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Selective Photodegradation Using Titanate Nanostructures

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Abstract

Adsorption and photocatalytic degradation are considered as the most important ways of treating water from organic compounds. It would be very useful if the adsorption and photocatalytic properties are combined in the same catalyst used in the treatment. Titania is one of the best well-known photocatalysts. However, due to its poor selectivity, it is unfavorable for photocatalytic removal of highly toxic low-level organic pollutants in wastewater in the presence of other less toxic high-level pollutants. Recent trials to introduce selectivity for titania have been achieved via controlling the catalyst morphology or by modifying the catalyst surface. This chapter summarizes the control of selectivity of titanate nanostructures toward adsorption and/or photocatalytic degradation of toxic organic dyes. In the first part, the effect of morphologies of titanites on selective photocatalytic degradation of three food dyes (color yellow sunset, red allura, and red carmoisine) was discussed. In changing the morphology of titanite, each dye is being preferably adsorbed by one morphology and decomposing more rapidly. In the second part, the selective adsorption and/or photocatalytic degradation of methylene blue dye from mixed dye solution using sodium titanate (NaTNT), cobalt-doped titanate nanotubes (co-doped TNT), and the decorated one with gold nanoparticles has been discussed.

Keywords: titanate, selectivity, TiO_2 , photocatalysis, dyes, water treatment

1. Introduction

Advanced oxidation process (AOP) is considered as one of the innovative technologies that is used for degradation of various organic pollutants by generating highly reactive species [1]. Heterogeneous photocatalysis is one of the most effective methods leading to complete

mineralization of organic pollutants to carbon dioxide, water, or low molecular weight compounds under visible or ultraviolet (UV) light radiation [2–5]. Photocatalytic degradation of various families of organic pollutants had been studied using semiconductors such as TiO_2 , ZnO , Fe_2O_3 , CdS , GaP , and ZnS [6–15]. Titanium dioxide (TiO_2) is considered as one of the most important photocatalysts used in water treatment application where it is stable, inexpensive, nontoxic, insoluble, and potentially reusable in water [2, 16–19].

As it is well known, the mechanism of degradation of an organic pollutant using TiO_2 nanostructures depends mainly on producing hydroxyl radicals ($\cdot\text{OH}$). TiO_2 absorbs in the UV region and produces electron-hole pairs. The electron-hole (e^- - h^+) pairs generate superoxide ions ($\text{O}_2^{\cdot-}$), peroxide radicals ($\cdot\text{OOH}$), hydroxyl ions (OH^-), and H^+ ions. All these species will finally form the desired hydroxyl radicals ($\cdot\text{OH}$). Free radicals are aggressive species and highly active in the chemical reactions; these radicals attack the organic pollutants forming different oxygenated intermediates and finally converting them into CO_2 and H_2O .

TiO_2 with variable morphologies, rods, spheres, tubes, fibers, sheets, and interconnected architectures, can be prepared with many methods such as hydrothermal method, sol-gel method, electrodeposition, chemical vapor deposition, and microwave method [20, 21].

The photocatalytic activity of TiO_2 depends on many factors such as specific surface area, size, pore structure, pore volume, exposed surface facet, and crystalline phase [20, 22, 23]; achieving selectivity in degradation using TiO_2 in some cases depends on crystallinity and crystal facet [24–26], and also depends on introducing molecular sites on TiO_2 surface which produce selective adsorption and degradation for targeted compounds are also introduced [27].

2. Selective photocatalytic degradation of dyes

2.1. Selective photocatalytic degradation by controlling titanate morphology and crystal structure

The adsorption stage is a very important stage in the photocatalytic process; many factors affect on the selectivity in this stage like changing the size, amount, surface, and morphology of the photocatalyst, as well as the size or type of the target compounds. Recent studies revealed that altering the exposed surfaces of TiO_2 nanoparticles is by controlling the morphologies of these particles. Sofianou et al. [25] found that the calcined TiO_2 nanoplates showed the highest photocatalytic activity toward oxidizing NO gas to NO_2 and NO_3^- ; on the other hand, the washed TiO_2 nanoplates, preserving the initial morphology, showed the best photocatalytic activity toward acetaldehyde decomposition. It was concluded that the dominant exposed $\{1\ 0\ 1\}$ or $\{0\ 0\ 1\}$ crystal facet of the TiO_2 nanoplates is considered as the key factor in controlling the selectivity in adsorption of these air pollutants. Also, it was demonstrated by other researchers that modifying the surface of TiO_2 microspheres by varying the degree of the etching of $\{0\ 0\ 1\}$ facets exhibited tunable photocatalytic selectivity toward the decomposition of azo dyes in water [28].

Recently, Zaki et al. [22] used three different colors (color yellow sunset, color red allura, and color red carmoisine) to test the selectivity of degradation of three different morphologies of TiO_2 (spherical, layered, and tubular); the TEM images of these morphologies are shown in **Figure 1**. It is clear from **Figure 1a** that the starting TiO_2 powder consists of nanosized particles, while **Figure 1b** shows the TEM image of the synthesized TiO_2 nanosheets, and **Figure 1c** shows the TEM images of the obtained TiO_2 nanotubes. The tubes have a diameter of about 16 nm, and they are randomly oriented with nearly homogenous dimensions with some intercalated tubes.

