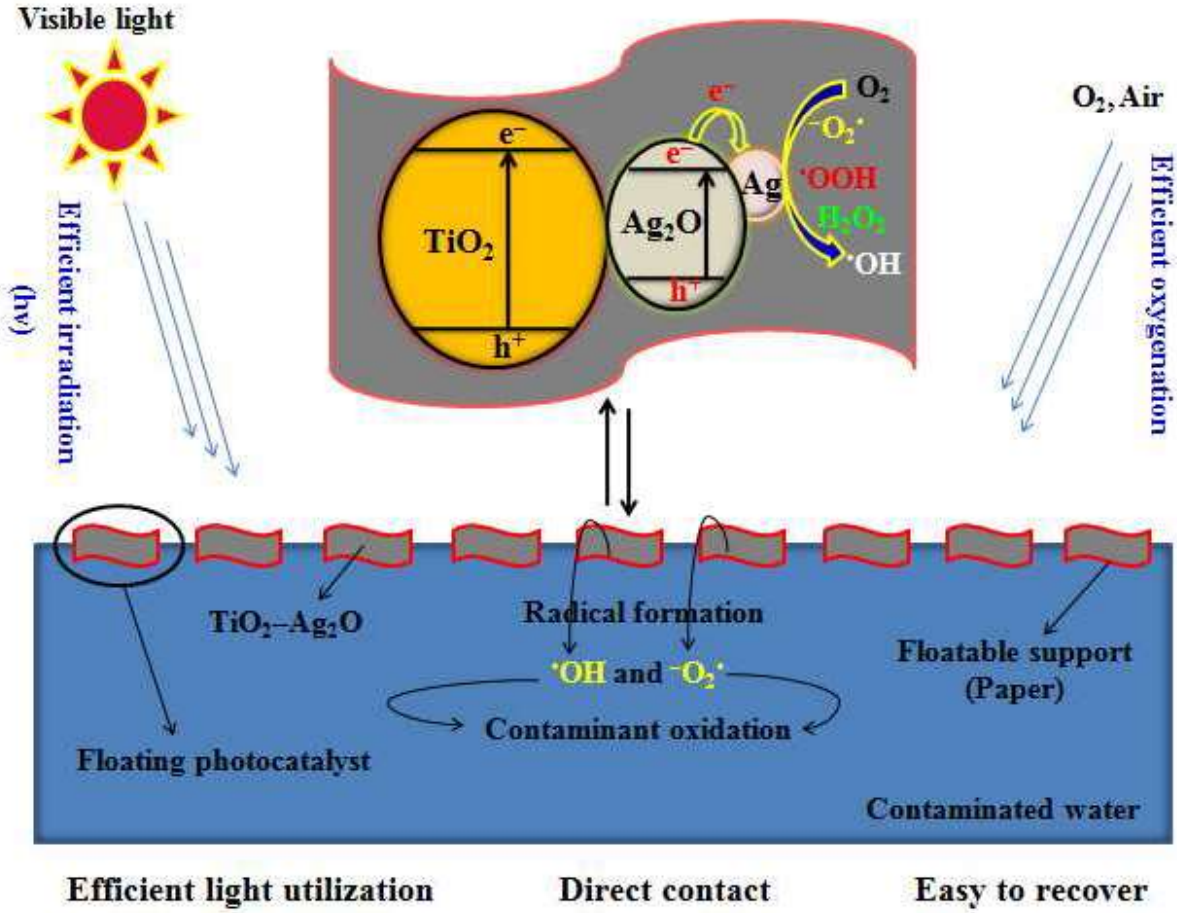
Highlights

- Paper–TiO_2 decorated with Ag_2O nanoparticles was prepared by a facile method.
- Generation of TiO_2 anatase and Ag_2O phases was confirmed by XRD, Raman and XPS.
- Paper–TiO_2–Ag_2O exhibits excellent photodegradation activity toward of aniline.
- Paper–TiO_2–Ag_2O displays good antibacterial activity against E. Coli under sunlight.

Graphical Abstract



TiO_2/Ag_2O immobilized on cellulose paper: A new floating system for enhanced photocatalytic and antibacterial activities

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Abstract

Paper–TiO_2–Ag_2O floating photocatalysts were produced under mild condition and their photocatalytic activity for the degradation of aromatic amine under sunlight stimulant was investigated.

Characterization by Raman, XRD, XPS, DRS and PL was used to confirm the presence of TiO_2 and Ag_2O, and the morphology of the appended TiO_2/Ag_2O layer was probed by FE-SEM. The photocatalytic activity of the prepared samples was investigated by the degradation of aniline (AN) in water under simulated sun-light illumination and constrained conditions, i.e. non-stirring and non-oxygenation. The presence of Ag_2O combined with TiO_2 was shown to improve the resistance of paper to bacteria attack, thus increasing the durability of the photocatalyst. Thanks to its hydrophobic character, the paper–TiO_2–Ag_2O NPs can be employed as useful floating photocatalyst and can be reused without separation during the photocatalytic reaction.

Keywords: Paper, TiO_2–Ag_2O heterojunction, Self-cleaning, Surface functionalization, Floating photocatalyst.

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1. Introduction

Since the discover of light-assisted water splitting by a single crystal TiO_2 semiconductor electrode in the early 1970 (Fujishima and Honda, 1972), photocatalysis has become a topic of surge interest with many applications, such as detoxification of effluents, as well as hydrogen production and photosynthesis. Photocatalysis is an economic and energetically advantageous process taking place in mild conditions, usually at ambient temperature and under sunlight, without any chemical reagents. Compared to other photocatalysis, titanium dioxide (TiO_2) has low cost, is an ecologically friendly material thanks to its nontoxicity, has good chemical inertness and long–term stability (Wang et al., 2013).

Nevertheless, there are still some limitations that hinder the widespread industrial application of TiO_2. Indeed, being a very fine and light powder, TiO_2 when dispersed in a water solution, easily deposits at the bottom of the water and its recovering is even worse due to the tendency of powder agglomeration. Moreover, titania has limited photoactivity in the visible domain due to the weak absorption edge (~390 nm for TiO_2 anatase) and its activity is further weakened underwater, even if UV light are used, since only 1% of UV light can penetrate up to 0.5 m (Shan et al., 2010; Xing et al., 2018).

To overcome such difficulties in using TiO_2 powder, several attempts to immobilize titania over a support have been carried out. A floating support, cheap to manufacture, represents a convenient solution to immobilize titania powder. It allows the easy recover and reuse of the catalyst, especially for application in solution, such as for water purification and enhances the photocatalytic activity thanks to full illumination due to high air-water interface (Xing et al., 2018; Wang et al., 2017; Zhou et al., 2014; Wang et al., 2017; Zhang et al., 2015; D'Souza et al., 2013 ; Sboui et al.,2017). Among various substrates reported in the literature, cellulose paper has attracted great interest owing to its low price, abundance, lightness, and non-toxicity (Pelton et al., 2006; Abdel Rehim et al., 2016; Sboui et al., 2018). Moreover, cellulose containing surface hydroxyl groups favors the adhesion of TiO_2 on the fibers through the formation of surface–O–Ti bridges (Daoud and Xin, 2004). Therefore, cellulose is an excellent carrier for the nucleation of nanostructured TiO_2 and represents a substrate deserving further research.

