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Photocatalytic Decomposition of Trypan Blue over Nanocomposite Thin Films[1]

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Abstract—The photocatalytic activity of titanium dioxide and gold modified TiO_2 (Au/TiO_2), supported on polymethylmethacrylate (PMMA) thin film, was evaluated in the photodegradation of Trypan Blue (TB) under sunlight irradiation. The effect of parameters such as the photocatalyst amount and pH on TiO_2 photocatalytic activity is investigated. Oxygen flow stream was applied to enhance the decomposition process of TB. The maximum photoactivity was attained using Au/TiO_2–PMMA thin film at pH 2.

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The existence of organic dyes in wastewaters has become a serious problem because of the synthetic nature of organic dyes [1]. Trypan blue (TB) is an azo dye that is reported as a carcinogenic agent [2]. It has a complex structure with a high photostability [3]. So there is a need for an efficient economic method for the degradation of such stable compounds. The use of solar energy to drive the destruction of pollutants presents an indubitable advantage from the environmental viewpoint [4]. It also improves the economic achievability of the process, making it competitive with other technologies for wastewater management, such as ozone or H_2O_2/UV-C [5].

It has been reported that some semiconductor fine particles coated with polymer are excellent photocatalysts [6], due to their unique electronic and optical properties. This facilitates efficient photon-induced generation and the separation of charges that can be utilized for selective oxidation and reduction reactions at the semiconductor's surface [7].

TiO_2 is the most widely used catalyst, essentially because of its photostability, non-toxicity, low cost and water insolubility under most environmental circumstances [8]. Even though nanocrystalline TiO_2 has been shown to be an extremely active photocatalyst [9], this technology has not yet been successfully commercialized because of the problems linked to the separation of TiO_2 particles from the suspension after treatment. In order to solve this problem, supported photocatalysts have been developed [10–12]. Many research efforts have been focused on the holding of titania nanoparticles onto silica materials using different reactor configurations, such as silica gel particles slurries [13], glass electrodes [14], and fluidized beds [15]. TiO_2 supported on clinoptilolite was used efficiently as a catalyst for photocatalytic degradation of azo dye Disperse Yellow 23 in water. This study shows that pH is one of the main affecting factors on the degradation of azo dye Disperse Yellow 23 [16]. TiO_2 codoped with Fe^{3+} and Ho^{3+} ions was more powerful in the photocatalytic degradation of methyl orange than TiO_2 alone. This was ascribed to the fact that some elements such as Fe^{3+} and Ho^{3+} broaden the absorption profile, generate more electron–hole pairs and retard the recombination of photo-generated electrons and holes [17].

The goal of this work is to develop a method for the immobilization and easy separation of the used nanoparticles (Au/TiO_2) by supporting them into polymethylmethacrylate (PMMA) thin film. PMMA was chosen because this type of plastic is UV transparent and easy mouldable [1]. Moreover, photocatalytic thin films can shatter down organic dirt, kill bacteria and destroy harmful molecules in water and air by using light as the energy source [18].

In this study, TiO_2 and surface modified TiO_2 with Au (Au/TiO_2) particles supported on PMMA thin film were used for the photocatalytic degradation of the azo dye TB (carcinogenic hazardous water contaminant) under irradiation with sunlight.

Photodegradation of organic compounds using a semiconductor catalyst takes place when the catalyst is illuminated with light of energy $h\nu$ more than or equal to the band gap energy. Electron–hole pairs are gener-

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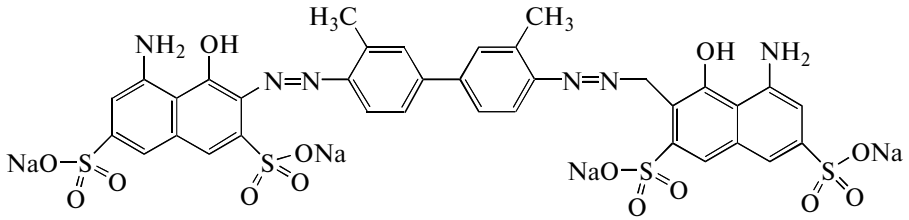


TB Chemical Formula: $C_{34}H_{24}N_6Na_4O_{14}S_4$

Scheme 1. TB chemical structure.

ated in the bulk. These charge carriers migrate towards the catalyst surface, where they take part in redox reactions with adsorbed organic molecules.

