# SUPER HYDROPHILIC PROPERTY AND PHOTOCATALYTIC ACTIVITY OF Na DOPED K/$TiO_2$ THIN FILMS COATED ON Ti SUBSTRATES UNDER VISIBLE LIGHT IRRADIATION

P. KONGSONG[a,*], M. MASAE[b], A. JEENARONG[c]
[a]*Department of Materials Engineering, Faculty of Engineering and Architecture, Rajamangala University of Technology Isan, Nakhon Ratchasima 30000, Thailand*
[b]*Department of Industrial Engineering, Faculty of Engineering, Rajamangala University of Technology Srivijaya, Songkla 90000, Thailand*
[c]*School of Health Science, Traditional Chinese Medicine, Mae FahLuang University, Chiangrai 57100, Thailand*

In this context, the present work was dedicated to the tailored synthesis of Na doped K/$TiO_2$ thin films for their hydrophilic property and photocatalytic activity. In particular, the systems were synthesized by a sol–gel route and thoroughly characterized by field emission scanning electron microscopy (FESEM) and X-ray photoelectron spectroscopy (XPS). The photocatalytic activities degrading methylene blue (MB) in solution were determined, expecting these activities to correlate with the hydrophobic property. The results showed that 3Na/K/$TiO_2$ thin film has super-hydrophilicity and photocatalysis under fluorescence light irradiation. The high hydrophilic property was mainly related to the high level of $OH^-$ radicals on its surface. The super-hydrophilicity of all new doped $TiO_2$ thin films was found at room temperature for 15 min. Moreover, 3Na/K/$TiO_2$ thin film was proven to have excellent photocatalysis and hydrophilicity in the visible region simultaneously, which made the application of 3Na/K/$TiO_2$ thin film as self-cleaning and anti-fogging material practical under everyday condition.

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*Keywords*: Na doped K/$TiO_2$; Photocatalytic activity; Hydrophilicity property; Sol-gel method

## 1. Introduction

Titanium dioxide ($TiO_2$) and $TiO_2$-based materials have been extensively studied. This has been driven by their important applications in many fields such as heterogeneous catalysis, energy storage and transfer, photovoltaic solar cell production, sensor design, pigment production, corrosion protection, optical coating, ceramic manufacturing, electric device design, wastewater purification and self-cleaning coatings. Recent studies show that the wettability of the anatase $TiO_2$ surface changes before and after UV irradiation. This is based on the measurements of the water contact angle using single crystal, polycrystalline films and nanocrystal films [1]. $TiO_2$ surface is well known to exhibit super-hydrophilic wettability, with water contact angles less than 58°, as a result of ultraviolet (UV) irradiation [2]. The water contact angle represents the hydrophilicity or hydrophobicity of a surface. If the contact angle is less than 90°, it is hydrophilic and in contrary, if the contact angle is greater than 90°, it is hydrophobic. For the super-hydrophilicity and super-hydrophobicity, the contact angles are smaller than 10° and larger than 150° respectively. For the surface which is super-hydrophobic or super-hydrophilic, it is usually considered as self-cleaning surface [3].

The modification of $TiO_2$ by doping with alkali and the cooperative actions of doping were investigated to improve the photocatalytic activity. The improvement in both spectral response and the photocatalytic efficiency could be achieved through a combined approach of doping with alkali with some other action [4].

*Corresponding author: physics_psu@windowslive.com

This paper focuses on the surface morphology and contact angle measurement of as-deposited and annealed $TiO_2$ films using X-ray diffraction (XRD), field emission scanning electron microscope (FESEM) and surface wettability techniques. $TiO_2$ films were fabricated on the polished Ti substrates using sol-gel and sintering methods. The influence of Na doping content into $K/TiO_2$ films on their hydrophilicity and photocatalysis are also investigated in this study.

## 2. Experimental

### 2.1 Preparation of $Na/K/TiO_2$ thin films

In a typical preparation procedure, titanium (IV) isoproxide (TTIP, 99.95%, Fluka Sigma-Aldrich) was added drop-wise under vigorous stirring into the mixture solution containing ethanol (99.9%; Merck Germany), 10 mL glacial acetic acid, potassium oxalate ($(COOK)_2 \cdot H_2O$) corresponding to different K/Ti proportions of 3 mol% [4] and sodium nitrate $Na(NO_3)$ corresponding to different Na/Ti proportions of 3, 5 and 7 mol% and stirred for 60 min at room temperature; after that, $Na/K/TiO_2$ sol was coated on Ti sheets by dipping at room temperature. Gr-2 commercially pure Ti sheets (25.4 × 25.4 × 0.5 $mm^3$) were bought from Prolog Titanium Corporation Co., Ltd. (Thailand). After polishing with SiC sandpaper, the Ti substrates were cleaned with ultrasonic for 15 min, washed with distilled water and dried at 60°C for 15 min. Then, the sol could be homogeneously coated on the substrate at the dipping speed of 0.1 mm/s. The coated substrates were dried at 60°C for 30 min and then heated at a temperature of 400°C for 1 h with a heating rate of 10°C/min [4].

