

Facile Synthesis of Silver-salicylic acid (modified)/TiO₂-nanotube/Ti plates for UV-light Promoted Dye Degradation

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Abstract. Salicylic acid (mod)-Ag/TiO₂NTs/Ti photocatalyst plates were prepared using chemical modification process of TiO₂-nanotubes/Ti plates with salicylic acid and silver nanoparticles. Morphology studies exhibit that esterification between salicylic acid and -OH groups on TiO₂ surface as well as deposition of Ag has been led to formation of uniform deposits on the walls of TiO₂-nanotubes/Ti plates. The photocatalytic activity of the plates was tested on the degradation of Methylene Orange (MO) dye. The activity tests showed that the photodegradation efficiency for salicylic acid(mod)-Ag/TiO₂NTs/Ti is higher than for Ag/TiO₂NTs/Ti, salicylic acid(mod)/TiO₂NTs/Ti and TiO₂NTs/Ti plates, showing the integration the photocatalytic advantages of both Ag-TiO₂ and salicylic acid-Mod-TiO₂ composites. The modified plates can eliminate 96.6% of MO under UV light irradiation after 1 h, while can be recycled 4 times with 72.9% degradation ratio. Improved surface adsorption of MO, fast charge separation and slow electron-hole recombination are the main factors being responsible for the increase the photocatalytic activity of salicylic acid (mod)-Ag/TiO₂-nanotubes/Ti plate.

Keywords: Chemical modification; TiO₂-nanotubes/Ti; Salicylic acid; Silver nanoparticles; Methylene orange; Photocatalyst.

Resumen. Se prepararon placas de fotocatalizador de ácido salicílico (mod)-Ag/TiO₂NTs/Ti, utilizando un proceso de modificación química de placas de nanotubos/TiO₂-TiO₂, con ácido salicílico y nanopartículas de plata. Los estudios morfológicos muestran que la esterificación entre el ácido salicílico y los grupos -OH en la superficie de TiO₂, así como la deposición de Ag, ha llevado a la formación de depósitos uniformes en las paredes de las placas de nanotubos de TiO₂/Ti. La actividad fotocatalítica de las placas se probó en la degradación del colorante naranja de metileno (MO). Las pruebas de actividad mostraron que la eficiencia de fotodegradación para el ácido salicílico (mod)-Ag/TiO₂NTs/Ti es mayor que para las placas Ag/TiO₂NTs/Ti, ácido salicílico (mod)/TiO₂NTs/Ti y TiO₂NTs/Ti, mostrando la integración de las ventajas fotocatalíticas de los compuestos de Ag-TiO₂ y ácido salicílico-Mod-TiO₂. Las placas modificadas pueden eliminar el 96.6% del MO bajo la irradiación con luz UV después de 1 h, mientras que pueden reciclarse 4 veces con una relación de degradación del 72.9%. La mejora de la adsorción superficial de MO, la rápida separación de la carga y la lenta recombinación del hueco de electrones son los principales factores responsables del aumento de la actividad fotocatalítica del ácido salicílico (mod)-Ag/TiO₂-nanotubos/placa de Ti.

Palabras clave: Modificación química; TiO₂-nanotubos/Ti; Ácido salicílico; Nanopartículas de plata; Naranja de metileno; Fotocatalizador.

Introduction

Semiconductor photocatalysis has recently attracted great attentions for environmental remediation and purification through advanced oxidation processes [1,2]. Heterogeneous semiconductor photocatalysis was reported as a suitable approach to detoxification from both industrial and biological pollutants in many researches [3,4]. Among the semiconductors investigated, anatase TiO_2 is one of the most commonly used materials for photocatalytic degradation of chemical and microbiological pollutants due to its non-toxic nature, low cost, abundance, UV-driven high activity, photo and thermal stability [5,6]. Nevertheless, the photocatalytic activity of TiO_2 is constrained by two main problems which are the wide band gap energy (E_{bg}) that limit its application to ultra-violet region and the fast recombination of photogenerated electrons and holes [7,8]. Both of these drawbacks have been studied to resolving by using several approaches such as doping the TiO_2 with metallic or nonmetallic elements, dye sensitization and surface coupling with other semiconductors to form a heterojunction [9-11], that cause of improving the photocatalytic activity of TiO_2 for degradation of organic pollutants by shifting the light absorption of TiO_2 to visible-light region and retarding the recombination of electron and hole [9,12]. Moreover, the affinity interaction between the catalyst TiO_2 and pollutants should be paid more attention to enhance the photocatalytic efficiency. Since aromatic compounds are common pollutants, it has been proven that surface modification of TiO_2 with aromatic organic acid compounds as surface modifiers can improve not only adsorption efficiency of aromatic pollutants, but also lead to an increase in the light utilization [13-15]. These modifiers can enhance the surface coverage of the pollutants on TiO_2 through phenyl group interaction. Wang et al. found that surface modification of TiO_2 nanotubes/Ti with salicylic acid can be carried out in saturated solution of salicylic acid through an ester-like bond between -COOH group and the surface -OH groups of TiO_2 [16]. They concluded that salicylic acid-modified TiO_2 can enhance photoactivity of TiO_2 nanotubes/Ti in degradation of *p*-nitrophenol due to improved surface adsorption properties and light utilization. Moreover, it has been known that the coupling of Ag nanoparticles (AgNPs) with TiO_2 can spread the light absorption spectrum of TiO_2 toward the visible-light region and promote the separation of photogenerated electron-hole (e^-h^+) pairs to facilitate the electron transfer from TiO_2 to AgNPs [17-19]. According to the mentioned reasons, it seems that the fabrication of salicylic acid-Mod-Ag/ TiO_2 ternary composite can be investigated as a good approach to merge the photocatalytic advantages of salicylic acid-Mod- TiO_2 and AgNPs- TiO_2 composites and therefore improve the photocatalytic activity of TiO_2 for photocatalytic degradation.