Since the first work by Matsubara in the mid-1990s on paper functionalized with TiO_2 (Matsubara et al., 1995), such hybrid systems have attracted significant attention for a wide variety of environmental applications, such as the water treatment (Chauhan and Mohanty,

2014), air purification (Sboui et al., 2018) and antibacterial applications (Abdel Rehim et al., 2016; Chauhan and Mohanty, 2014). Paper–TiO_2 was also used as a colorimetric sensor (Li et al., 2014), as anodes of the lithium-ion batteries (LIBs) (Zhao and Shao, 2012), as dye-sensitized solar cells (DSSCs) (Bellaa et al., 2017).

Nevertheless, cellulose paper functionalized with TiO_2 has still a limited capability to absorb visible light. The modification of TiO_2 with plasmonic NPs such as Ag, Au or Pt is a promising approach to shift the activity of the photocatalyst towards the visible domain and further boost the photocatalytic response through the plasmon effect of the appended noble metal NPs.

In fact, beyond their absorption of visible light, Ag, Au or Pt NPs behave as a sink for generated charge carriers (e^-/h^+) reducing the strong tendency of the recombination of e/h in TiO_2 (Mohamed and Al-Sharif, 2013; Xiang et al., 2013; Rosario and Pereira, 2014). Only few works have been reported, concerning the association of TiO_2 with Ag NPs in paper–TiO_2 composite materials. Wang et al., (2013) have prepared cellulose fiber–TiO_2 nanobelt–silver nanoparticles hierarchically structured by assembling cellulose fibers with silver nanoparticles loaded TiO_2 nanobelts. Such paper functionalized with silver-loaded TiO_2 nanobelts has shown to be effective for the photocatalytic degradation of methyl orange in aqueous solution, under UV illumination, and exhibited high antibacterial activity. In another recent work (Mihaly-Cozmuta et al., 2017) cellulose paper modified with TiO_2, Ag–TiO_2 and Ag–TiO_2–Zeolite nanocomposites has been applied for bread packaging to preserve the nutritional compounds. The zeolite–Ag–TiO_2 has a positive antimicrobial effect by inhibiting the multiplication of yeasts and molds. In that article, no photoactivity of the composite materials was discussed. A part these two papers, no other works have been reported concerning such topic.

Due to the lack of scientific investigations carried out on TiO_2/Ag_2O systems immobilized on a support and considering the absence of scientific data on the photocatalytic degradation by TiO_2/Ag_2O under sunlight of the aniline a carcinogenic compound, that is the waste product of paint factories, we have considered worthy to investigate the coupling effect of Ag_2O and TiO_2 on aniline photodegradation efficiency.

In this study, a floating photocatalyst TiO_2/Ag_2O immobilized on cellulose paper was prepared under mild temperature conditions, characterized by using several techniques and its photocatalytic activity was investigated for the degradation of aniline in water under solar light irradiation. Its antibacterial properties were also evaluated against Escherichia coli (E. coli) bacteria.

2. Materials and methods

2.1. Materials

In this research work, all chemical reagents used were furnished by Aldrich (Grenoble, France): $Ti(OBu)_4$ (≥97%), $AgNO_3$ (≥99.8%), CH_3CO_2H (≥99.7%), $(CH_3)_3COH$ (≥99.0%), NaOH and aniline (AN). The commercial paper used was manufactured by SOTEFI Industry (Tunisia).

2.2. Synthesis of paper–TiO_2–Ag_2O

As a first step, paper–TiO_2 was prepared by dipping the paper for 180 min in a pre-prepared solution consisting of 1.25 (w/v)% of $Ti(OBu)_4$ and a mixture of tert–butanol plus acetic acid (90/10 wt%). The sample paper was dried at 55 °C for 90 min in oven, subjected to hydrothermal treatment, within 180 min, at 130 °C and, again, dried at 55 °C for 150 min. The so prepared sample was labeled as PT.

For the synthesis of the paper–TiO_2–Ag_2O, the PT sample was soaked in a solution of $AgNO_3$ at different concentrations (at pH = 14 for 180 min). Then, after removing from the solution, it was rinsed with distilled water several times and dried at 55 °C for 150 min. The resulting photocatalysts prepared with different concentrations of $AgNO_3$ ($5x10^{-4}$, $1x10^{-3}$, $5x10^{-3}$ and $1x10^{-2}$ M) were labeled as PTG1, PTG2, PTG3 and PTG4, respectively.

2.3. Characterization

In this research work, the prepared samples were characterized by several experimental techniques that include: The UV−vis diffuse-reflectance spectrophotometer (DRS, UV-2550, Shimadzu, Japan) and Photoluminescence (PL) spectroscopy (Fluorolog 3–21, Horiba Jobin Yvon, France) in order to check the optical properties of the samples, Raman spectroscopy (Horiba Jobin Yvon, France) and X-ray diffractometer (XRD, Bruker AXS, Madison, USA) in order to determine the crystalline phase, field emission scanning electron microscope (FE–SEM) from Carl Zeiss (ZEISS SUPRA40, Germany) in order to study surface morphology, X–ray photoelectron spectroscopy (XPS) using a (VG Microtech ESCA 3000Multilab, ISMN-CNR, Italy) in order to study the chemical components of the samples and Dataphysics OCA 25 apparatus in order to measure the contact angle of the paper photocatalytic.

2.4. Photocatalytic tests

The photocatalytic efficiency of the paper–TiO_2–Ag_2O was studied in aqueous solution using aniline as pollutant probe molecule. The experiments were carried out as follows: the paper sample (4 x 4 cm) was placed in a crystallizer containing 50 mL of a solution of aniline with a concentration of 30 mg/L. Before light exposure, the catalyst was maintained in the solution in a dark place for 60 min to achieve sorption equilibrium of aniline on the catalyst. After that, the crystallizer was lit by Xenon lamp (50 W).

An UV-Vis Spectrophotometer (UV-6300, Mapada) was approved to calculate the concentration of aniline before the experiment and during the photocatalytic degradation. The degradation rates of aniline according to a pseudo-first-order kinetic model were measured using the following Eqs. (1) and (2):

$$\text{Degradation}(\%)=\frac{C_0-C_t}{C_0}\times 100 \quad (1)$$

$$\ln\left(\frac{C_0}{C_t}\right)=kt \quad (2)$$

where, C_t (mg/L) is the concentration of aniline after certain time t and C_0 (mg/L) is the initial concentration, and k represents the rate constant of photodegradation of aniline (min^{-1}).