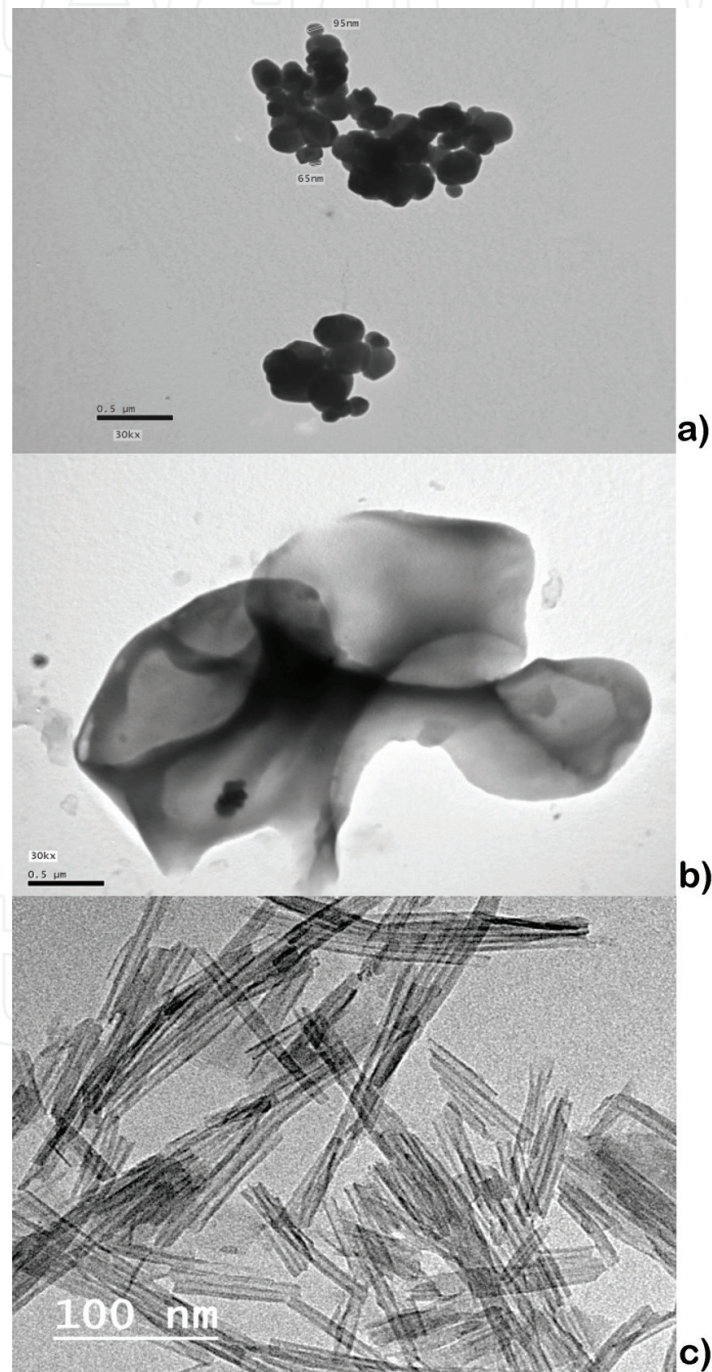


Figure 1. TEM image of spherical TiO_2 (a), TiO_2 nanosheets (b), and TiO_2 nanotubes (c).

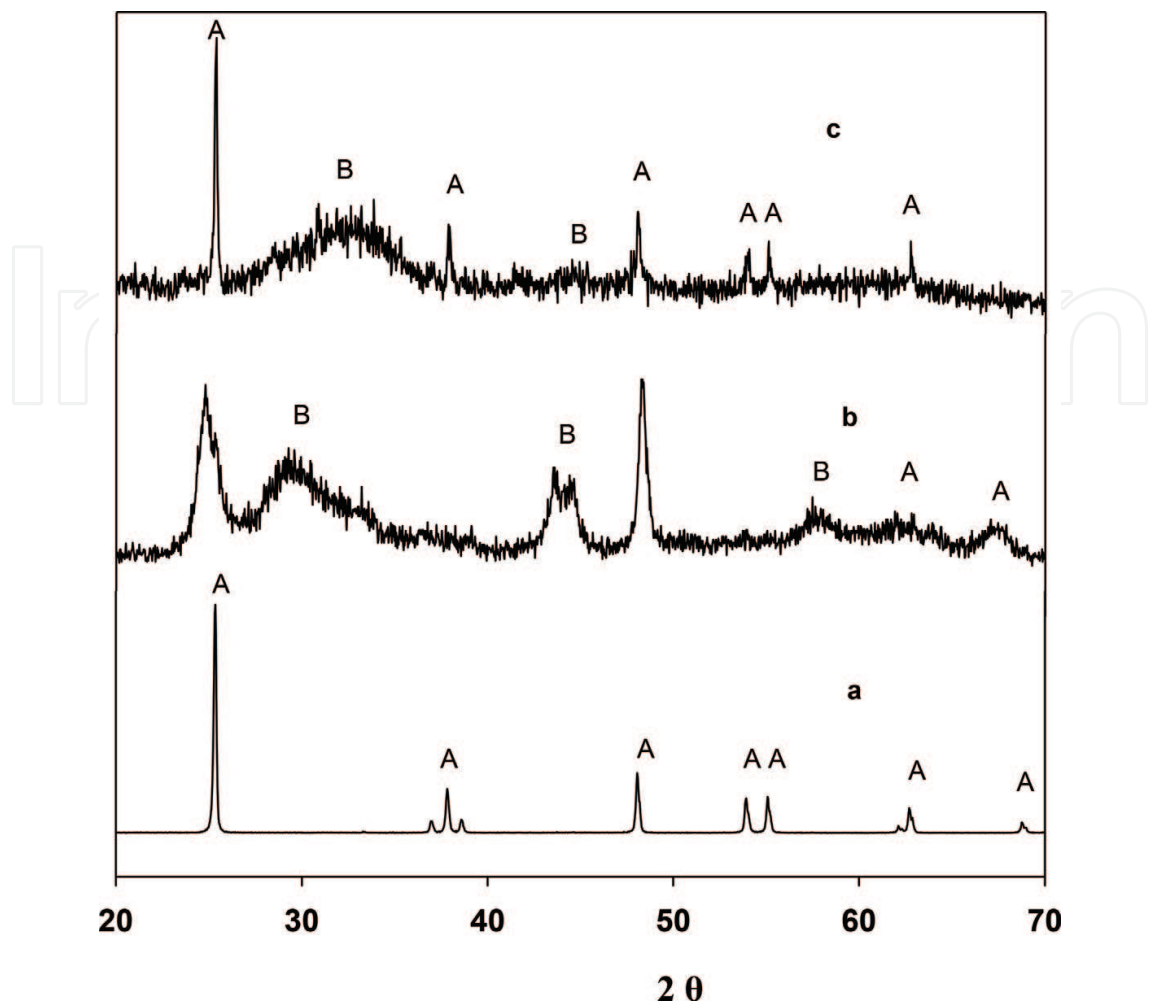


Figure 2. XRD patterns of spherical TiO₂ (a), TiO₂ nanotubes (b), and TiO₂ nanosheets (c). A, anatase; B, TiO₂ (B).