In the present study, we described an experimental investigation of simple surface chemical co-modification of TiO_2 nanotubes/Ti plates with salicylic acid and AgNPs. Methylene Orange (MO) dye was chosen as the model pollutant to investigate the photocatalytic activity of the modified plates in the presence of UV light irradiation.

Experimental

Catalyst preparation

Titanium dioxide nanotubes arrays (TiO_2NTs) were growth on pure Ti plates by potentiostatic anodic oxidation process according to our previous work [20]. Very briefly, Ti plates (purity 99%) with geometric area of 3 cm^2 were mechanically polished with different emery papers and then ultrasonically washed in acetone and deionized water bath. The anodizing process was performed in a mixed solution containing of glycerol/water (75:25, vol.%) + 0.5 wt.% NH_4F under magnetic stirring in two electrode configuration, where cleaned Ti plate and Pt sheet were used as anode and cathode at an applied voltage of 20 V in 25 °C. The $\text{TiO}_2\text{NTs}/\text{Ti}$ plates were modified by immersing of the plates in the mixture of saturated solution of salicylic acid and 0.3 M AgNO_3 at 45 °C for the duration of 45 min. Finally, the prepared plates were directly calcined at 450 °C for 2 h. The yellow colored, homogeneous and adherent coatings were successfully obtained on the $\text{TiO}_2\text{NTs}/\text{Ti}$ plates. The yellow color is due to esterification between salicylic acid and -OH groups on surface of $\text{TiO}_2\text{NTs}/\text{Ti}$ plate according to following mechanism (Fig. 1) reported in [13]. These chemically modified plates were denoted as salicylic acid(mod)-Ag/ $\text{TiO}_2\text{NTs}/\text{Ti}$ plate.

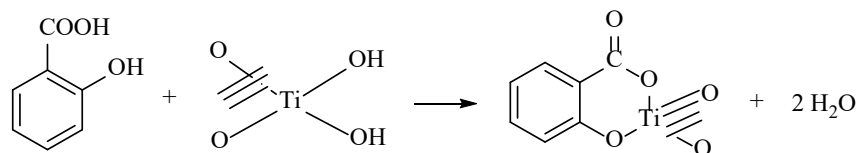


Fig. 1. Suggested mechanism of esterification between salicylic acid and -OH groups on TiO₂ surface in [13].

Characterization and electrochemical studies

The surface morphology of the plates was characterized with a scanning electron microscope (Philips, Model XL30). FT-IR spectrometry was conducted using a Fourier transform infrared spectrophotometer (Nexus 670, Thermo Nicolet USA). Electrochemical measurements were carried by Autolab PGSTAT302N potentiostat.

Photocatalytic degradation of Methylene Orange (MO)

The photocatalytic activities of the bare and modified TiO₂NTs/Ti/Ti plates were tested by the degradations of MO dye as a chemical pollutant under UV light irradiation. In a general photocatalytic measurement, four plates (geometric area of 3 cm²) were put around the beaker (500 mL) containing aqueous solution of MO (10 ppm) and irradiated under magnetic stirring in a photoreactor set-up equipped with a 250-W high-pressure mercury lamp. The photoreactor setup was explained in our previous reports [20]. The initial pH of MO solution (10 ppm) was at about 6.2 and all photocatalytic tests were done in this pH. Prior to the irradiation, the adsorption efficiency for MO removal was tested. In this regard, the MO suspensions including the plates were magnetically stirred in the dark for 30 min to establish the adsorption/desorption equilibrium and subsequently, the reaction was started. At a given time interval (15 min), 5 mL of solution was withdrawn periodically and MO concentration was determined by measuring the UV-Vis absorption.