2.5. Antibacterial Activity Tests

In order to access the antibacterial properties of the prepared catalysts, tests were carried out by using the method of the disc diffusion in presence of E. coli ATCC 25,922 as (Gram-) bacterium, according to experimental conditions previously applied by us (Sboui et al., 2020).

3. Results and discussion

3.1. UV–vis spectroscopy

In order to verify the effect of $AgNO_3$ concentration on the optical properties of paper–TiO_2–Ag_2O, the absorption spectra were studied for all the prepared samples. Fig. 1 shows the optical properties of PT and paper–TiO_2–Ag_2O with different concentrations of $AgNO_3$.

For the sample PT, the absorbance in the ultraviolet area with an edge of absorption at about 390 nm corresponds to the band gap (≈ 3.2 eV) for TiO_2 anatase powder. After loading Ag_2O onto the TiO_2 layer, the absorption spectra of all samples, paper–TiO_2–Ag_2O, showed better absorption efficiency in visible light. According with the literature, the good absorption

properties of paper–TiO_2–Ag_2O into the visible region can be attributed to the presence of silver (I) oxide and as well to the effective coupling between two semiconductors (p-type semiconductor (Ag_2O) and n-type semiconductor (TiO_2) (Zhou et al., 2010; Paul et al., 2016; Sarkar et al., 2013). Moreover, looking at the effect of $AgNO_3$ concentration on the properties of the resulting Ag_2O-modified materials, it is worth to note that the diffuse reflectance spectra presented a red-shift and an increased absorbance in the visible range depending on the $AgNO_3$ concentration. According to Fig. 1, the diffuse reflection spectrum of PTG3 experienced the largest shift compared to the other spectra.

In general, we can conclude that the visible light absorption of the hybrid photocatalysts (paper–TiO_2–Ag_2O) is affected by the change in $AgNO_3$ concentration. This finding will also affect the photocatalytic performance of the prepared photocatalysts.

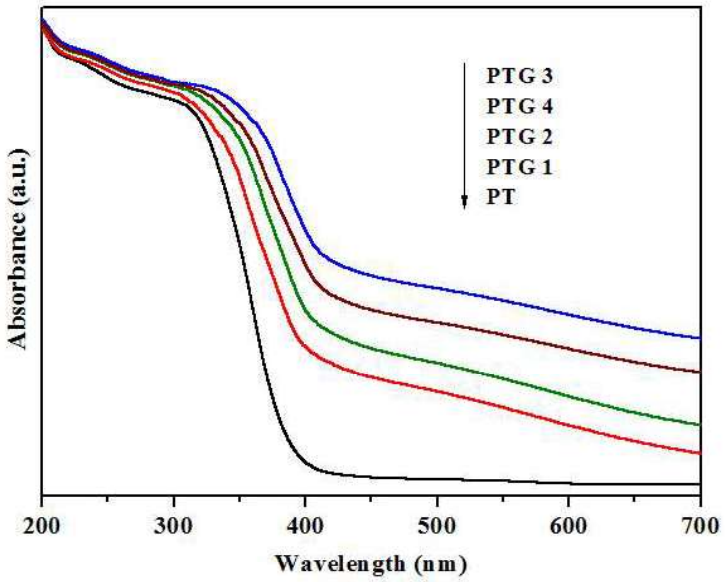


Fig. 1. UV–vis spectra of PT and paper–TiO_2–Ag_2O with different concentrations of $AgNO_3$.

3.2. PL analysis

The Photoluminescence (PL) properties of PT and paper–TiO_2–Ag_2O with different concentrations of $AgNO_3$ were also studied to evaluate the effect of these concentrations on the luminescence behavior of the photocatalyst.

Results shown in Fig. 2, revealed a decrease in the intensity of the PL signal after the loading of Ag_2O NPs to the surface of the TiO_2. If we consider that the origin of the PL emission is the recombination of electrons and holes following the excitation of TiO_2 by illumination, then the decrease in the PL intensity in after inclusion of Ag_2O in comparison with PT sample, pointed toward a decrease in the recombination rate of charge

carriers in TiO_2. This results in a higher probability of generated e^-/h^+ in TiO_2 to combine with O_2 and H_2O producing highly reactive oxygen species (ROS) with strong capacity to degrade organic molecules via an oxidation process, as well highlighted in the literature data (Zhou et al., 2010; Zhou et al., 2010).

Notably, the weakest emission peak was for paper–TiO_2–Ag_2O with a concentration value of $5x10^{-3}$ M of $AgNO_3$ solution (PTG3), indicating that $5x10^{-3}$ M is the optimal concentration to improve charge separation and inhibit recombination.

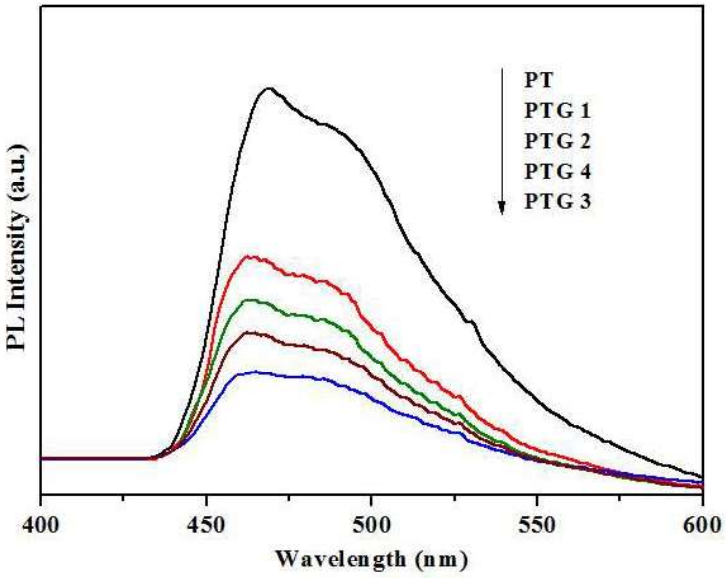


Fig. 2. PL spectra PT and paper–TiO_2–Ag_2O with different concentrations of $AgNO_3$.

3.3. Raman analysis

The Raman spectra of the untreated paper and the PT and PTG3 samples are shown in Fig. 3.

After functionalization of cellulose paper with TiO_2 (Fig. 3, curve b), three new bands appeared at 147 cm^{-1}, 517 cm^{-1} and 636 cm^{-1}, typical of TiO_2 anatase corresponding to E_g, (A_{1g}+ B_{1g}) and E_g, respectively (Sboui et al., 2018, 2020; Ohsaka et al., 1978).The characteristic features of cellulose at 329, 376, 438, 1095 and1115 cm^{-1} (Sboui et al., 2018, 2020; Liu, 1998) remained unchanged after the functionalization process, and their intensity was not much reduced, suggesting the formation of a thin layer (several µm thick) of appended TiO_2 on cellulose fibers.