In this study, sunlight was used as an energy source for the excitation of catalyst electrons from filled valence band (**vb**) to empty conduction band (**cb**). The photocatalyst, in presence of sunlight and oxygen flow stream, decomposes the organic species to CO_2 and H_2O [19].

The most commonly proposed mechanism for the mineralization of most organic pollutants is the following [20, 21]:

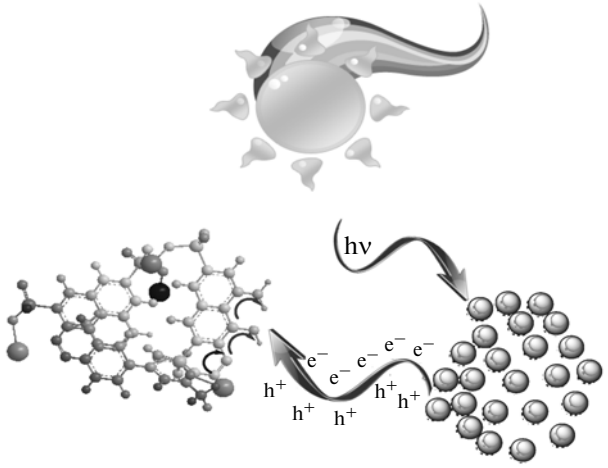
(1) absorption of efficient photons

$$TiO_2 + h\nu \rightarrow e^-_{cb} + h^+_{vb},$$

where h is the Plank's constant, ν—the light frequency, e^-_{cb}—the electron of conduction band and h^+_{vb}—the hole of valence band;

(2) oxygen adsorption leading to $O_2^{\bullet -}$ free radicals

$$(O_2)_{ads} + e^-_{cb} \rightarrow O_2^{\bullet -};$$



TB Au/TiO_2 embedded into PMMA

Scheme 2. TB photocatalytic degradation process.

(3) formation of $^{\bullet}OH$ radical by photo-holes

$$(H_2O \rightarrow H^+ + OH^-)_{ads} + h^+_{vb} \rightarrow H^+ + {}^{\bullet}OH;$$

(4) oxidation of organic species (R) by $^{\bullet}OH$ radical or holes

$$R + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2O,$$

$$R + h^+ \rightarrow R^{\bullet +} \rightarrow \text{degradation products}.$$

Scheme 2 illustrates the mechanism of TB photocatalytic degradation process using Au/TiO_2-PMMA thin film and sunlight irradiation.

EXPERIMENTAL

Chemicals

The P25 TiO_2 (ca. 80% anatase, ca. 20% rutile) supplied by Degussa, with a typical surface area of 50 ± 15 m^2/g, average primary particle size 21 nm and band gap 3.03 eV for rutile and 3.18 eV for anatase.

Preparation of Au/TiO_2

50 ml aqueous solution contains 0.08 g TiO_2 and 5 ml of 5×10^{-3} mol/dm^3 $HAuCl_4$ (Aldrich) was stirred whilst heating until boiling. Then 1 ml of 0.5% solution of sodium citrate (Puriss, Fluka) was added during heating until the colour changed. The deposition of gold nanoparticles on TiO_2 is confirmed by the colour change of the modified oxide powder, turning from white into deep purple, a colour deriving from the surface plasmon resonance of Au^0 islands [22]. The solution was removed, centrifuged, washed 3 times with methanol and 6 times with water, and dried overnight at 90°C.

Polymer Synthesis

PMMA polymer was prepared according to the free radical polymerization process [23]. Methyl methacrylate (99.0%, Fluka) was purified via distillation under reduced pressure. About 100 ml (density 0.943 g/ml) of purified methyl methacrylate monomer was taken in a Pyrex glass jar. Traces of benzoyl peroxide were added to catalyze the radical polymerization.

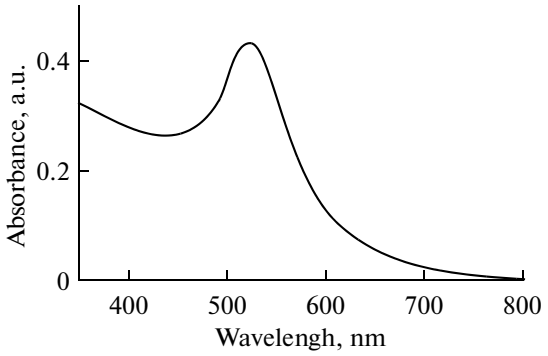


Fig. 1. Absorption spectra of the synthesized gold (0.025 mg/ml) nanoparticles using optical path length of 1 cm.