Results and Discussion

Structural and morphological characteristics

SEM micrograph of TiO₂ nanotubes layer electrochemically grown on Ti plate by applying a constant voltage of 20 V are shown in Fig. 2a. From the top-view, it can be observed that the diameter of the nanotubes is about 70 nm and the wall thickness is around 10 nm. Fig. 2b, shows the TiO₂NTs/Ti after surface chemical modification process with salicylic acid. As can be seen from Figure, esterification between salicylic acid and -OH groups on TiO₂ surface has been led to formation of uniform deposits on the walls of TiO₂NTs/Ti plates where the walls are almost closed. Fig. 2c, presents the microstructure of the salicylic acid(mod)-Ag composite coated on TiO₂NTs/Ti plate. As can be seen from the figure, the composite has completely covered the entire surface of TiO₂NTs/Ti plate, where nanotubular structure is disappeared. In order to probe the chemical composition, the plate material was further characterized by EDX. Fig. 2d, shows the EDX spectrum of the salicylic acid(mod)-Ag/TiO₂NTs/Ti plate that confirms the presence of carbon and silver on TiO₂NTs/Ti.

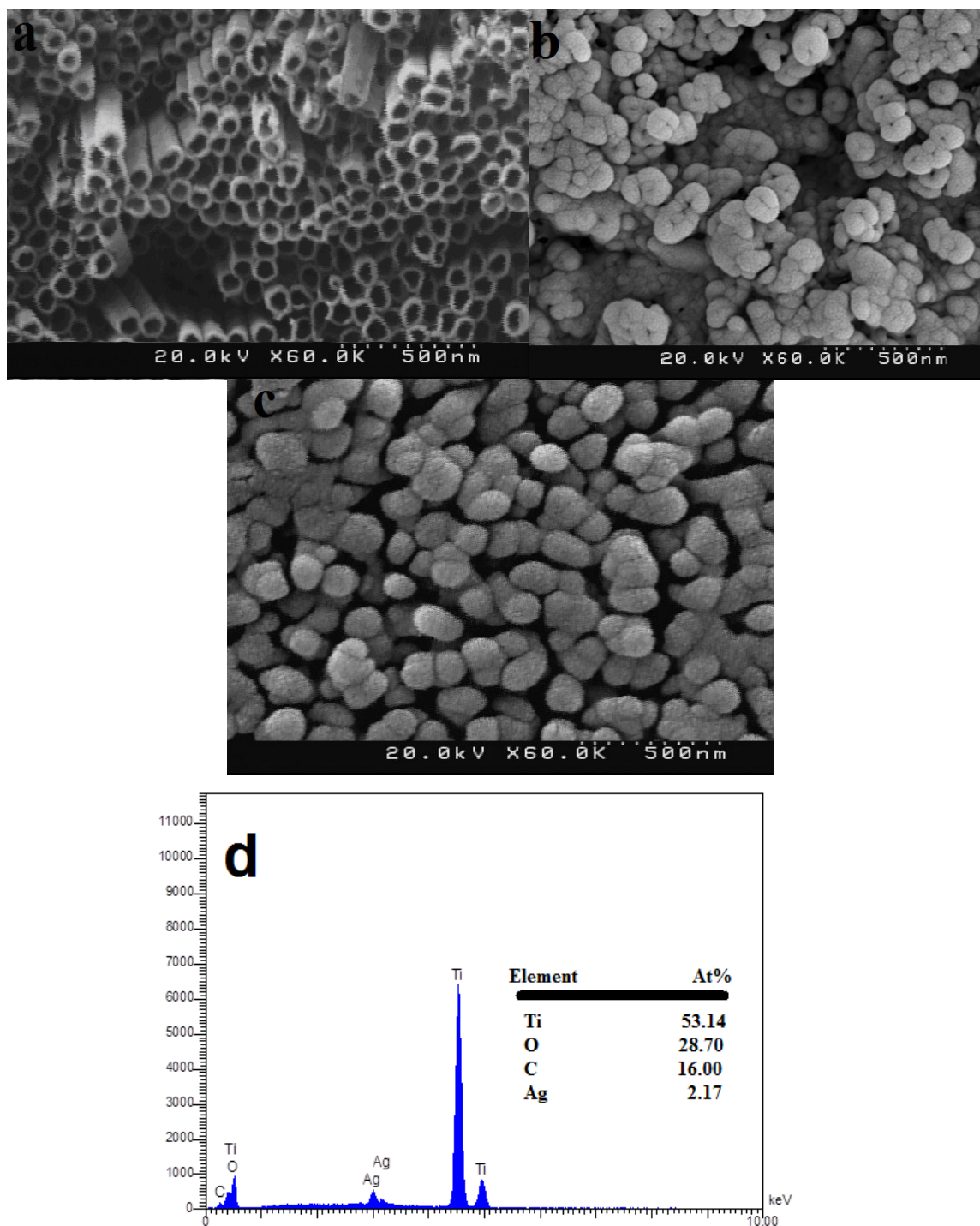


Fig. 2. SEM images of bare TiO₂-NTs/Ti plate (a), Salicylic acid(mod)/TiO₂NTs/Ti plate (b), Salicylic acid(mod)-Ag/TiO₂NTs/Ti plate (c) and EDX spectra obtained of salicylic acid(mod)-Ag/TiO₂NTs/Ti plate (d).