Figure 2 shows XRD patterns of the three morphologies; it is clear from these patterns that the crystallinity of TiO₂ nanotubes and TiO₂ nanosheets is generally poor; this may be attributed to the small sizes of the prepared samples, which are confirmed by the presence of broad peaks. All the detected peaks confirmed the presence of anatase phase for spherical TiO₂ nanoparticles; in the case of nanosheets and nanotubes, there is a contribution of TiO₂ (B) with different ratios depending on the morphology; accordingly, we have preferred three. The crystal sizes of the three morphologies were calculated using Scherrer’s formula and are listed in **Table 1**.

| Catalyst | | <i>K (min⁻¹)</i> | | |
|-----------------------------|-------------------|---|--|--|
| Morphology | Crystal size (nm) | <i>K (min⁻¹) for Yellow sunset</i> | <i>K (min⁻¹) for Red allura</i> | <i>K (min⁻¹) for Red carmoisine</i> |
| Spherical TiO ₂ | 95 nm | 0.0065 | 0.0098 | 0.0082 |
| TiO ₂ nanosheets | 67.9 nm | 0.0513 | 0.0059 | 0.0103 |
| TiO ₂ nanotubes | 27.1 nm | 0.0324 | 0.0060 | 0.0189 |

Table 1. Structural and kinetic parameter TiO₂ nanostructures.

Zaki et al. in this work reported that changing the morphology of TiO_2 from spherical to layered and tubular shape made each morphology preferentially decompose one dye of the three dyes [22]. From **Figure 3a–c**, it is clear that the photocatalytic degradation strongly depends on the morphology of TiO_2 . To test photocatalytic performance of all morphologies, they started the test with yellow sunset as a model, and they found that as moving from the spherical to the tubular structure via the sheet structure, the time of degradation reduced from 400 min for spherical, 75 min for nanotubes, and 55 min for nanosheets, while in the case of the other two colors, red allura and red carmoisine, they found other trends, as shown in **Figure 4a–c**, where the best

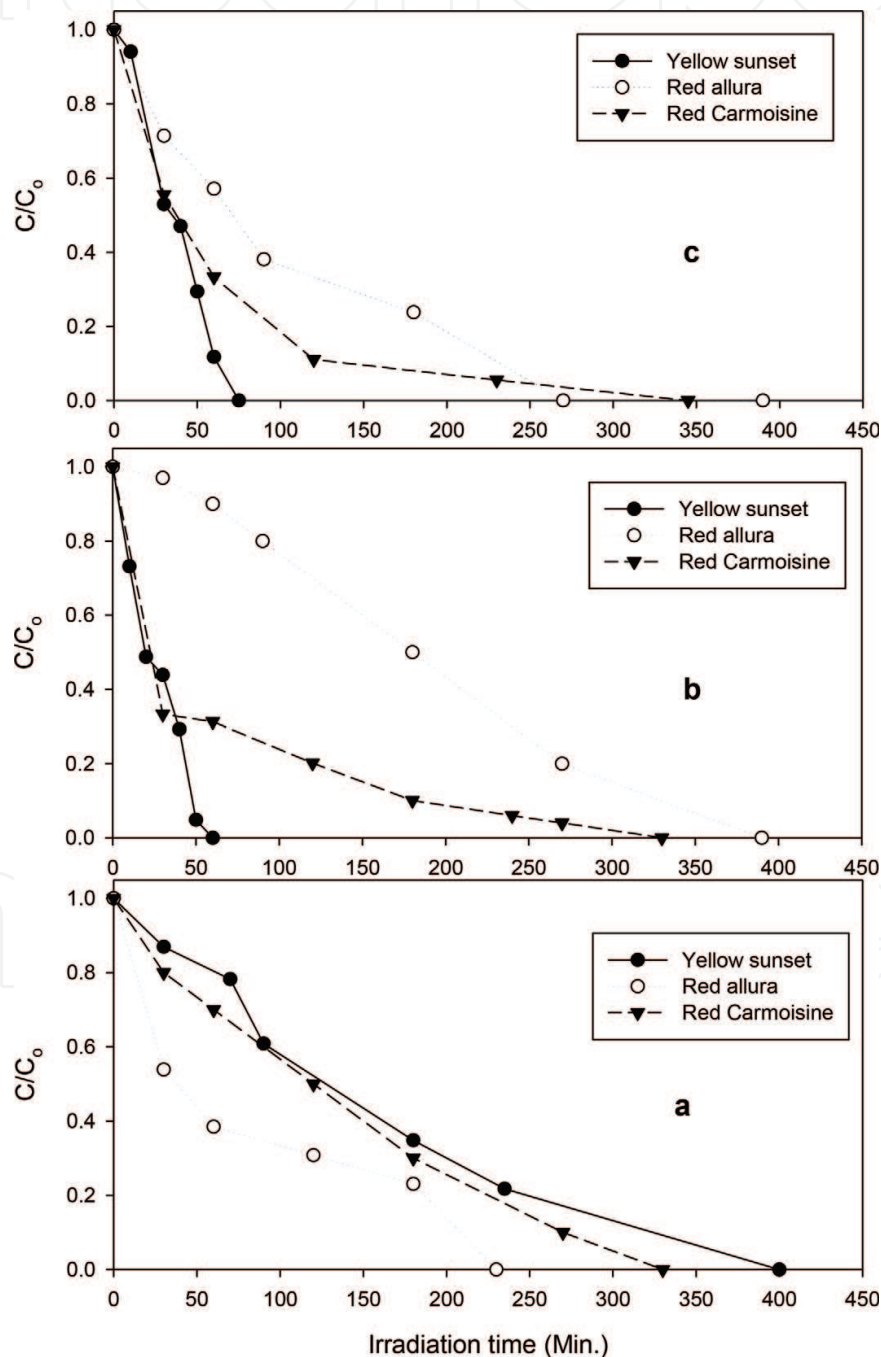


Figure 3. Photocatalytic activity of spherical (a) TiO_2 nanosheets and (c) TiO_2 nanotubes.

