

**SYNTHESIS AND PHOTOCATALYTIC ACTIVITY OF TiO₂/Ag**

S. A. P. V. T. de Carvalho, E. A. Pereira, M. A. Montanhera & Y. J. Dias, F. R. de Paula*

Departamento de Física e Química, Universidade Estadual Paulista-UNESP, Ilha Solteira, SP, 15385-000 Brazil

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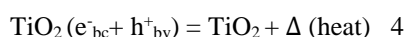
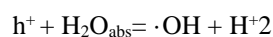
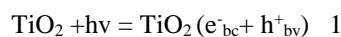
Abstract

Over the last decade, titanium dioxide (TiO₂), in particular, anatase phase became the most studied semiconductor photocatalyst due to its high photocatalytic efficiency under UV irradiation, low cost, high stability, and low toxicity. These characteristics allow the degradation of toxic and biological waste present in air and water, efforts have been devoted to modify and enhance them. In this work, TiO₂ samples were synthesized with different silver carbonate (Ag₂CO₃) concentrations. Under UV light, the results showed an enhancement in photocatalytic performance in degradation of Rhodamine-B dye compared to pure TiO₂. An increase of 25% on Rhodamine-B by TiO₂/Ag degradation was noticed.

Key words: photocatalysis, titanium dioxide, semiconductor, silver, Rhodamine-B**Introduction**

Nowadays water and air pollution, with dye and toxic waste, has been a warning factor for protecting the environment. Over the past decades, a great deal of effort has been devoted to the investigation of photocatalytic degradation of these pollutants by photocatalysis¹⁻³. Up to now, great deals of semiconductor photocatalysts have been developed, such as TiO₂^{4,5}, ZnO⁶, SnO₂⁷, ZnS⁸, etc. Among these reported photocatalysts, TiO₂ is the widely investigated photocatalyst. TiO₂ is a semiconductor with wide-bandgap (3.2 eV for anatase and 3.0 eV for the rutile phase), is not toxic to the environment, low cost and, has strong oxidizing power and good stability in photocatalytic reactions⁹.

The photocatalytic process begins when the TiO₂ under UV light irradiation receives photons with energy equal to or greater than the band gap. In this process, the electron in the valence band is excited generating a lacuna (h⁺) in the valence band and electron (e⁻) conduction band (Eq. 1). Part of the photogenerated e⁻ and h⁺ was consumed by producing thermal energy through the combination process. On the hand, other photogenerated e⁻ and h⁺ can migrate to the surface of TiO₂ and react with the adsorbed species. When the adsorbed species is water (H₂O), these lacunas (Eq. 2 e3) have the potential to generate hydroxyl radicals (·OH), highly oxidant capable of degrading any organic compound (Fig. 1). The reactions that describe these processes are:



Those hydroxyls are so strong that their oxidizing capacities are even stronger than Fluorine and Ozone¹⁰.

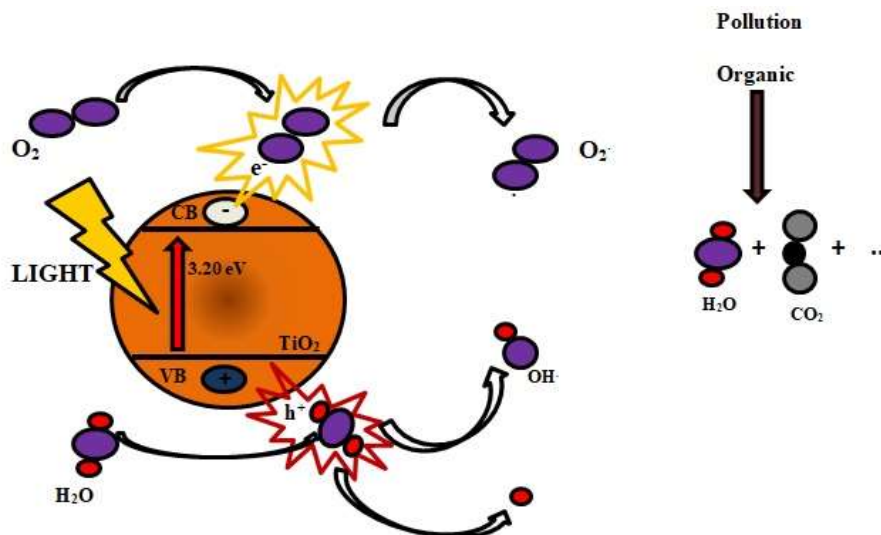


Figure 1: Scheme of TiO₂ excitation by light absorption leading to electron holes in the conduction band.