The FT-IR spectra of the TiO₂NTs/Ti and salicylic acid(mod)/TiO₂NTs/Ti plate are shown in Fig. 3. There are obvious differences in the FT-IR spectra of the TiO₂ nanotubes and salicylic acid modified TiO₂NTs/Ti plates. In contrast to FT-IR spectrum of the bare TiO₂ nanotubes, the spectrum of the salicylic acid(mod)/TiO₂NTs/Ti consists of absorption bands at ~2351 cm⁻¹ (attributed adsorbed CO₂ molecule), ~1650 cm⁻¹ (C=O stretching) and ~1450 cm⁻¹ (C=C stretching in the aromatic rings) [13,14]. All these results clearly reveal the esterification between salicylic acid and -OH groups on surface of TiO₂NTs/Ti plate.

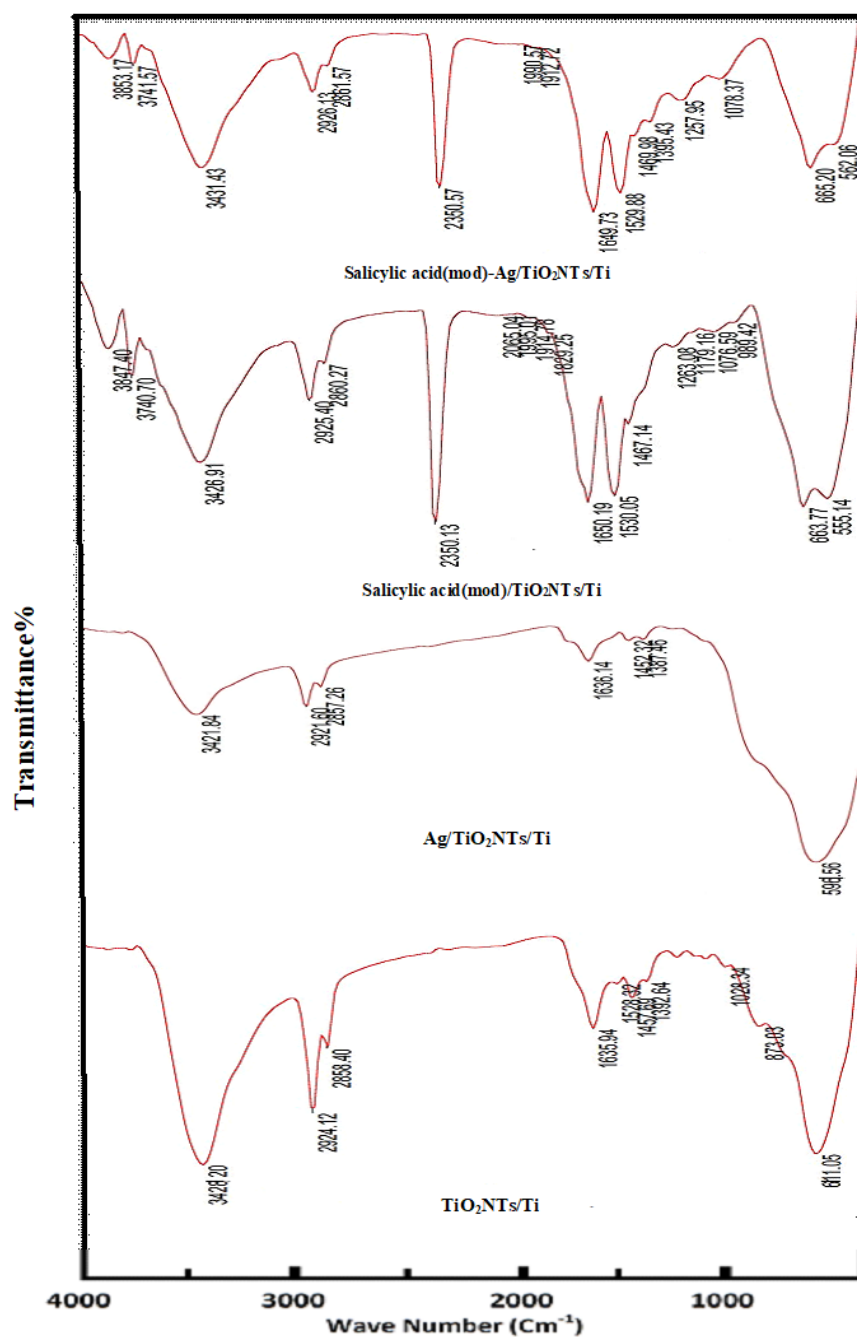


Fig. 3. FT-IR spectra of Salicylic acid(mod)-Ag/TiO₂NTs/Ti, Salicylic acid(mod)/TiO₂NTs/Ti, Ag/TiO₂NTs/Ti and TiO₂NTs/Ti plates.

Photoelectrochemical performance

Photocurrent response is an important parameter for studying the separation efficiency and transfer performance of the photoinduced charge carriers of the fabricated plates. Thereby, the photocurrent response of fabricated plates was analyzed according to Fig. 4, by several on-off cycles of intermittent irradiation (50 s) at -0.2 V versus Ag/AgCl in 0.1 M Na₂SO₄ solution. The dark currents of the all plates are almost zero. In presence of UV light, the photocurrent of salicylic acid(mod)-Ag/TiO₂NTs/Ti is about 500 μ A which is approximately 1.5 times higher than Ag/TiO₂NTs/Ti and salicylic acid(mod)/TiO₂NTs/Ti plates, indicating that the photogenerated electron transfer efficiency on salicylic acid(mod)-Ag/TiO₂NTs/Ti plate was higher than that of other plates under similar condition [21,22].