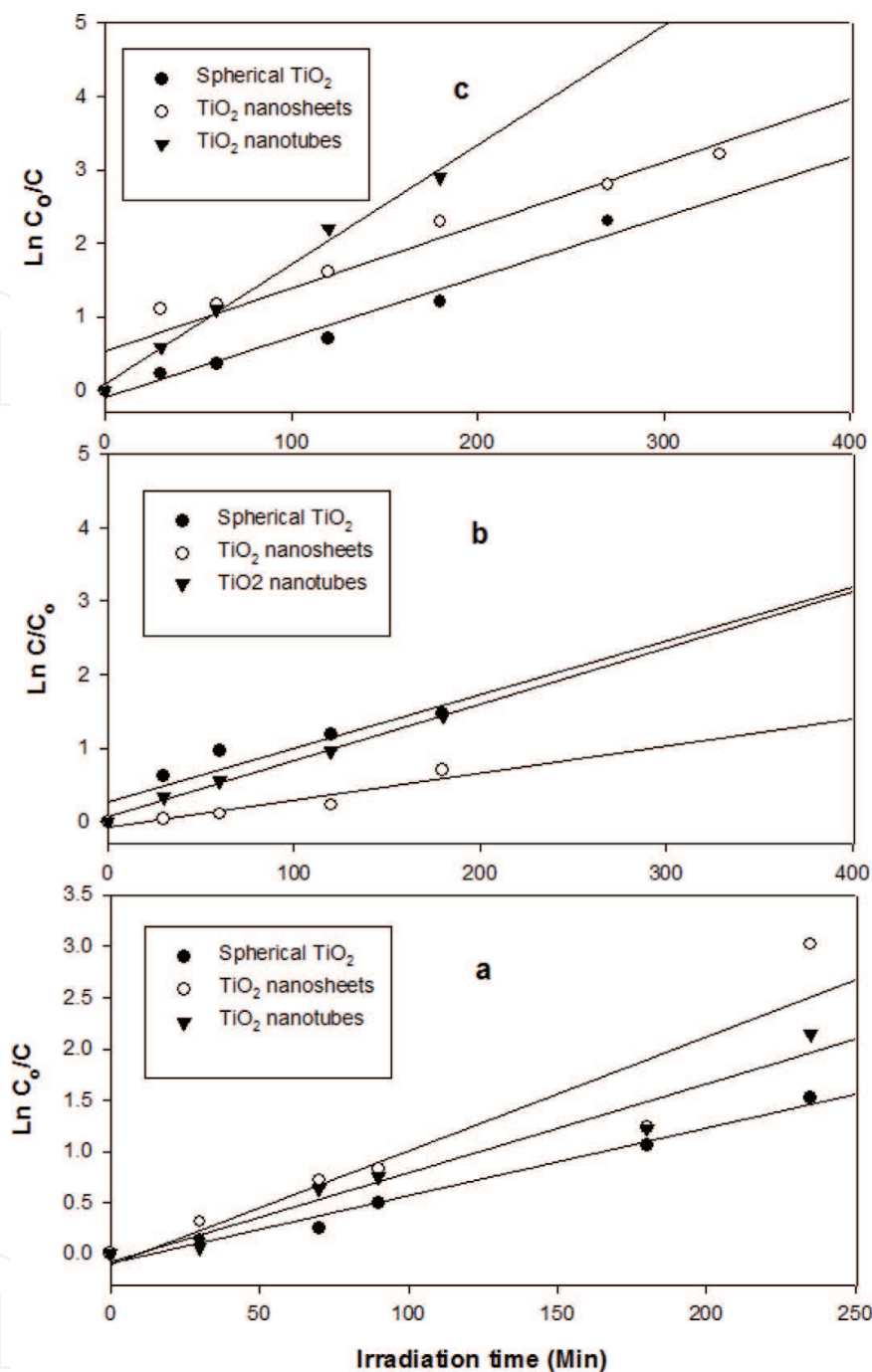


Figure 4. Linear transform $\ln (C_0/C) = f(t)$ of kinetic curves.

degradation rate for yellow sunset was achieved by TiO_2 nanosheets, by spherical TiO_2 for allura and by TiO_2 nanotubes for carmoisine. Finally, they concluded that the preferred orientation of each morphology made it more specific in action; each dye is adsorbed preferentially by one of the three morphologies and decomposed more rapidly.

3. Selective adsorption and degradation over decorated titanate nanotubes

There is a major concern on contamination of water by organic pollutants [29–31]. Nowadays, intensive efforts have been devoted for water treatment especially when the problem of water shortage has begun to loom in some cities and countries, particularly in Africa and the Middle East. This problem has made scientists think of reusing water again after treatment. Therefore, many methods of treatment have been used such as filtration [32], biodegradation [33], adsorption [34], and photocatalytic degradation [35] of contaminant especially the organic molecules. Among these methods, adsorption is the simplest, cheapest, and most versatile technique for treating water pollutants [30, 36]. Photocatalytic degradation is also considered as one of the promising technologies used for wastewater treatment, where a suitable catalyst is used for the degradation of toxic organic molecules under irradiation with light [35, 37, 38].

Titanium dioxide (TiO_2) is considered as one of the most important photocatalysts used in water treatment application where it is stable, inexpensive, nontoxic, and potentially reusable in water; however, its adsorption ability is very low. Therefore, the key challenge of using TiO_2 for the treatment of industrial dye-mediated wastewater is to provide adsorption characteristics through surface or structure modification. Another drawback of TiO_2 is the low selectivity due to the formed reactive species (radicals) by means of light irradiation which is difficult to be controlled. In addition, TiO_2 efficiently degrades organic pollutants but requires ultraviolet light for activation. Thus, the ideal solution to it is to acquire TiO_2 selective **adsorption** property which will be a powerful technique for imparting selectivity to photocatalytic degradation also.

Transformation of TiO_2 nanoparticles to the tubular titanate forms could give some unique photocatalytic properties because of the one-dimensional (1D) geometry, which will enable the electron transfer faster for long distance. Moreover, its nanotubular structure will provide a large specific surface area and pore volume which is very important for providing more active sites for adsorption and photocatalytic degradation.

The treatment of highly enduring toxic dyes and leaving the alterable pollutants to be treated by the low-cost biological treatment systems are considered as great aims for scientists interested in wastewater treatment. Thus, provision of selective materials may be of great benefit. Therefore, one of the important challenges in water treatment is to possess a highly selective method for adsorption and photodegradation of contaminants [39].