Due to its wide band gap (range 3.0 - 3.2 eV), UV light is required to generate electron/hole pairs, this significantly limits TiO₂ as an effective photocatalyst since UV light accounts for only 5 % of total solar radiation. Additionally, the photocatalytic efficiency of TiO₂ depends on the competition between the process where the electron is removed from the semiconductor's surface, and the process recombination electron-hole pair, which results in liberation heat (Eq. 4)¹¹⁻¹³. Many attempts have been to inhibit these charge recombination process. In this regard, an effective way to facilitate charge separation involves a combination of TiO₂ with metals. The presence of metals on the surface of TiO₂ can produce traps to capture the photoinduced electrons or holes, leading to the reduction of electron/hole recombination and as consequence improved photocatalytic efficiency.

The aim of the present work is to verify the influence of the presence of silver (Ag) nanoparticle (NP) on the surface of TiO₂ chemically synthesized on the photocatalytic degradation of dye Rhodamine-B (Rhod-B). Metallic silver was incorporated into TiO₂ by decomposition of Ag₂CO₃ at 600 °C¹⁴.

Materials and methods

In the preparation of titanium precursor, 0.02 g/mol of TiOSO₄ was dissolved in 2.50 ml of water at 10 °C under vigorously magnetic stirring and then after 30 min. 0.007 mol/l of H₂O₂ was added to the solution. A yellow colored acidic solution with a yellow precipitate was formed indicating the formation of peroxo-hydroxo titanium complexes. After the preparation of precursor were incorporated different concentrations of Ag₂CO₃: 2.00; 0.20; 0.10 and, 0.05 %, percentage in function of the quantity of TiOSO₄ used. Finally, the precipitate was annealed in air at 600 °C for 4 h to obtain crystalline Ag/TiO₂.

The photocatalytic activity of the samples for the oxidation of Rhod-B was tested under UVC light illumination. The powders were placed in beakers and immersed in 100 mL of a Rhod-B aqueous solution (2.5 mg L⁻¹). The beakers were placed in a photo-reactor at 30 °C and illuminated by an OSRAM 125 W high-pressure mercury-vapor lamp (bulb free). All the tests were performed under vigorous stirring. The photocatalytic oxidation of Rhod-B was monitored by taking UV-vis measurements at various light exposure times.

The structures of the samples were studied by X-ray diffraction (XRD) at room temperature by SHIMATZU XRD-6000 model which provides CuK_α radiation (λ=1.544 Å). Measurements were taken in θ-2θ configuration from 20° to 65°, with a step size of 0.02°. SEM images were obtained with ZEISS model EVO LS15 with an acceleration voltage of 0.1 to 20 kV.



Results and discussion

3.1 XRD and EDX Analysis

The crystalline property of the prepared sample is reported via patterns which are illustrated in Fig. 2. XRD of Ag/TiO₂nanocomposite shows the presence of metallic Ag and TiO₂. As seen in Fig. 2, the strong diffraction peaks at $2\theta = 25.3^\circ, 37.7^\circ, 48.04^\circ, 54.0^\circ, 55.1^\circ$ and 62.6° , are corresponding to (101), (004), (200), (105), and (211) planes, relatively, which are systematically ascribed to the anatase-TiO₂. We can also see diffraction peaks at $2\theta = 38.3^\circ, 44.3^\circ$ and 65.0° , which can be indexed to crystallite planes of (111), (200) and, (220) of fcc Ag. Figure 2(b) gives the EDX spectrum of one small particle over TiO₂ and confirm the presence of metallic Ag.