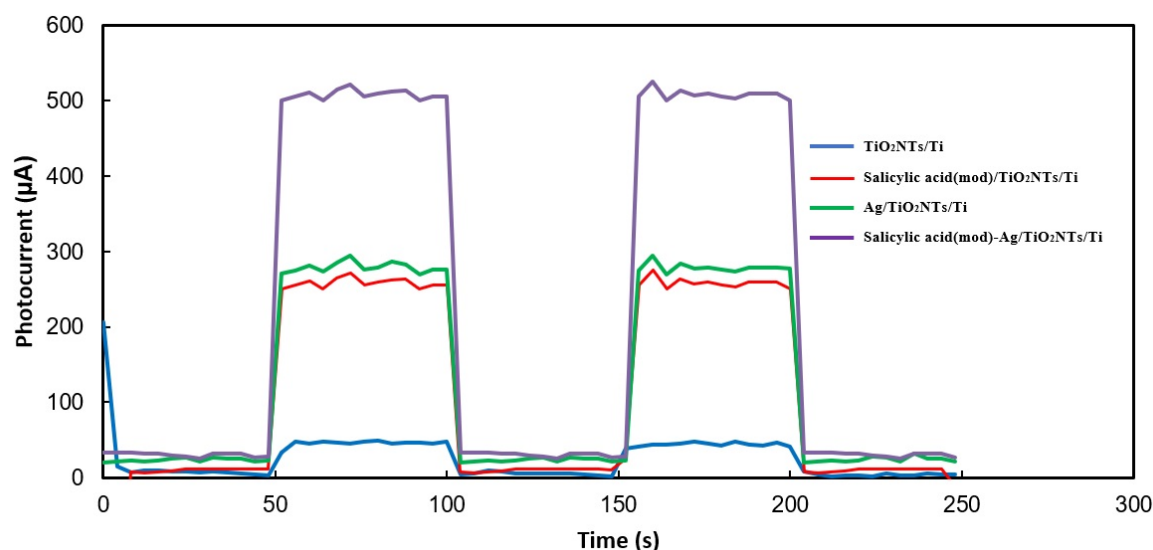


Fig. 4. Photocurrent density of the fabricated plates at -0.2 V.

Photocatalytic activity

The photocatalytic activity of TiO₂NTs/Ti and modified plates was investigated during MO degradation under UV light irradiation in aqueous solution. As can be seen from Fig. 5a, the photodegradation efficiency of the salicylic acid(mod)/TiO₂NTs/Ti plate is higher compared to bare TiO₂NTs/Ti plate. The formation of ester with stabile six-member ring could avail the esterification between salicylic acid and -OH groups on TiO₂ surface which can lead to formation of weak charge transfer between the aromatic system and Ti⁴⁺ center [13]. In addition, the higher photocatalytic activity of the salicylic acid(mod)/TiO₂NTs/Ti plate can be attributed to improved surface adsorption properties between MO and the plate. In case of Ag/TiO₂NTs/Ti, silver can trap the excited electrons from TiO₂NTs under UV light irradiation and leave the holes for the degradation of pollutants, improving the charge carrier separation and therefore photocatalytic activity [17,19]. The salicylic acid(mod)-Ag/TiO₂NTs/Ti plate has maximum photocatalytic performance compared to the other plates in MO degradation. It seems that the fabrication of salicylic acid(mod)-Ag/TiO₂NTs ternary hybrid integrate the photocatalytic advantages of salicylic acid(mod)-TiO₂ and Ag-TiO₂ hybrids and therefore maximize the photocatalytic activity. Fig. 5b, shows the absorbent spectrums of MO degradation with various fabricated TiO₂NTs/Ti plates under UV light illumination for 15 min. As seen, the decrease amount of MO concentration for salicylic acid(mod)-Ag/TiO₂NTs/Ti is higher compared to other TiO₂NTs/Ti plates. The synergetic effect among salicylic acid(mod), Ag and TiO₂NTs motivate a fast charge separation, a slow electron-hole recombination and improved surface adsorption, thus increasing the photocatalytic performance of the salicylic acid(mod)-Ag/TiO₂NTs/Ti plate. The comparison of the photodegradation efficiency of the

salicylic acid(mod)-Ag/TiO₂NTs/Ti plate with previously reported photocatalysts for degradation of MO is summarized in Table 1. It is clear that the photodegradation efficiency of final modified TiO₂NTs/Ti plate is comparable with values reported in previous literatures.