Titanate nanotubes (TNTs) produced from the hydrothermal treatment of TiO_2 nanoparticles in the presence of high concentration of NaOH (10 M) at 160°C have been used for selective adsorption of specific dyes from water [40, 41]. The obtained sodium titanate (Na_2TiO_3 , NaTNT) nanotubes were characterized before using as an adsorbent. In the TEM micrograph (**Figure 5a** and **b**), a clear tubular structure of about 5 nm inner cavity with a mean length of $148 (\pm 35)$ nm and thickness of $8 (\pm 1)$ nm is seen. Due to NaTNTs having a large bandgap (more than 3 eV), it needs high-energy light (UV light) for initiating its photocatalytic activity. Thus, for improving the photocatalytic properties of NaTNTs, gold (Au) nanoparticles were

deposited on the surface where the Au nanoparticles have a plasmonic response in the visible light. The in situ photoreduction deposition method was used for forming a good contact between the gold nanoparticles and NaTNTs. From **Figure 5c** and **d**, a homogeneous distribution of highly crystalline spherical Au nanoparticles with a mean diameter of $7.7 (\pm 1)$ nm was formed at the surface of the NaTNTs, and there is no any aggregation of Au particles.

As mentioned before, the adsorption ability of TiO_2 nanoparticles is extremely low. El Rouby et al. reported that the titanate form can adsorb up to 55% of the methylene blue (MB) dye initial concentration after 180 min compared to the TiO_2 nanoparticles which show negligible adsorption for MB (**Figure 6a**) [40]. This high adsorption ability of NaTNTs is due to their high porosity, large specific surface area, and strong electrostatic interaction between the positively charged dye and the negatively charged surface of NaTNTs. In addition, the internal cavity of the tubular structure can contribute to further extend the area on which organic molecules can be adsorbed.

The photocatalytic activity of NaTNTs and Au-decorated NaTNTs has been assessed under simulated solar light (350–2400 nm). Twenty-seven percent degradation of MB was achieved

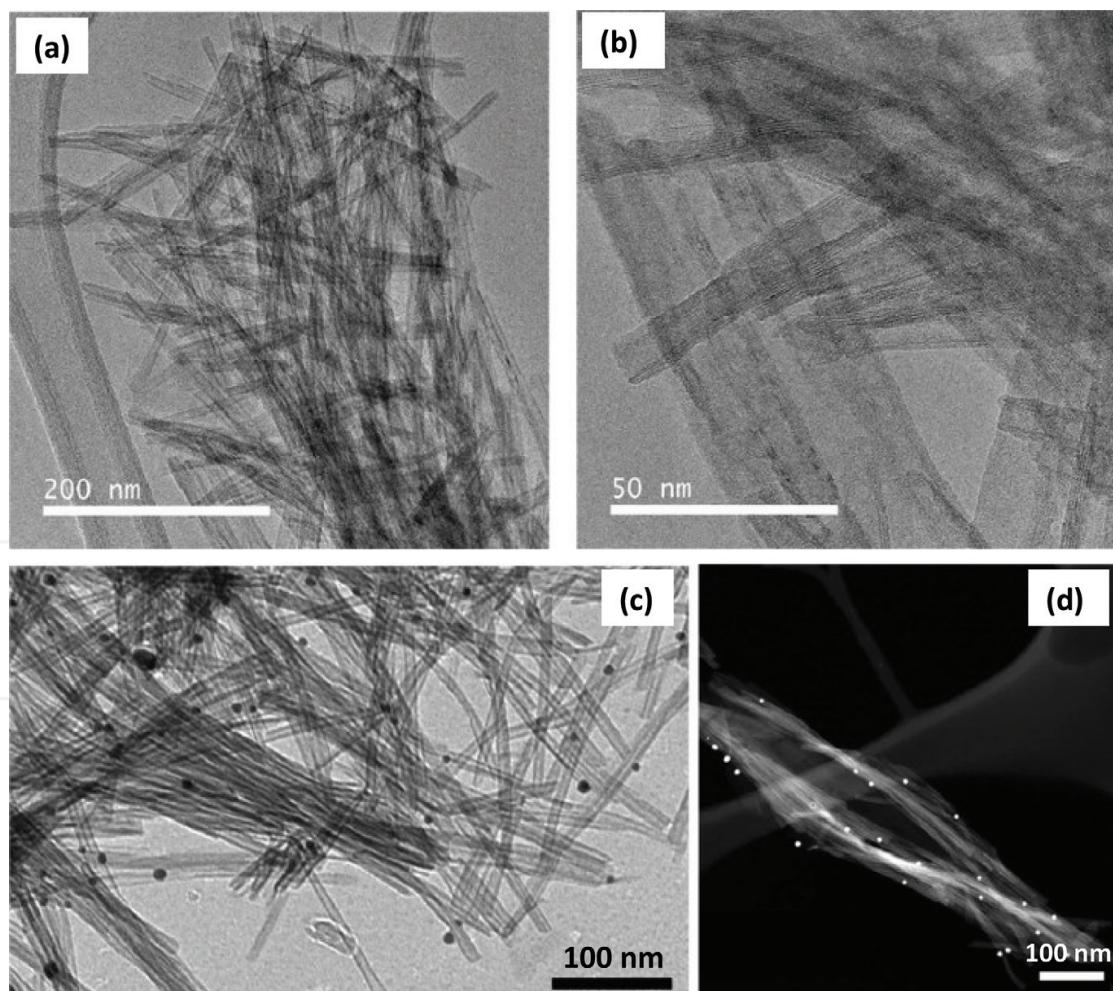


Figure 5. (a) Low and (b) high magnification TEM images of the NaTNTs, (c) TEM images of au-NaTNTs, and (d) STEM images of the Au-NaTNTs [12] (copyright 2017, IOP Publishing Ltd).