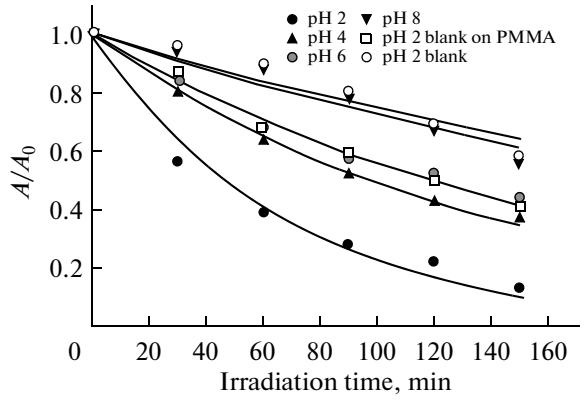


Fig. 2. Effect of different pHs on TB (1×10^{-5} mol/dm^3, $\lambda_{max} = 585$ nm) degradation efficiency using 0.08 g TiO_2–PMMA thin film and sunlight irradiance 500–600 W/m^2.

The mixture was deoxygenized by purging with argon. Oxygen may cause oxidative degradation of macromolecules that have already been formed [24]. The jar is then sealed and kept undisturbed for 48 h at 55°C. The temperature was raised gradually to 90°C for 5 h to get rid of the remaining traces of unreacted initiator and monomer by evaporation [25]. Before taking the samples out of the oven, its temperature is decreased slowly to 25°C over a period of 24 h.

Preparation of TiO_2 Thin Film

First, 300 mg PMMA was dissolved in 10 ml tetrahydrofuran (Fluka). A proportional amount of TiO_2 (0.04 or 0.08 g) powder was suspended in the dissolved polymer. The mixture was uniformly distributed in a Pyrex glass Petri dish (100 mm in diameter) and left to dry for 24 h at room temperature. Au/TiO_2 thin film was prepared by the same method.

Preparation of Gold Nanoparticles

Gold nanoparticles was prepared by chemical reduction of $HAuCl_4$, according to Turkevich's method [26]. 95 ml of a chlorauric acid ($HAuCl_4$) solution containing 2.5 mg of Au was refluxed and 5 ml of 1% sodium citrate solution was added to the boiling solution. The solution is further boiled for 30 min and is then left to cool to room temperature.

Figure 1 shows the absorption spectra of gold nanospheres. The spectrum of the gold nanospheres has an intense band at 521 nm assignable to the plasmon absorption of a 22 nm particle diameter of gold [27, 28].

Photocatalysis Experiment

The photocatalysis experiment was carried out by exposing 100 ml of the aqueous TB samples over the PMMA thin film in a Petri dish to outdoor sunlight. The dried PMMA thin film was maintained in the bottom of the Pyrex glass Petri dish (100 mm in diameter) by holding large lipped paper clips vertically across the dish boundary. The values of natural sunlight irradiance were measured on the Three Channel Eldonet Dosimeter (Germany), and the concentration of TB was 1×10^{-5} mol/dm^3. Two control experiments were carried out. In the first, TB solution only was exposed to sunlight. In the second, TB solution over blank PMMA thin film (without nanoparticles) was exposed to sunlight. The effect of pH on the photodegradation of TB was investigated over the pH range of $2–8 \pm 0.1$ by addition of HCl and NaOH. The temperature was maintained at 22–25°C by using an ice-water bath. Airing by oxygen was done in all experiments using a battery powered (3 V) portable aquarium fish tank air pump (R-104). Samples (3 ml) were taken out at regular time intervals for analysis using a Perkin Elemer λ_{40} spectrophotometer (USA). Data acquisition and manipulation were performed using UV-winlab λ_{40} and Origin 7 computer based programs.

RESULTS AND DISCUSSION

Effect of pHs

TiO_2-PMMA thin film was used to examine TB photostability in neutral, acidic and basic media. The pH of the sample is an important parameter in the photodegradation taking place on semiconductor particle surfaces, since it is related to the surface charge properties of the photocatalyst. The pH of an electrolyte can vary the surface charge of the photocatalyst and also shifts the potential of some redox reaction. Thus, it affects the adsorption of organic solutes [29]. On the other hand, TiO_2 surface charge is zero at pH 6.3. This means that the TiO_2 surface is positively charged ($Ti\text{-}OH_2^+$) when the pH is lower than this value and