### 2.2 Materials characterization

The surface morphology was investigated by field emission scanning electron microscopy (FESEM, JEOL, JSM). The chemical composition of the films was investigated by X-ray photoelectron spectrometer (XPS; AXIS ULTRA$^{DLD}$, Kratos analytical, Manchester UK.) Spectrums were processed on software "VISION II" by Kratos analytical, Manchester UK. The base pressure in the XPS analysis chamber was about $5x10^{-9}$ torr. The samples were excited with X-ray hybrid mode 700x300 µm spot area with a monochromatic Al $K_{\alpha\ 1,2}$ radiation at 1.4 keV. X-ray anode was run at 15kV 10 mA 150 W. The photoelectrons were detected with a hemispherical analyzer positioned at an angle of 45$^o$ with respect to the normal of the sample surface.

### 2.3 Photocatalytic reaction test and contact angle

The photocatalytic activity of pure $TiO_2$ and Na doped $K/TiO_2$ thin films were tested by means of photodegradation of MB solution 5 mL having an initial concentration of $1x10^{-5}$ M as an indicator under the fluorescence light of 50 W. The distance between a testing substrate and a light source is 32 cm. The photocatalytic reaction test was done in a dark chamber under visible light irradiation at various times up to 4 h. The remaining concentration of MB was determined by UV-Vis spectroscopy. Hydrophobic properties were investigated by measuring the contact angle using a contact angle meter (OCA 15EC). Several deionized water droplets of 0.5 µL volume were spread on the samples and water contact angles were measured at different points on the thin film surface for statistical purpose.

## 3. Results and discussion

### 3.1 Morphology of thin film surface

The morphology of pure $TiO_2$ and Na doped $K/TiO_2$ thin films annealed at 400ºC were observed by FESEM as illustrated in Fig. 1. As be served from the FESEM image, the obtained sample is mainly composed of solid film structure, and some small particles dispersed on the $TiO_2$ surface (Fig 1a, c, and e). Fig. 1 b, d and f show FESEM images of the cross-section of $TiO_2$ composite films coated on the Ti substrates. The thickness of pure $TiO_2$, K/$TiO_2$, and 3Na/K/$TiO_2$ films were found to be nearly 250, 300 and 450 nm respectively.

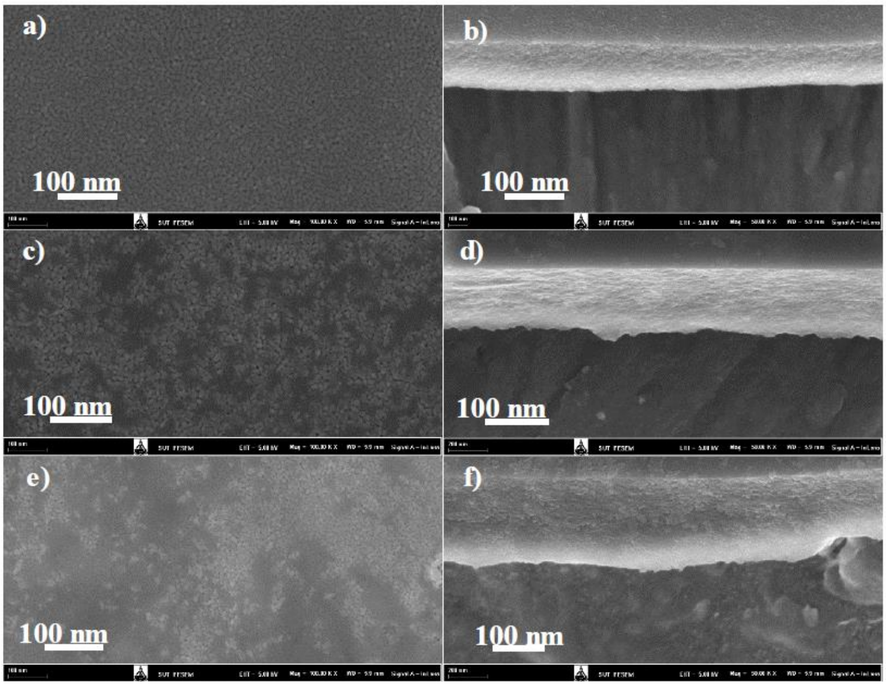


*Fig. 1. FESEM images of (a) pure $TiO_2$ and (b) cross-section, (c) K/$TiO_2$ and (d) cross-section, (e) 3Na/K/$TiO_2$ and (f) cross-section films.*