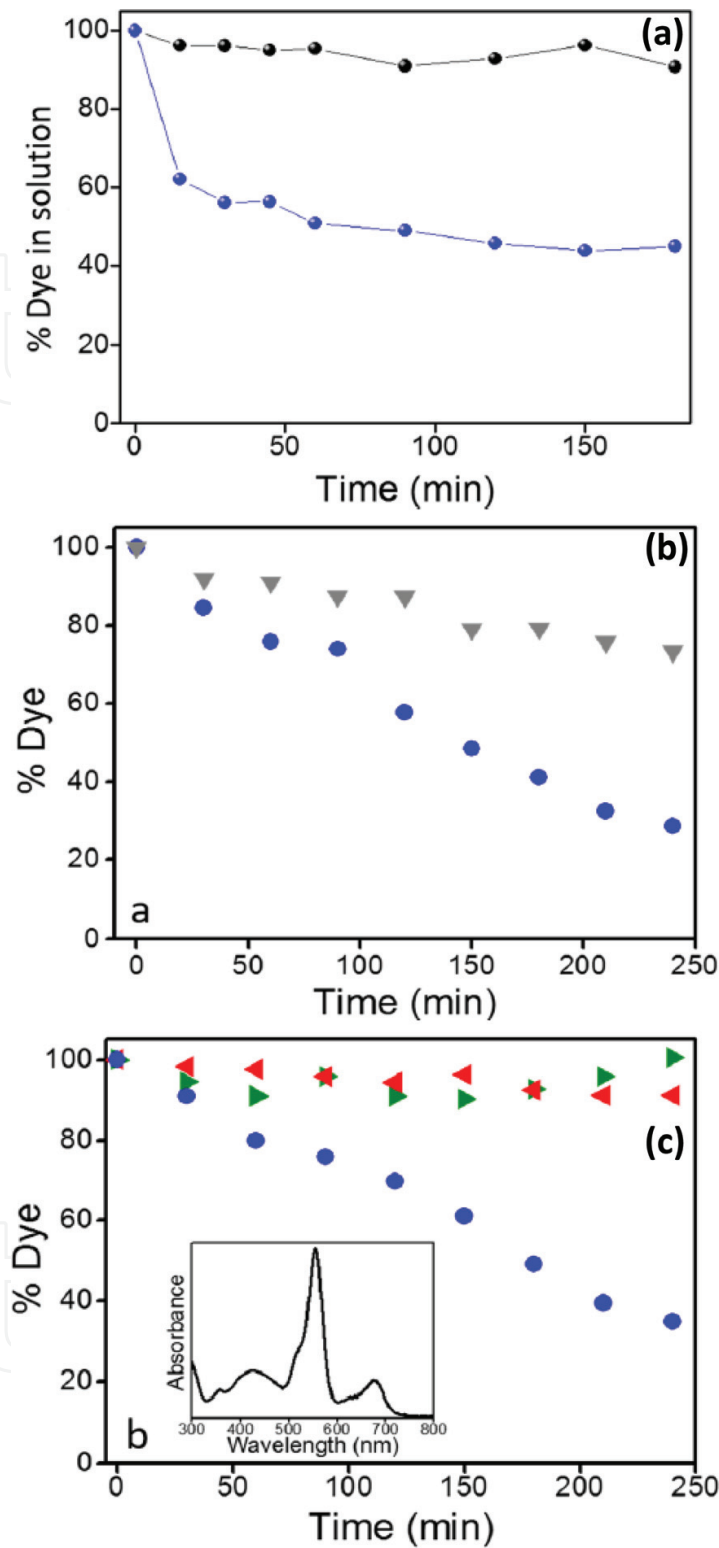


Figure 6. (a) Effect of contact time on MB dye adsorption in the presence of TiO₂ nanoparticles (black) and NaTNTs (blue) under agitation in the dark. (b) Photodegradation of MB in the presence of NaTNTs (gray triangles) and Au-functionalized NaTNTs (blue circles). (c) Photodegradation of the three mixed organic dyes: Tz (green triangles), RhB (red triangles), and MB (blue circles) using Au-functionalized NaTNTs as catalysts. The inset shows the absorption spectrum of the mixture after adsorption/desorption equilibrium and prior to the photocatalytic degradation. The absorption maxima for each dye in such a solution are 421 nm (Tz), 555 nm (RhB), and 674 nm (MB) [12] (copyright 2017, IOP Publishing Ltd).

by NaTNTs that may be ascribed to the small portion of UV light irradiated from the solar simulator (350–400 nm). When Au-decorated NaTNTs were used as a photocatalyst, a remarkable 72% degradation of MB is observed (**Figure 6b**). This is due to the plasmonic photosensitization of gold nanoparticle which is considered as an effective way for increasing the photocatalytic activity of semiconductors holding large bandgaps such as TNTs.

The well-established Au-decorated NaTNT photocatalyst was applied for selective degradation of MB from dye mixture. Three different dyes as model (MB, rhodamine B (RhB), and tartrazine (Tz)) have been used where the absorption spectra of the three dyes allow for interference-free monitoring of the photodegradation for each one of them, thus facilitating their tracking over time through the change in its absorbance. As shown in **Figure 6c**, 65% of MB was decomposed after 240 min, while Tz and RhB remain in solution showing no trace of reaction after that time. These results clearly evidence for the selectivity of Au-NaTNT composite to MB degradation. This selectivity toward MB is attributed to the net charge of the dyes under consideration [40]. Through electrotactic interaction, the surface of the NaTNTs governs the preferential adsorption of the positively charged dye (MB), thus facilitating a high degree of contact between MB and the photocatalyst. On the other hand, in the case of Tz, it remains intact in solution due to its negatively charged surface which makes repulsion with the negative charges on NaTNTs. In a similar way, the interaction of RhB with the NaTNT surface is significantly weakened, due to the deprotonation of the RhB carboxyl group when dissolved in water and thus the formation of a zwitterionic species [40].

For the photocatalytic degradation of organic dyes in a highly concentrated solution, it will be difficult for the catalyst to achieve degradation unless it has a good adsorption property. This is because during the photocatalytic process by any semiconductor, the light strikes the catalyst surface leading to excitation of valence band electrons forming holes in the valence band that can make degradation for the pollutants. But in the case of high-concentrated dye solution, the dyes can strongly absorb the incident light and prevent the light to reach the catalyst surface forming impermeable solution. Thus, the electrons cannot be exited, and the degradation process will not start. Thus, in that case, it is very useful to use a catalyst with high adsorption property especially in addition to its high photocatalytic degradation properties.