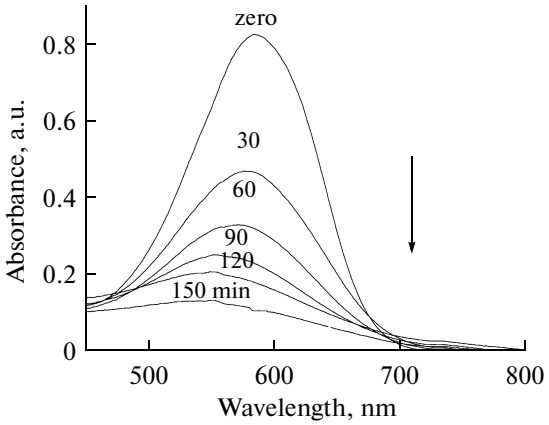


Fig. 3. The photobleaching of TB (1×10^{-5} mol/dm^3) at pH 2 irradiated in sunlight (500–600 W/m^2) using 0.08 g TiO_2–PMMA thin film.

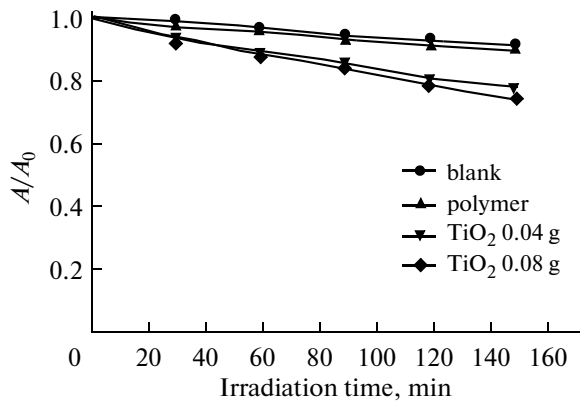


Fig. 4. Normalized absorption of TB (1×10^{-5} mol/dm^3, λ_{max} = 585 nm) against the irradiation time at sunlight irradiance 500–600 W/m^2 using 0.04 and 0.08g TiO_2–PMMA at pH 7 (optical path length of 1 cm).

negatively charged (Ti–O) when the pH is higher than this value [30].

With raising the pH value the rate of photodegradation efficiency decreases (Fig. 2). Shifting the pH from highly acidic pH 2 towards pH 6 decreases the photodegradation rate due to decreasing the positive charge at the surface. As a result, the adsorption and electron injection on the surface will decrease. At pH > 6.3 TiOH and TiO^- species are present [31]. TB and TiO_2 surface existed under negative forms. Therefore, repulsions are much more marked because both species are negatively charged, thus preventing interactions and delaying degradation.

These interactions of the catalyst at acidic and basic pHs are going to accelerate or retard the degradation rate respectively [29].

TiO_2-PMMA

High degradation of trypan blue (pH 2) over 0.08 g TiO_2-PMMA thin film is given in Fig. 3. This behaviour depends on the type of interactions between TB molecules and the catalyst surface. In strong acidic media, interactions between $TiOH_2^+$ and TB anions are very strong and allow TB to be degraded more easily. Furthermore, for the azo dyes with sulfonic groups in their structures, at low pH range, electrostatic inter-

TB (1×10^{-5} mol/dm^3) photodegradation rate and percentage according to exposure time at pH 2 and λ_{max} = 585 nm

Nanoparticle	Weight of particles, g	Time, min	Photodegradation, % $(A_0 - A_t) \times 100$	Photodegradation rate $(A_0 - A_t)/t$, mol dm^{-3} s^{-1}
Blank	0	150	20	2.2×10^{-5}
TiO_2	0.04	150	79	8.8×10^{-5}
TiO_2	0.08	150	87	9.7×10^{-5}
Au/TiO_2	0.08	105	90	1.4×10^{-4}

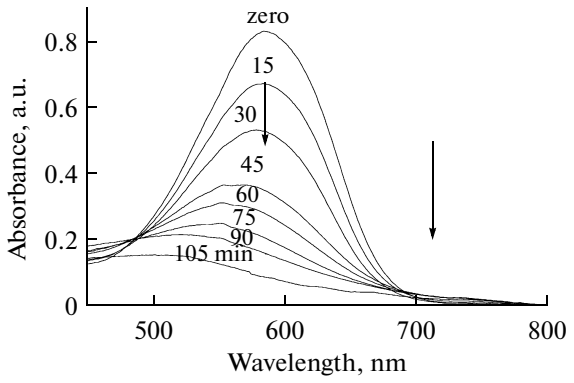


Fig. 5. The photobleaching of TB (1×10^{-5} mol/dm^3) at pH 2 irradiated with sunlight (500–600 W/m^2) on Au/TiO_2–PMMA thin film.