For the PTG3 (Fig. 3, curve c), new peaks appeared at 429 cm^{-1} and 490 cm^{-1} that are related to Ag_2O (Waterhouse et al., 2001) in addition to the bands of cellulose I and TiO_2 anatase.

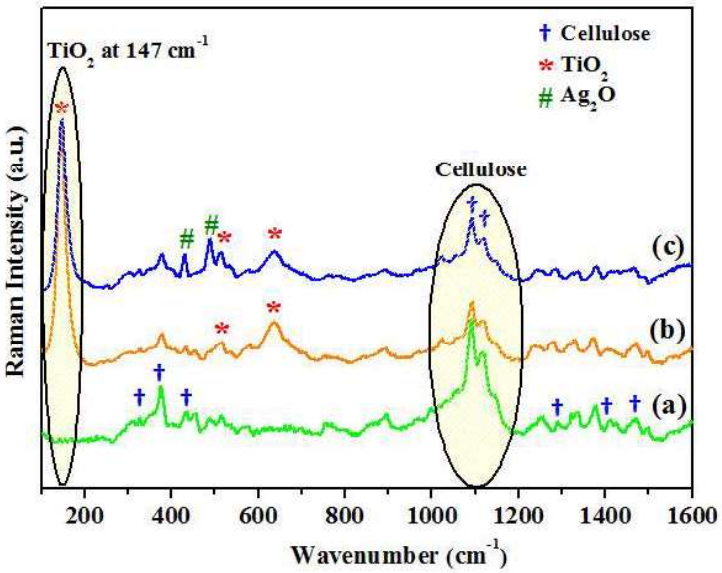


Fig.3. Raman spectra of neat paper (a), PT (b) and PTG3 (c).

3.4. XRD analysis

XRD analysis of the PTG3 was performed to further identify the crystalline composition of the appended layer on the paper (Fig. 4). In addition to the main diffraction peaks of cellulose I at 14.9°, 16.6°, 22.65° and 34.4° ascribed to (1-10), (110), (200) and (004) plane (Sboui et al., 2020), other minor features emerged at 2θ around 25.3°, 33.0°, 38,3°, 48.1°, 54° and 55.2°, as shown in Fig. 4, curve b. Though, the intensity of these peaks was not enough to assert with certitude their assignment, it is likely to claim the presence of TiO_2 anatase (2θ=25.3°, 48.1°and 54°) and Ag_2O (2θ=33.0°, 38.3° and 55.2°) (Ren and Yang, 2017; Liu et al., 2019; Liu et al., 2017). No other peaks were detected, indicating high purity of the phases.

The PTG3 sample was analyzed by XRD also after photocatalytic test. As display in Fig. 4, curve c, a new peak at 44.3 ° was detected, which was indexed to the (200) plane of metallic Ag (JCPDS 04-0783). The formation of Ag^0 after photocatalytic test is likely due to the photoreduction of Ag_2O by exposure to the UV fraction of Xenon light. The photosensitivity of Ag_2O is well known in the litterature (Lalitha et al., 2010) and the formation of metallic Ag on Ag_2O under exposition to light was also reported earlier (Wang et al., 2011).Other authors found that after a certain amount of Ag^0 is formed on the surface of Ag_2O, Ag_2O becomes more stable (Ren and Yang, 2017; Wang et al., 2011; Xu et al., 2013; Yu et al., 2012). On this basis, the photo-induced electrons move from Ag_2O to Ag^0, thus the separation process of charges is improved, contributing to strengthening the performance of the catalyst. Therefore, based on the so far results, PTG3 can be considered as a stable and

effective photocatalyst under visible light, opening new horizons for its use in the environmental field.

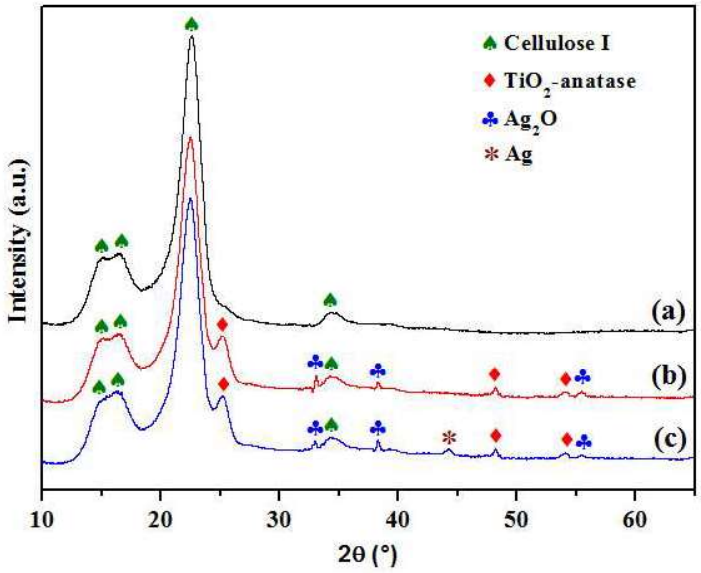


Fig. 4. X-ray diffractograms of neat paper (a), fresh PTG3 (b) and PTG3 after photocatalytic test (c).

3.5. SEM analysis

The FE–SEM images were recorded on the neat paper, after being treated with TiO_2 and also after depositing Ag_2O. According to Fig. 5 (A), the neat paper is composed of an entangled and welded fibrous network, with organization of fibers in random planes orientation, which is at the origin of the strength of paper.

After treating the paper with TiO_2 (Fig. 5 (B)), the fine elements of cellulose fibers can no longer be observed, while a continuous layer of TiO_2 covering the surface of cellulose appeared. In the PTG3 sample (Fig. 5 (C)), the surface of the paper was coated with a continuous layer associated with TiO_2, on top of which NPs with size around 100–150 nm are visible, as shown in Fig. 5 (D), which are assumed to be compatible with the Ag_2O NPs.