In another work, El Rouby [41] tried to increase the adsorption ability of NaTNTs through doping by transition metal (Co). It was found that replacement of Na⁺ by Co²⁺ leads to increase the specific surface area as shown in **Table 2** which will directly affect the adsorption extent.

| Sample | BET (m ² /g) | Surface area of pores (m ² /g) | Pore size (Å) | Pore volume (cm ³ /g) |
|----------------|-------------------------|---|---------------|----------------------------------|
| NaTNT | 132.15 | 144.37 | 51.09 | 0.900 |
| Co-doped TNT 1 | 161.47 | 163.25 | 53.23 | 0.243 |
| Co-doped TNT 2 | 162.62 | 177.94 | 49.33 | 0.226 |
| Co-doped TNT 3 | 170.83 | 185.14 | 51.62 | 0.255 |

Table 2. Effect contents on surface area, pore size, and pore volume of Co-doped TNT samples [13] (copyright 2018, Elsevier).

This increase of specific surface area is due to the formation of a large number of pores because of the removal of sodium ions (larger ions) and insertion of cobalt ions (smaller ions). This leads to the increase in the surface area of pore as the cobalt content was increased in the samples (**Table 2**). It was found that MB uptake on NaTNTs was about 89 mg/g after 35 min. This indicated its ferocity to remove MB from water in a very short time at room temperature. In replacing the Na^+ by Co^{2+} , the surface area and number of pores were increased as mentioned previously. Thus, the available adsorption active sites will be more than in the case of NaTNT. This was reflected on the adsorption capacity of Co-doped TNT samples, where the uptake was increased by increasing the dopant content. The adsorption capacity reached 92.5, 91.9, and 91.8 for Co-doped TNT 1, Co-doped TNT 2, and Co-doped TNT 3, respectively, depending on the concentration of Co^{2+} in NaTNTs (**Figure 7**).

The problem in Co-doped TNT catalysts is its wide bandgap as in the cases of TiO_2 and NaTNTs. So, for adding a photocatalytic property, the prepared Co-doped TNTs were calcined at 500°C for enhancing its crystallinity and thus the photocatalytic activity. But, after calcination, the adsorption property was decreased, and the degradation was low (**Figure 8a**) due to light shielding by the high concentration of MB. The decrease in adsorption is due to the decrease in surface area which is caused by means of wall collapse and loose of tubular structure after calcination. Therefore, the previous concept of attaching Au nanoparticles to the surface of Co-doped TNTs was used. It was noticed that MB concentration (1×10^{-4} M) was decreased gradually with time up to (1.2×10^{-5} M) after 300 min, and with continuous illumination, MB was completely degraded (**Figure 8b**). The conclusion from these results is that a highly concentrated organic dye and pollutant solution can be photocatalytically degraded efficiently [41].

The prepared Au-decorated Co-doped TNT catalysts were used for the selective adsorption and degradation of MB in the same dye mixture (MB, RhB, TZ). From **Figure 9a**, the selective

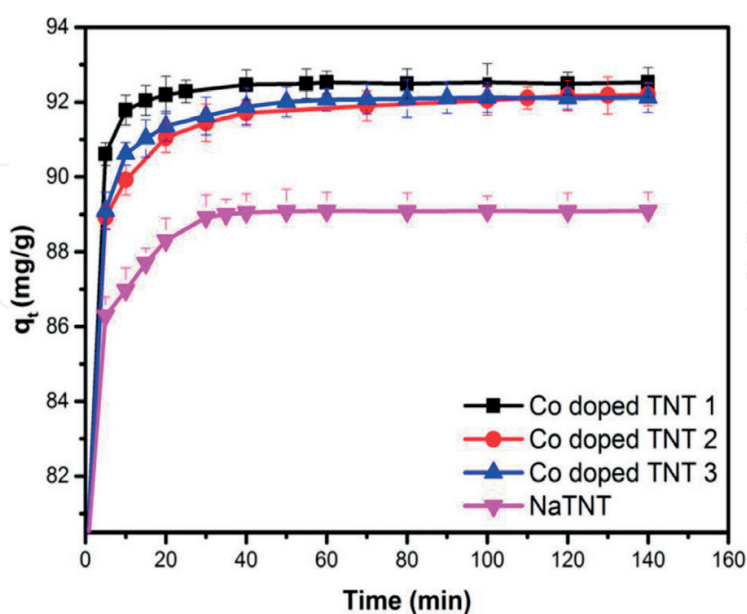


Figure 7. Methylene blue dye (1×10^{-4} M) uptake on titanate nanotubes doped with different ratios of cobalt (0.4 g/L) [13] (copyright 2018, Elsevier).