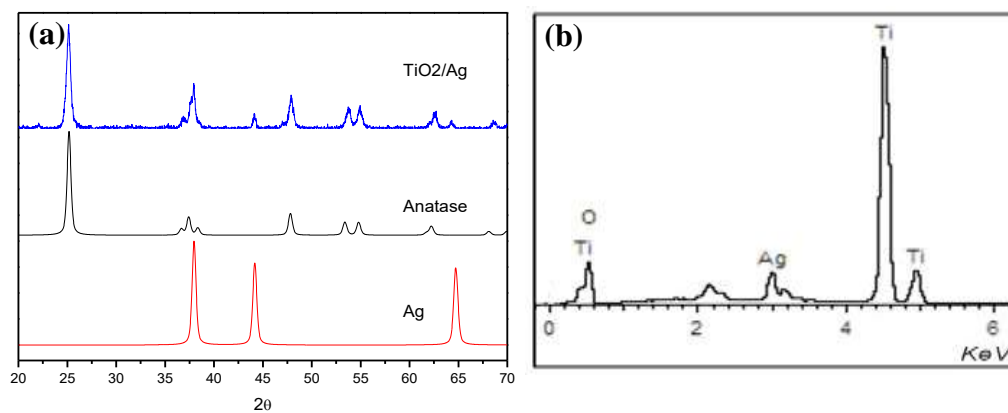


Figure 2: Analysis of X-ray diffraction the TiO₂/Ag (a), Characterization of TiO₂/Ag by the method EDX (b).

3.2 Scanning electron microscope (SEM)

The morphology of the Ag/TiO₂ samples was investigated by SEM images. The Fig. 03 clearly shows that Ag/TiO₂ samples exhibit TiO₂ completely aggregated with the presence on the surface of metallic Ag with sphere-like morphology

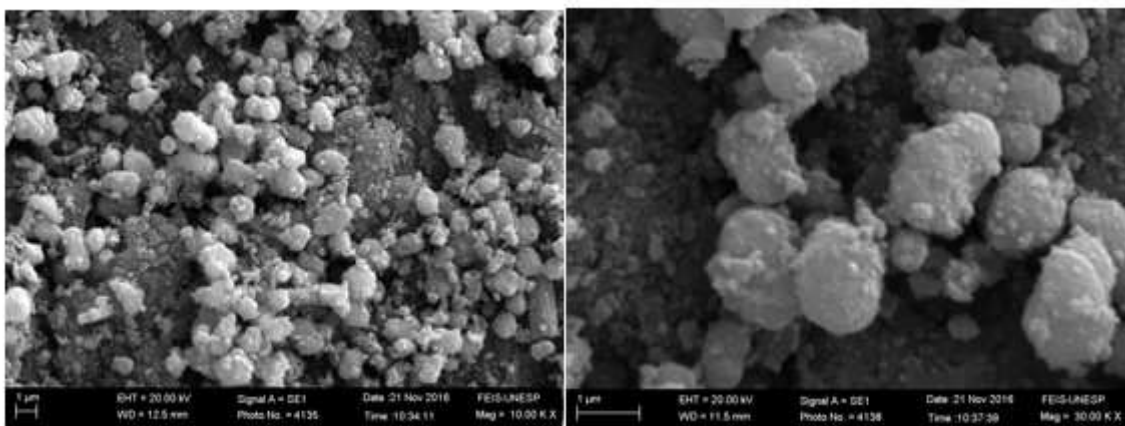


Figure 3: Images MEV of TiO₂/Ag.

3.4 Photocatalytic Performance Test

The photocatalytic performance of the pure TiO₂ and Ag/TiO₂nanocomposite was tested in decomposition Rhod-B under UV light. The results for the photocatalytic activity to the samples with a different concentration of Ag are present in Fig. 4. The figure indicates that metallic Ag does not exhibit significant photocatalytic



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activity, on the hand, pure TiO₂ and Ag/TiO₂nanocomposite exhibit activity. The presence of trace of metallic Ag NPs on the surface of TiO₂can increase the photocatalytic activity. The optimal concentration of Ag₂CO₃ incorporated in the titanium precursor was the found as 0.20 %. The result was 25% higher when compared to pure anatase TiO₂.