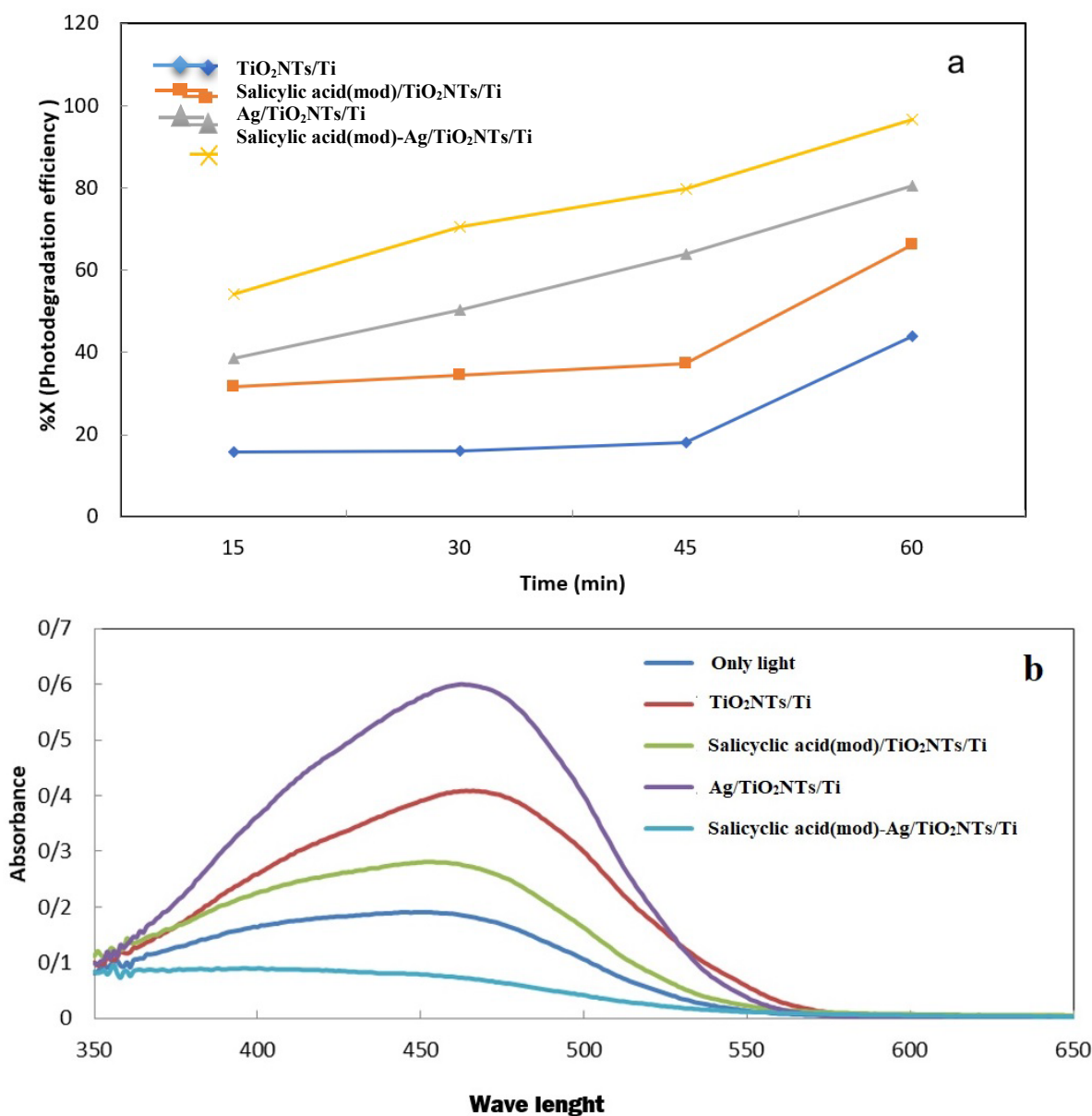


Fig. 5. The degradation efficiency of MO under UV light illumination for the salicylic acid(mod)-Ag/TiO₂NTs/Ti, Ag/TiO₂NTs/Ti, salicylic acid(mod)/TiO₂NTs/Ti and TiO₂NTs/Ti plates (a) and Typical absorbent spectra of the MO solution illuminated by UV light (b).

Table 1. The comparison of photodegradation efficiency of the salicylic acid(mod)/TiO₂NTs/Ti plate with previously reported photocatalysts for degradation of MO.

| Photo-Catalyst | Pollutant | Lamp Source | Photodegradation Efficiency (%) | Time (min) | Refrence |
|---|---------------|-------------|---------------------------------|------------|---------------|
| TiO ₂ /Cu ²⁺ | Methyl Orange | UVc lamp | 81 | 90 | [23] |
| TiO ₂ /TENA | Methyl Orange | UVc lamp | 76 | 120 | [24] |
| TiO ₂ /Zeolite | Methyl Orange | UVc lamp | 86.2 | 30 | [25] |
| TiO ₂ /Ce | Methyl Orange | UVc lamp | 78 | 240 | [26] |
| Salicylic acid (mod)-Ag/TiO ₂ NTs/Ti | Methyl Orange | UVc lamp | 96.6 | 60 | Present study |