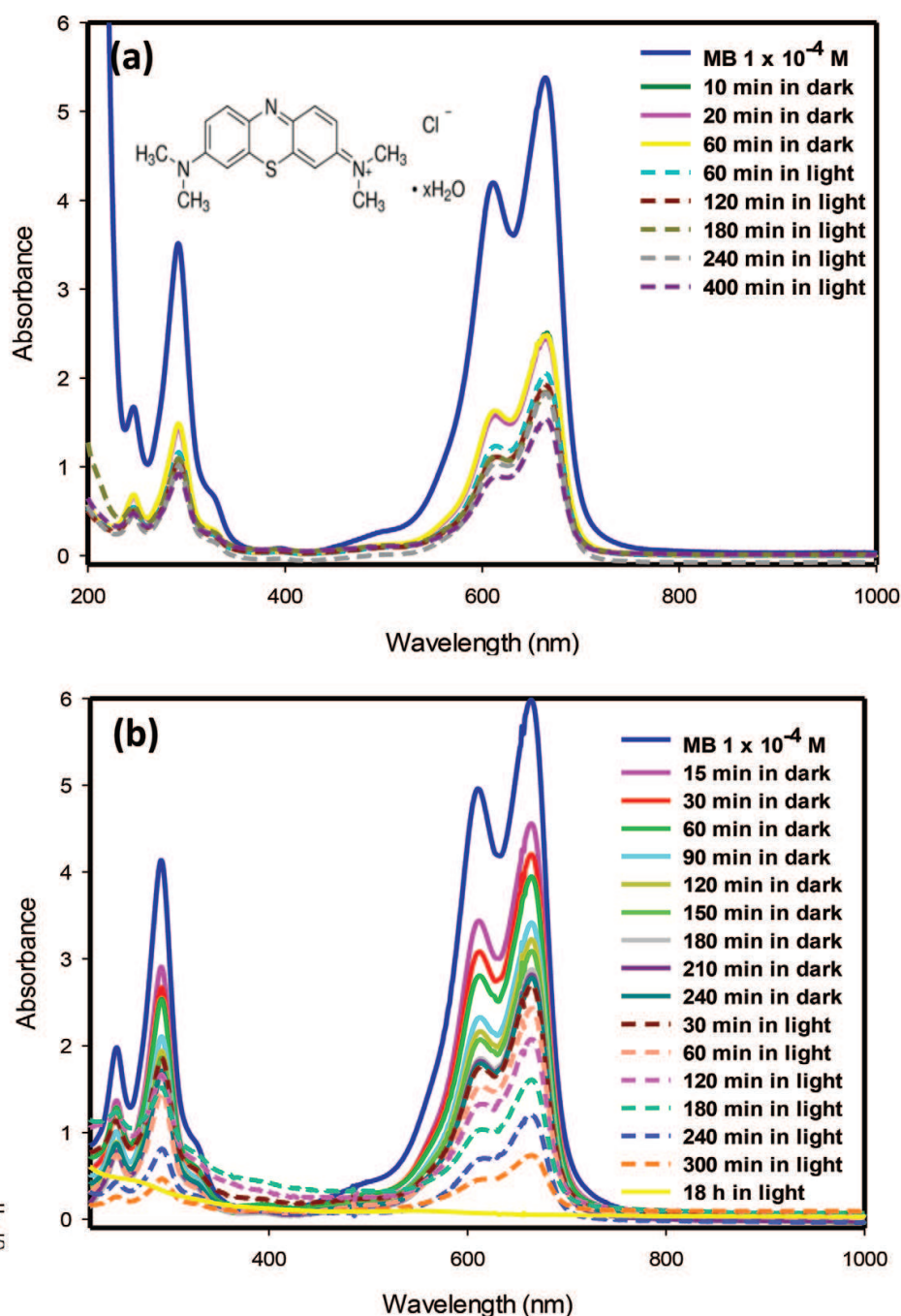


Figure 8. Absorption spectra of MB dye (1×10^{-4} M) in presence of (a) Co-doped TNT 1 calcined at 500°C for 2 h and (b) Co-doped TNT 1 at Au in dark and under illumination [13] (copyright 2018, Elsevier).

adsorption of MB from the dye mixture is clear for the same reason of surface charge as discussed before. After adsorption and subjecting the dye solutions to illumination of simulated light, the degradation of MB was started (**Figure 9b**). According to postulates of any photocatalytic process, the catalyst will initially adsorb the reactant, catalyze the reaction, and finally leave the products. By the same concept, the adsorbed dye was degraded, while dyes in the solution remained without effect [13].

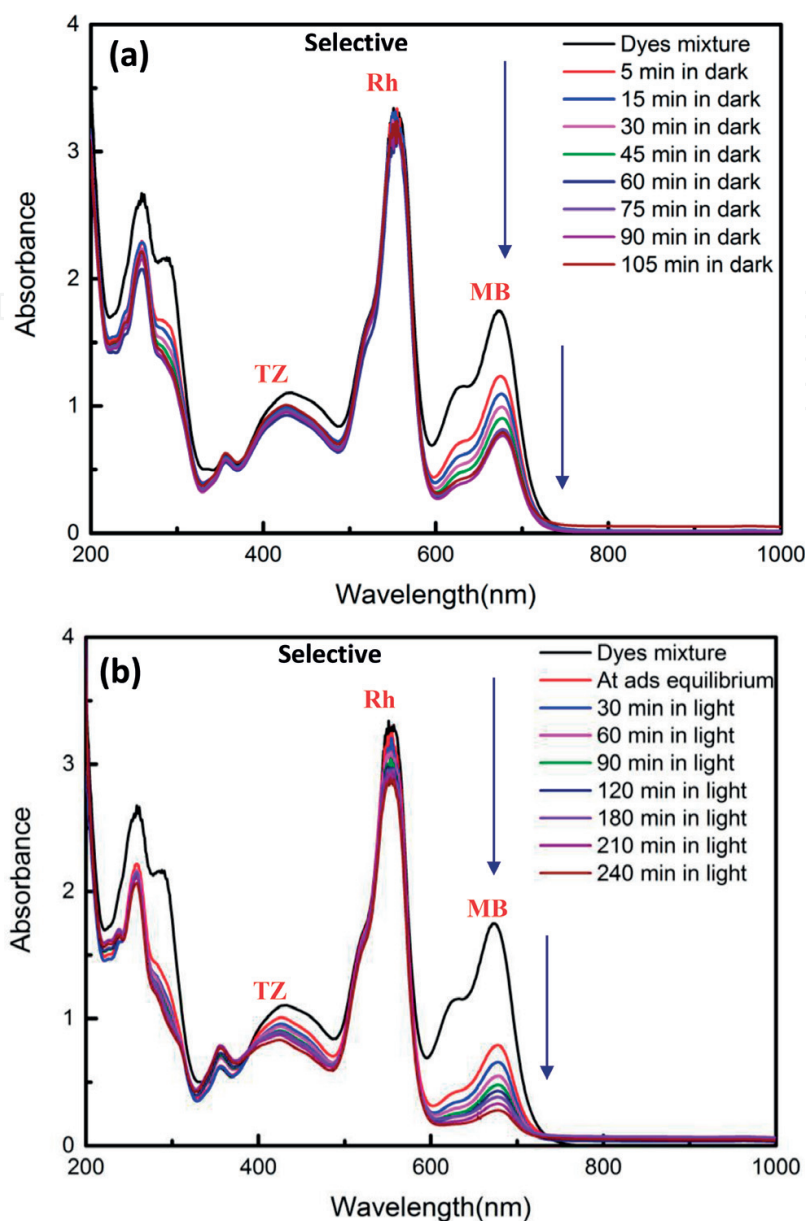


Figure 9. Selective adsorption (a) and selective degradation (b) of MB dye from dye mixture (methylene blue, rhodamine B, and tartrazine dye [5×10^{-5} M]) in dark and under simulated solar light illumination using Au-decorated Co-doped TNT 1 as a catalyst (0.4 g/L) [13] (copyright 2018, Elsevier).

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