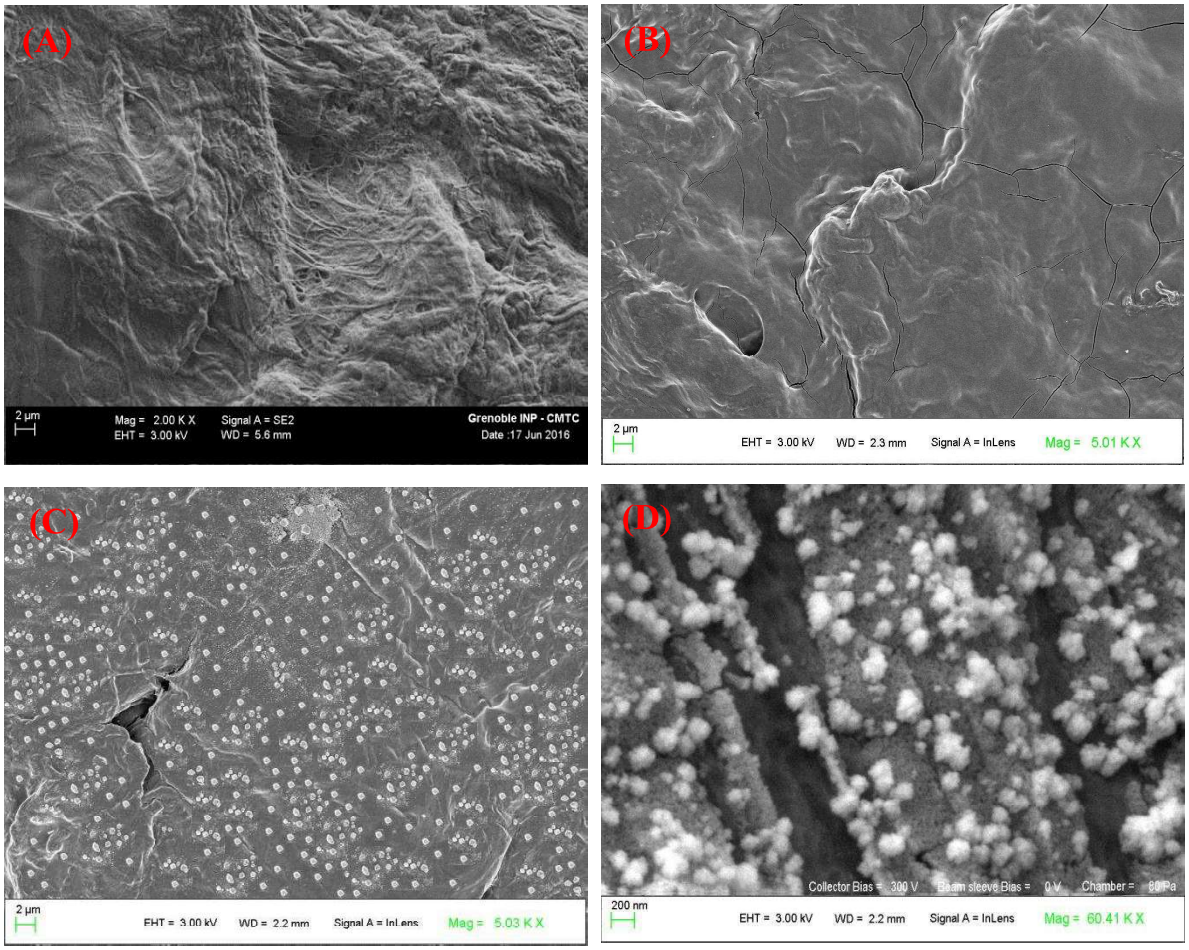


Fig. 5. FE–SEM images of neat paper (A), PT (B) and PTG3 (C and D).

3.6. XPS analysis

In order to investigate the surface chemical composition and oxidation state of the prepared samples, XPS analyses were carried out. Fig. 6 (A) displays the survey spectra of neat paper and PT, Fig. 6 (B) shows the XPS survey of PTG3. In the inset the high resolution O1s and Ti 2p and Ag 3d regions are reported. By comparing the spectrum of the neat paper with that of the PT sample, the disappearance of the traces of silicon occurs. In addition, new peaks attributed to the titanium appeared. The Ti 2p spectrum shows binding energy values of 458.8 eV (Ti $2p_{3/2}$) and 464,5 eV (Ti $2p_{1/2}$) characteristic of TiO_2. Furthermore, the effective coverage of the surface paper is demonstrated by the decrease of the O1s component at 533 eV related to the hydroxyl groups of the paper, while two components at 529.9 ± 0.1 eV and 531.9 ± 0.1 eV attributed to O–Ti–O and Ti–OH or Ti–O–C, respectively, were detected (Damasceno Da Silva et al., 1995; Jiao et al., 2015).

The XPS spectra of PTG3 are represented in Fig. 6 (B). The coverage of the surface by TiO_2 is confirmed by the presence of Ti2p peaks (458.8 eV) and by the presence of O1s peaks

at 529.9 eV and 532.0 eV. Alongside these peaks, new peaks appeared related to Ag_2O. In the high-resolution XPS spectra of Ag 3d, the peaks located at 367.9 eV (Ag $3d_{5/2}$) and 374.0 eV ($Ag3d_{3/2}$) usually assigned to Ag_2O (Murray et al., 2005; Chen et al., 2016). Furthermore, no other peaks were detected; such finding is consistent with the Raman and XRD data highlighting phases purity.

Based on the so far reported results, generation of both TiO_2 anatase and Ag_2O NPs on the surface of the paper is confirmed.

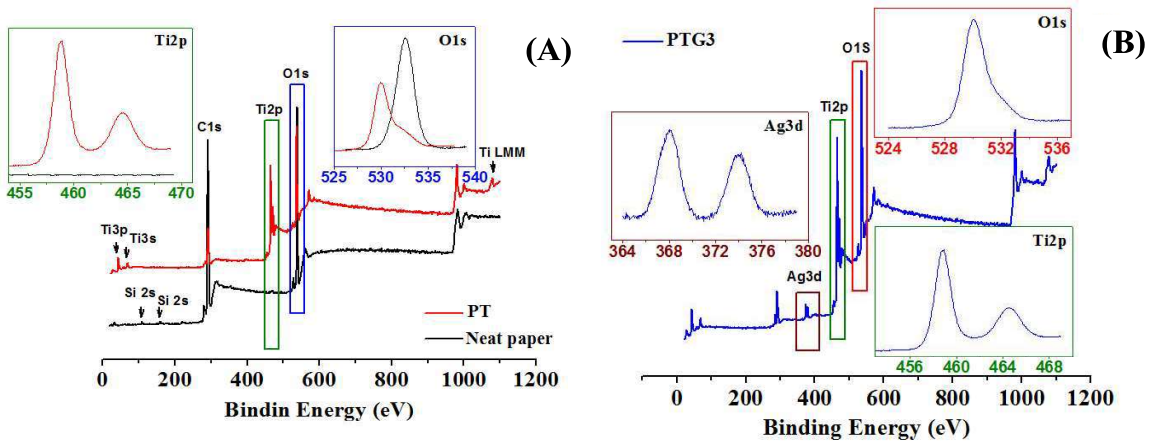


Fig.6. XPS survey of neat paper and PT (A) and PTG3 (B). In the inset, the O1s, Ti 2p and Ag 3d regions are reported.

3.7. Surface wettability

The evolution of the contact angle vs time for the neat paper, PT and PTG3 composites are shown in Fig. 7.