Kinetic study of photocatalysis

Fig. 6a, shows plotting the graph of $\ln(C_0/C_t)$ versus time(min) based on first-order model for all fabricated TiO₂NTs/Ti plates. According to Eq. 1, rate constant (k_{app}) can be obtained for MO photocatalytic degradation from plotting the graph of $\ln(C_0/C_t)$ versus t. For more clarifications, the obtained results for k_{app} are demonstrated for all fabricated plates in Fig. 6b. As can be seen from Fig. 6b, the salicylic acid(mod)-Ag/TiO₂NTs/Ti shows maximum rate constant compared to other plates, attributing to synergetic effect between Ag, salicylic acid and TiO₂ for photocatalytic degradation of MO.

$$\ln \left(\frac{C_0}{C_t} \right) = -kt \quad \text{Eq. 1.}$$

The stability of the salicylic acid(mod)-Ag/TiO₂NTs/Ti was evaluated in four consecutive experiments by using fresh aqueous solution of MO (10 ppm). Between each experiment, the photocatalyst plate was removed, then washed with distilled and used. According to results of Fig. 7a and 7b, during the 4 cycle experiments, modified TiO₂NTs/Ti shown a slightly decrease in degradation efficiency from 96.6% in first cycle to 72.9% in fourth cycle experiment, showing modified TiO₂NTs/Ti plates have high chemical and photochemical stability in dye degradation under UV light illumination.

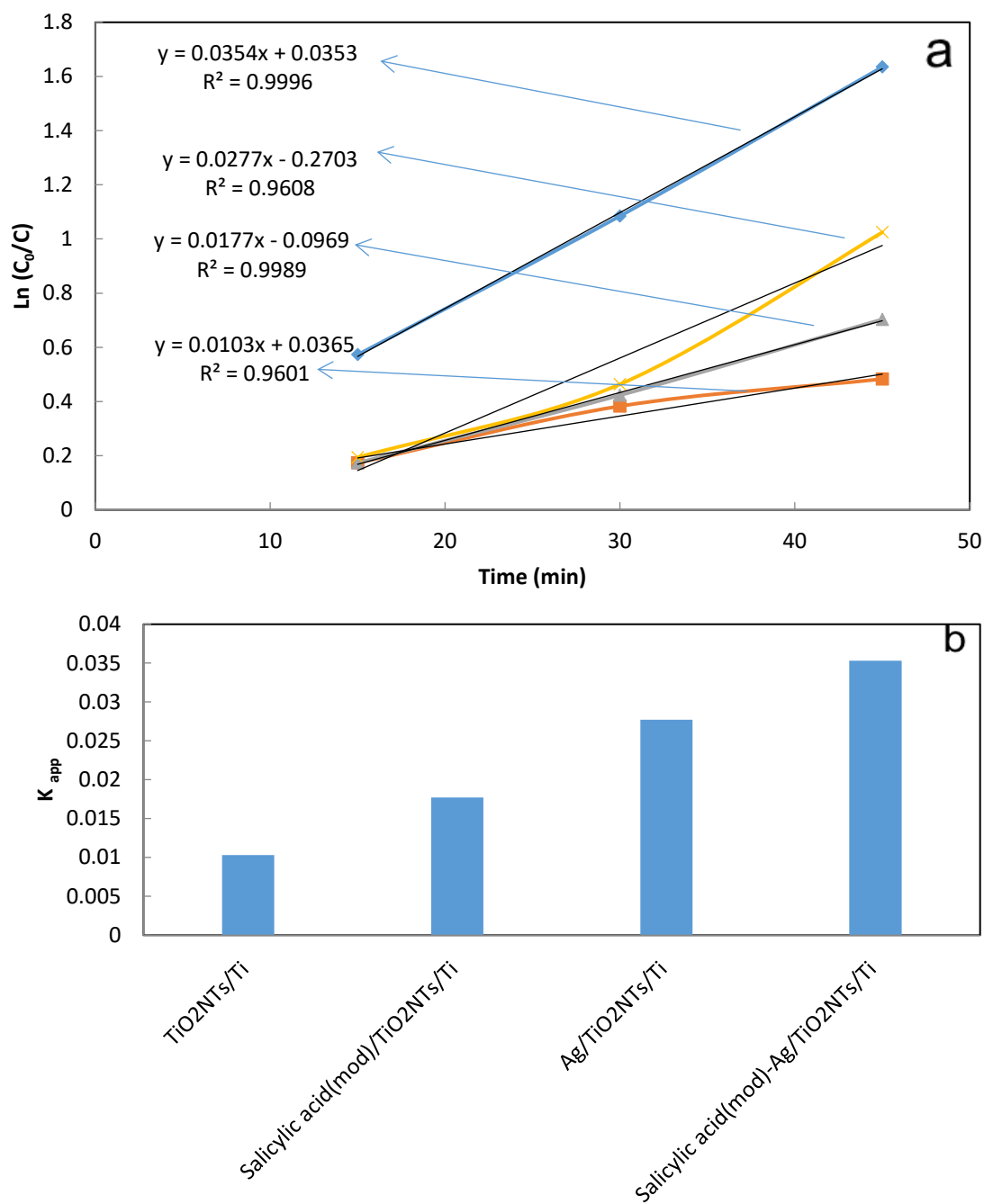


Fig. 6. Linear-log plot under UV light irradiation (a) and Rate constant for the degradation of MO under UV light irradiation (b) with various fabricated TiO₂NTs/Ti plates.