The reduction of efficiency is observed with increase of the concentration of metallic Ag. In the case, excessive coverage of TiO₂ limits the amount of light reaching to the TiO₂ surface, reducing the number of photogenerated e⁻ and h⁺ pairs and consequently the performance of the TiO₂

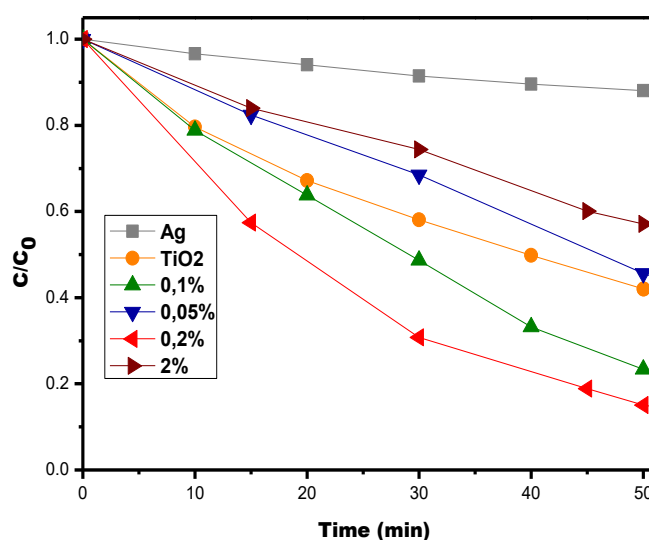


Figure 4: Profiles of photodegradation of Rhodamine-B dye, using TiO₂/Ag and TiO₂pure with light UV. Relation between C/C₀ vs. irradiation time.

A pseudo-first-order model expressed by the equation $\ln(C_0/C) = kt$ (C_0 the initial concentration; C the final concentration, k the pseudo-first-order rate constant) was applied to investigate the Rhod-B degradation kinetics. The obtained results are present in Table1. The results indicate a good correlation with pseudo-first-order reaction kinetics. The k constant confirms that the 0.20 % Ag/TiO₂ sample shows largest reaction rate constant, 2 times that pure TiO₂.

Table 1: Results of the pseudo-first-order rate constant in degradation of Rhod-B

Samples	UV light Irradiation	
	k	R ²
TiO ₂	0.01681	0.99309
Ag ₂ O	0.00255	0.98371
0.05% Ag/TiO ₂	0.01594	0.98223
0.1% Ag/TiO ₂	0.02894	0.98277
0.20% Ag/TiO ₂	0.03765	0.99833
2.00% Ag/TiO ₂	0.01117	0.99043

The schematic energy band model of the Ag/TiO₂ nanocomposite can be depicted as shown in Fig. 5. Under UV light irradiation, the excited electrons in the CB of TiO₂ can transfer to the CB of metallic Ag. Therefore, the formation of Ag/TiO₂ heterojunction, inhibit the recombination of photogenerated e⁻ and h⁺. As consequence,



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more hydroxyl radicals can be formed with larger reaction numbers of OH groups with h^+ photogenerated resulting in the enhanced photocatalytic efficiency observed in this work¹².

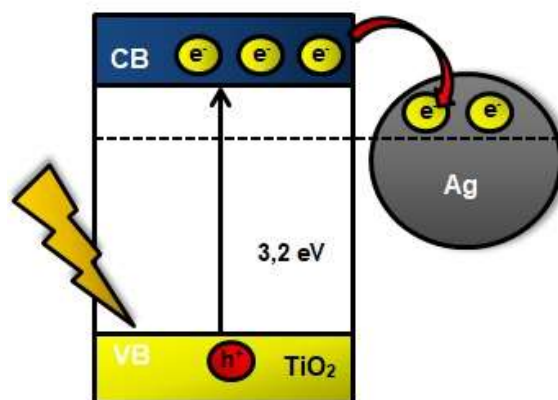


Figure 5: Illustration of TiO_2 electrons transference to the Ag under UV light irradiation.

Conclusions

Ag/ TiO_2 nanocomposite was obtained by adding Ag_2CO_3 in the titanium precursor and thermal treatment. The results showed that the presence of trace of metallic Ag nanoparticle increases the photocatalytic activity. The optimal concentration of Ag_2CO_3 incorporated in the titanium precursor was the found with 0.20 %. The result was 25% higher when compared to pure TiO_2 at anatase phase. The presence of trace of metallic Ag NPs on the surface of TiO_2 restrained the recombination rate photogenerated electron (e^-) and hole (h^+). In this case, the presence of metallic Ag provided additional active sites for the adsorption of reactive intermediates as well as improved charge mobility on the TiO_2 surface. These modifications prevent electron-hole recombination.

Acknowledgments

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