Untreated paper displays a hydrophobic surface as attested by the high contact angle value of about 120 °. The hydrophobic character can be attributed to two main factors: the presence of a silicon additive, as revealed by XPS measurements (Fig. 6 (A)) and the low surface porosity of the paper as revealed by SEM images (Fig. 5 (A)), which prevent the water absorption by capillarity inside the paper.

Unlike the original paper, after functionalization with TiO_2, the paper turned to hydrophilic as attested by the low value of contact angle around 40°. This evolution is likely due to the generation of TiO_2 layer bearing Ti–OH groups at the surface of the paper substrate.

However, after loading Ag_2O nanoparticles onto paper–TiO_2, the wettability of the paper–TiO_2 composite has become hydrophobic with an angle of contact of approximately

100 °. This finding can be explained by the decrease in the number of hydroxyl groups at the TiO_2 surface due to the growth of Ag_2O nanoparticles. This occurs because of the preferential adsorption of Ag^+ ions on the Ti–OH group during the process of dipping the paper–TiO_2 in $AgNO_3$ solution.

It is important to point out that the hydrophobic property is good for the photocatalyst because it inhibits the degeneration and disintegration of the cellulose support upon contact with water and provides it a self-cleaning property by preventing the adhesion of the by–product generated during water treatment.

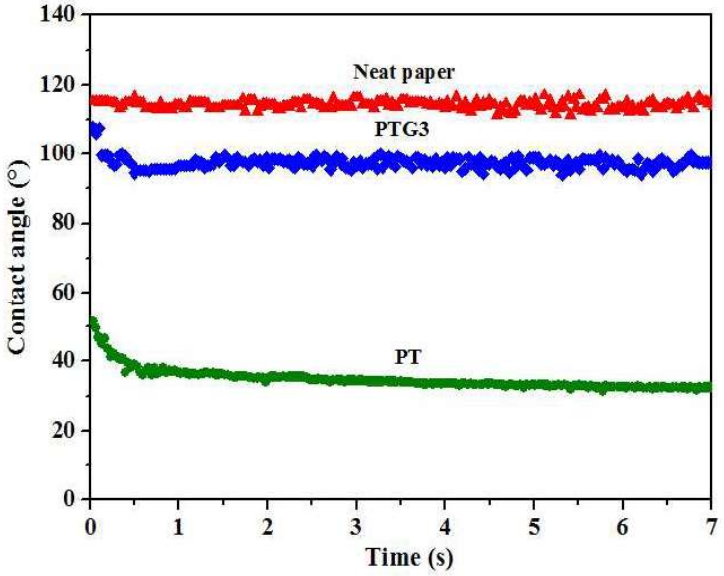


Fig. 7. Water contact angle evolution *vs* time for neat paper, PT and PTG3.

3.8. Photocatalytic activity study

3.8.1. Photodegradation of aniline

In this study, aniline was used as a model of aromatic pollutant soluble in water, because of its increased discharge into the aquatic environment due to its increased use in the chemical industry, including textiles, organic pigments, dyes, rubbers and herbicides to cite few of them (Szczepanik and Słomkiewicz, 2016; Najafi-Ashtiani et al., 2016). Aniline poses great risks to human life, as it causes many diseases such as lung cancer, anemia, osteoporosis and kidney disease (Bozkurt and Gul, 2019; Farmanzadeh and Keyhanian, 2019; Luongo et al., 2016; Jiang et al., 2016). In general, aromatic pollutants are hard to degrade via conventional biological pathway and additional specific tertiary treatments are needed to eliminate them.

Before starting the photodegradation process, the AN solution with the paper catalysts was maintained in the dark for 60 min to achieve sorption equilibrium of aniline on the

catalyst. Under dark condition, the vanishing fraction of AN did not exceed 6%, indicating a weak adsorption of AN of the modified paper. A negligible decrease in the concentration of AN was also noted, under illumination condition, when untreated paper was used, as shown in Fig. 8 (a).

In the presence of paper modified with TiO_2 or TiO_2/Ag_2O, a decrease in the concentration of residual AN was noted over time. Much more pronounced was the effect observed when Ag_2O was combined to TiO_2 in the functionalization of paper. For instance, after 180 min exposition to light, about 23 and 65% of AN was degraded in presence of PT and PTG3, respectively, and the degradation grade further grow after 300 min attaining about 31% and 97%. This huge improvement of the photodegradation efficiency when Ag_2O was associated with TiO_2, is presumably due to, (i) the reduced tendency to e^-/h^+ recombination favoring the possibility of the charge carriers generated through excitation of TiO_2/Ag_2O photocatalyst by light to generate ROS species, as has been demonstrated through PL study, (ii) to the enhanced light absorption in the visible domain brought by the presence of Ag_2O/Ag, and (iii) to the surface plasmon resonance (SPR) effect that contributed to feed the conduction band of TiO_2 with electrons. This later effect was widely discussed in the literature data (Abid et al., 2017) and is on the origin of the development of what is known as plasmonic photocatalyst (Wang et al., 2012) feeding the conduction band of the TiO_2 with electrons generated by surface plasmon resonance (SPR) of Ag and Ag_2O NPs. In addition, the improved performance of PTG3 compared to PT can be attributed to the hydrophobic nature of the PTG3 which contributed to enhancing its activity thanks to full illumination and oxygenation due to high air-water interface. As a result, the radical formation rate and the oxidation efficiency were highly improved (Xing et al., 2018; Wang et al., 2017 ; Sboui et al.,2017).

The important role that Ag_2O NPs has in the photodegradation process of AN has been confirmed by results of the kinetic analysis of AN degradation. Kinetic analysis of AN degradation is identical to the pseudo-first-order kinetic model, as shown in Fig. 8 (b). In light of this model, the values of the rate constant (k) were determined (see Table 1). These values indicate an improvement in the photocatalytic performance of the paper–TiO_2 after Ag_2O loading.

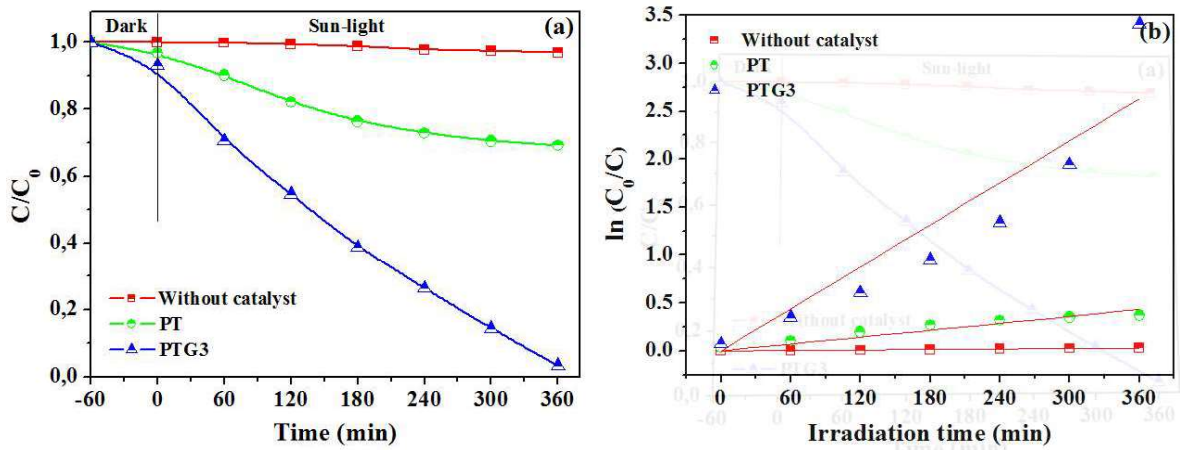


Fig. 8. (a) Photodegradation curves of aniline under Xenon lamp irradiation and (b) First-order kinetics.