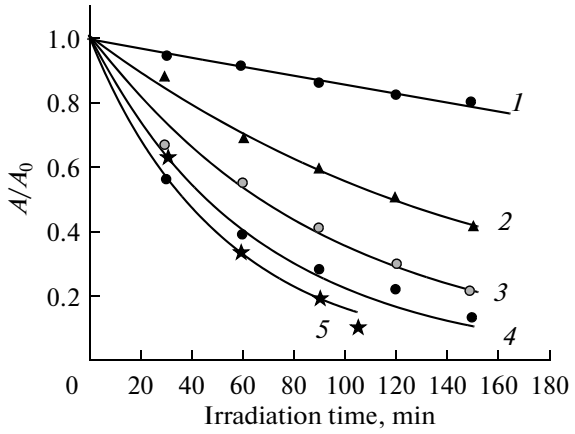


Fig. 6. Dependence of photodegradation of TB (1×10^{-5} mol/dm^3, $\lambda_{max} = 585$ nm) on the irradiation time at pH 2 and sunlight irradiance (500–600 W/m^2) using TiO_2–PMMA and Au/TiO_2–PMMA thin films: *1* – blank TB, *2* – blank TB on PMMA, *3* – 0.04 g TO_2–PMMA, *4* – 0.08 g TiO_2–PMMA, *5* – Au/TiO_2–PMMA.

actions between the positive catalyst surface and dye anions lead to strong adsorption of the dye anions on the metal oxide (TiO_2) support [30, 32, 33]. Therefore, efficient degradation is due to high electron injection rate from TiO_2 to the adsorped TB on the surface. From this figure it can be observed that 150 min sunlight irradiation of TB solution on 0.08 g TiO_2–PMMA thin film resulted in the decrease of TB up to 87% (see table) from its initial concentration.

Figure 4 illustrates similar characteristics in the normalized absorption spectra between the control samples (blank TB and blank TB on PMMA thin film). It also shows no remarkable changes in the normalized curves in cases of 0.04 and 0.08 g TiO_2. This may be due to that at pH 7, the TiO_2 surface charge is close to zero or slightly negative (i.e. no adsorption) [34]. Moreover, the molecular complexity of the diazo dye TB reduces the accessibility of the dye molecules to the TiO_2 surface [3]. Consequently, there is no significant difference between 0.04 and 0.08 g TiO_2 at pH 7. Hence the decrease of TB is 25%.

Au/TiO$_2$

The best photodegradation percentage (90%) was taken at pH 2 after 105 min using Au/TiO_2(0.08 g)–PMMA thin film as displayed in Fig. 5. The deposition of nanosized gold particles on the TiO_2 surface may possibly increase the photocatalytic action of the semiconductor oxide by increasing the efficiency of charge separation of the light-generated electron-hole pairs [35–39]. So the best photocatalytic activity was attained with Au/TiO_2–PMMA thin film. This means that actually Au/TiO_2–PMMA is an effective photocatalyst for the degradation of toxic materials in the wastewater.

Figure 6 confirms that the rate of decomposition assisted by the Au/TiO_2 nanocomposite is faster (105 min) and more effective than that catalyzed by TiO_2 alone (150 min) at the same pH value. The table gives the average rate of TB photodegradation. The rate was calculated according to the following equation:

$$\text{Rate} = (A_0 - A_t)/t,$$

where, A_0 is the absorpion spectra ($\lambda_{max} = 585$ nm) at zero time, A_t—the absorpion spectra ($\lambda_{max} = 585$ nm) at a time t, t—the irradiation time in s.

The table illustrates that the rate of photodegradation increases at pH 2 with using Au/TiO_2 (0.08 g). The time required for mineralization in case of TiO_2 (0.08 g) was longer and TiO_2 is less efficient than Au/TiO_2 (0.08 g). This may be due to the presence of gold nanoparticles which decrease the recombination rate between electron–hole pairs and consequently increasing the radicals produced in the medium and enhancing the efficiency of the photodegradation process.

Although TB is known for its high photostability we report a higher TB photodegradation rate using gold deposited on TiO_2 polymer film than using TiO_2 alone at the same pH value. In addition, the photocatalytic degradation was effective in acidic environment, the degradation of TB was at its greatest at acidic pH 2 while it was lowest at basic pH 8.

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