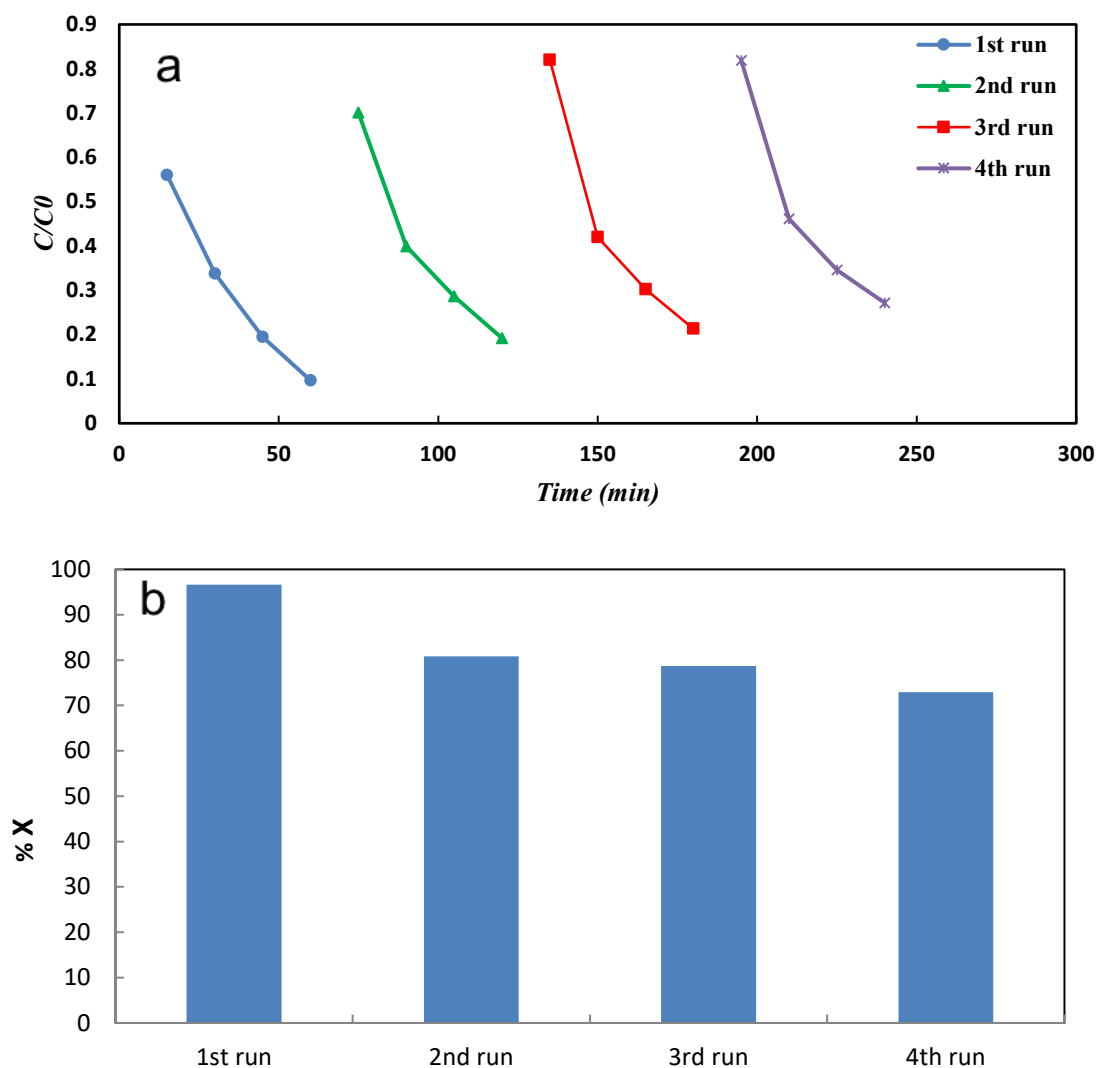


Fig. 7. Cyclic degradation curve (a) and the degradation efficiency of MO under UV light irradiation (b) for the salicylic acid (mod)-Ag/TiO₂NTs/Ti plates.

Conclusions

Synthesis and characterization of salicylic acid (mod)-Ag/TiO₂NTs/Ti plate as a photocatalyst in the photodegradation of methylene orange (MO) under UV light irradiation were carried out. Synthesis was conducted by immobilization of TiO₂NTs/Ti plates in the saturated solution of AgNO₃ and salicylic acid at 45 °C. The results showed the photochemically modified plates possess excellent photocatalytic performance for MO degradation under UV light irradiation when compared with that of the TiO₂NTs/Ti plate. These new plates may have potential applications in environmental area.

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