Table 1

k and R^2 of aniline degradation under Xenon lamp irradiation.

Catalyst name	k (min^{-1})	R^2
Without catalyst	8.5×10^{-5}	0.98
PT	0.00123	0.97
PTG3	0.0067	0.96

In order to check the stability of the composite (TiO_2/Ag_2O) on the cellulose paper, PTG3 was treated with ultrasound for 30 min and then its photocatalytic performance was tested. Results in Fig. 9 revealed no change of the photocatalytic efficiency of the sample after the sonication treatment, confirming the efficient binding of the composite onto the surface of the paper. Additionally, the PTG3 showed no sign of degeneration or disintegration after processing sonication and lengthened contact with water.

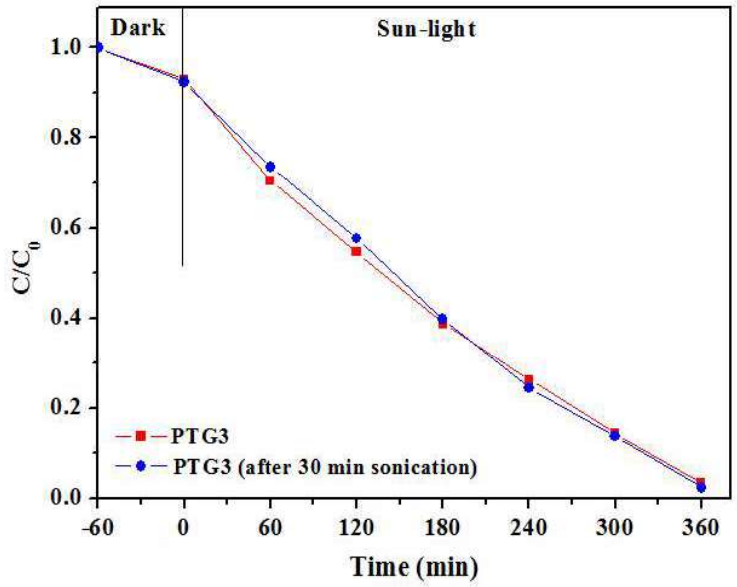


Fig. 9. Degradation of aniline under Xenon lamp illumination in the presence of PTG3 prior and after sonication during 30 min.

3.8.2. Effect of $AgNO_3$ concentration

To find out the effect of $AgNO_3$ concentration on aniline degradation, tests photocatalytic were performed of the prepared paper–TiO_2–Ag_2O samples with different $AgNO_3$ concentrations as shown in Fig. 10. According to Fig. 10, the photocatalytic performances of all samples were improved after loading Ag_2O onto the surface of TiO_2 and a gradual effect was registered by increasing the $AgNO_3$ concentration from 5 x 10^{-4} M to 5 x 10^{-3} M. Especially, the PTG3 sample prepared with a concentration of 5 x 10^{-3} M $AgNO_3$ solution showed the highest photocatalytic performance (97% of aniline photodegradation). Nevertheless, increasing the $AgNO_3$ concentration after this rate causes a decrease in the photocatalytic performance of the prepared sample, indicating that 5 x 10^{-3} M is the optimal concentration value.

In general, the photocatalytic performance of the prepared samples is in this order: PT<PTG1<PTG2<PTG4<PTG3. It is worth noting that the aniline photodegradation results are completely in agreement with the DRS and PL results, which show that Ag_2O NPs as visible-light sensitization enhances the photocatalytic activity of paper–TiO_2–Ag_2O samples and 5 x 10^{-3} M is the optimum concentration value of the $AgNO_3$ solution.

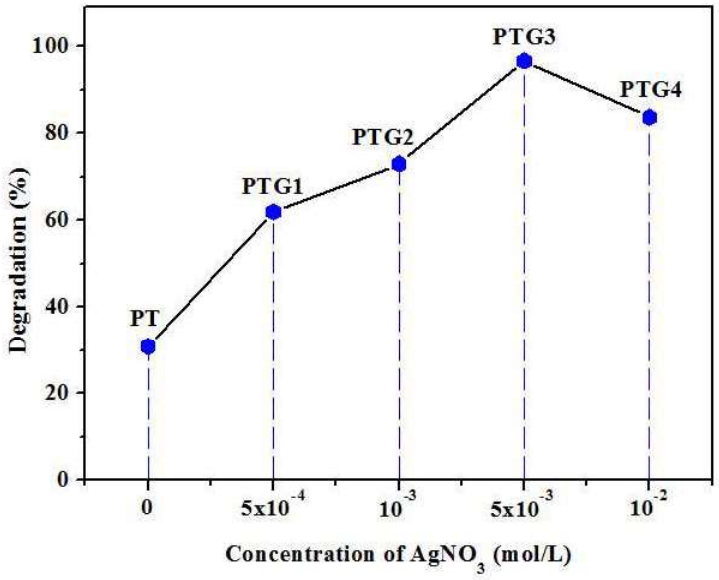


Fig. 10. Effect of the concentration of the $AgNO_3$ solution used to prepare paper–TiO_2–Ag_2O photocatalysts on the photodegradation of aniline after 6h of illumination.

3.8.3. Cyclic stability of photocatalysis

The stability of a photocatalyst is very important in environmental remediation. Therefore, recycling experiments on the degradation of AN by PTG3 were carried out to evaluate the degradation stability. As shown in Fig. 11, PTG3 generally showed similar degradation behavior under sunlight illumination for three cycles. 97% of AN could be degraded during the first cycle, while 92% of AN could still be degraded by PTG3 for the third cycle. These results indicate that the catalyst (PTG3) can be reused for several cycles without decrease its effectiveness. This makes it a potential candidate for several other applications, such as fighting bacteria and purifying the air from volatile organic compounds.

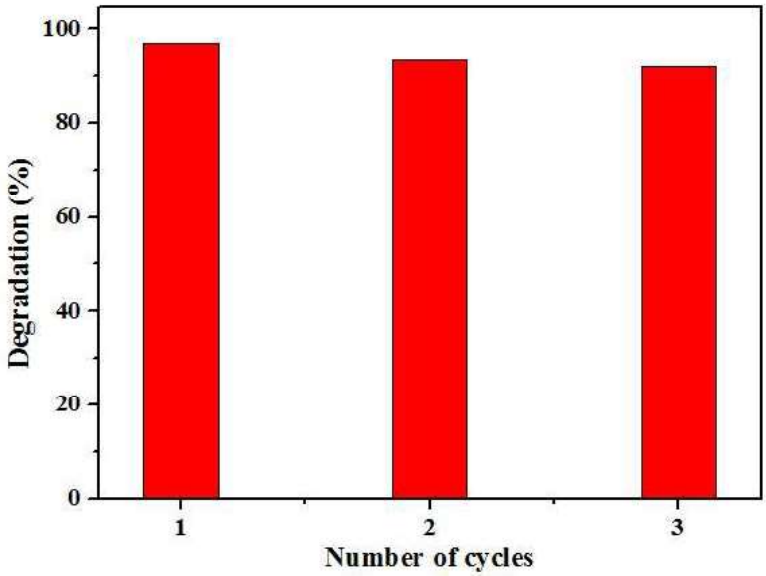
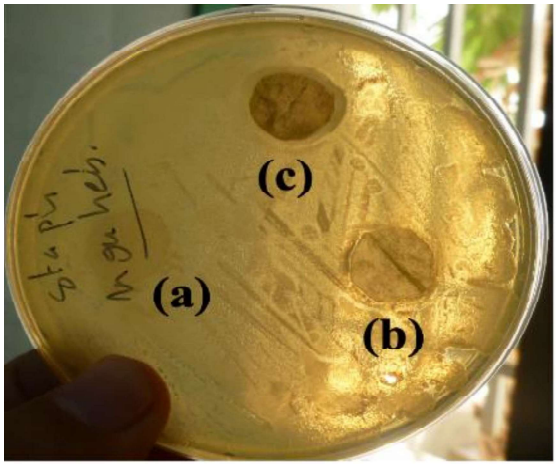


Fig. 11. Recycled activities of PTG3 for photodegradation of aniline under the Xenon lamp illumination for 6 h.

3.9. Antibacterial Properties of paper–TiO_2–Ag_2O

Given the sensitivity of cellulose-based material to bacterial proliferation, the presence of Ag_2O associated with TiO_2 might be beneficial to prevent any risk of bacteria growth on paper. To check the resistance of paper samples to bacteria attack, disk-diffusion method using E. coli as Gram–bacteria model was run (Fig. 12).



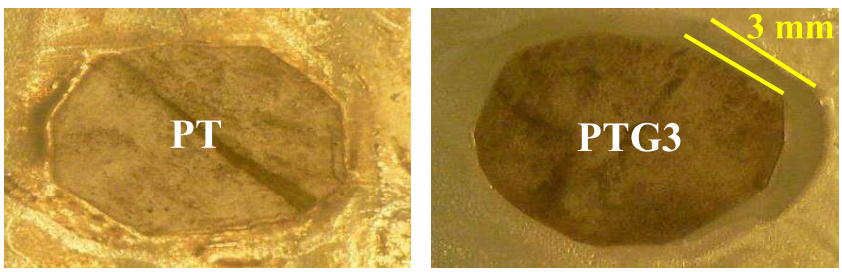


Fig. 12. Antibacterial activity against E. coli of neat paper (a), PT (b) and PTG3 (c). Magnified images of the inhibition test zone of the PT and PTG3.

From Fig. 12 it can be seen that the neat paper did not exhibit any resistance to bacterial growth, which is expected thanks to the sensitivity of cellulose to bacterial attacks. The paper treated with TiO_2 did not reveal any capacity to prevent bacteria from proliferation, as attested by the spread of bacteria over the sample. On the other hand, PTG3 sample revealed an apparent inhibition zone, confirming the aptitude of this sample to prevent bacterial growth and even to induce deactivation of bacteria in the nearby of the film. The improved activity of PTG3 sample compared to activity of PT sample can be attributed to several reasons (Reidy et al., 2013): (i) emitted silver ions from Ag_2O contribute to killing bacteria by disrupting their DNA; (ii) the damage of the bacterial membrane (Endo-Kimura et al., 2019; Lok et al., 2006) and (iii) the photocatalytic properties of PTG3 contribute to killing bacteria by reactive oxygen species (ROS) that are generated when Ag_2O/TiO_2 p-n heterojunction is exposed to illumination (Liu et al., 2017; Endo-Kimura et al., 2019; Zhao et al., 2017).In addition some scientific research proposed that Ag nanoparticles may attach to the cell membrane surface and penetrate it, leading to cell damage and then death it (Li et al., 2008; Sharma et al., 2009; Morones et al., 2005). Therefore, in addition to the enhancement of the photocatalytic activity under solar light exposition, the presence of Ag_2O NPs contributed to preserve the paper based photocatalyst from any risk of bacteria colonization, which will result in improved durability of the photocatalyst under humid condition.

4. Conclusions

In this study, a facile and eco-friendly strategy was presented to form titanium dioxide layer decorated with Ag_2O nanoparticles, which is well bonded to the paper surface. Paper–TiO_2–Ag_2O showed significant degradation ability towards aniline (AN) in water under simulated sunlight irradiation, indicating its ability to treat polluted wastewater. Moreover, the paper–TiO_2–Ag_2O showed very good antibacterial properties. The improved photocatalytic performance of the paper–TiO_2–Ag_2O is mainly due to the narrow band gap that is formed after loading the Ag_2O NPS onto the TiO_2 layer which contributed to the improvement of visible light absorption and reduced recombination of the generated charges. Also, the hydrophobic character helped to improve production of reactive oxygen species (ROS) due to the proximity to the air-water interface. This system (paper–TiO_2–Ag_2O) is reusable, inexpensive and eco-friendly. Furthermore, paper–TiO_2–Ag_2O can be used as useful floating

photocatalysts. They can float easily on liquid and are directly reused without separation during the photocatalytic reaction. In addition, the paper–TiO_2–Ag_2O can be directly applied in water treatment without having to stirring or artificial oxygenation during the photocatalytic reaction and it can be easily collected from the surface and therefore overcome the recycling problem. These results demonstrate that the paper–TiO_2–Ag_2O with high photocatalytic activity and excellent reusability have potential in wastewater treatment.

This work presents a new and feasible vision for preparing a floating photocatalytic paper that can be applied to purify polluted water from a large number of pollutants such as removing floating organic pollutants and soluble organic pollutants from wastewater, in addition to killing bacteria. It can also be used to purify the air, especially indoors.

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Conflict of Interest Statement

There are no conflicts to declare.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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