### 3.2 XPS analysis

Fig. 2 shows XPS spectra of Ti 2p core levels of pure $TiO_2$, K/$TiO_2$ and Na doped K/$TiO_2$ thin films. The respective spin orbits of Ti 2p3/2 and Ti 2p1/2 were clearly seen in all Ti 2p spectra, this indicated that the oxidation state of titanium atoms in the catalysts was in the form of $Ti^{4+}$. The binding energy of Ti 2p3/2 in 3Na/K/$TiO_2$ (458.2 eV) was lower than that of undoped $TiO_2$ (458.6 eV), indicating an increase in the electron density around titanium atoms [5]. The high-resolution XPS spectra of K 2p regions are shown in Fig. 3. In addition to assessing the state of potassium atoms in the 3Na/K/$TiO_2$ film, high-resolution XPS spectra of K2p region were generated. The XPS spectra in K 2p region of PWKT film was deconvoluted and four peaks at 292.9 eV (K 2p3/2) and 295.7 were obtained. The peaks at 292.9 eV (K 2p3/2) and 295.7 eV (K 2p1/2) were assigned to K-O groups [6]. The peak located at 1070.6 and 1071.6 eV corresponds to Na 1s showing the presence of Na in the lattice of the $TiO_2$ film (Fig. 4).

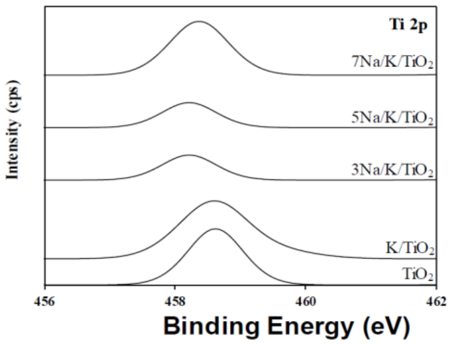


*Fig. 2. XPS spectrum of Ti 2p on the surface of $TiO_2$ and composite films.*

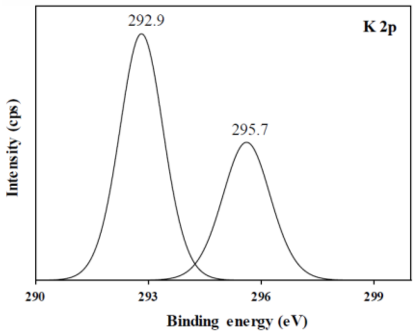


*Fig. 3. The high-resolution XPS spectra of K 2p on the surface of $3Na/K/TiO_2$ thin film.*

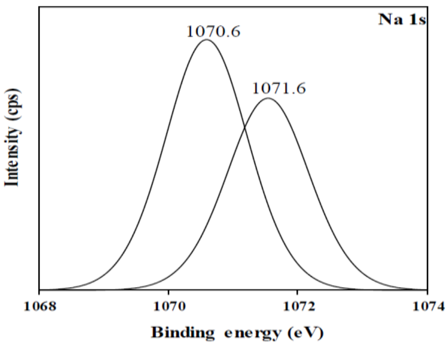


*Fig. 4. The high-resolution XPS spectra of Na 1s on the surface of $3Na/K/TiO_2$ thin film.*

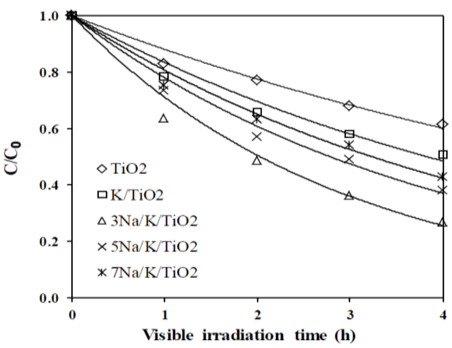


*Fig. 5. Photocatalytic performance curves of $TiO_2$ and composite films on degradation of MB under visible light irradiation.*

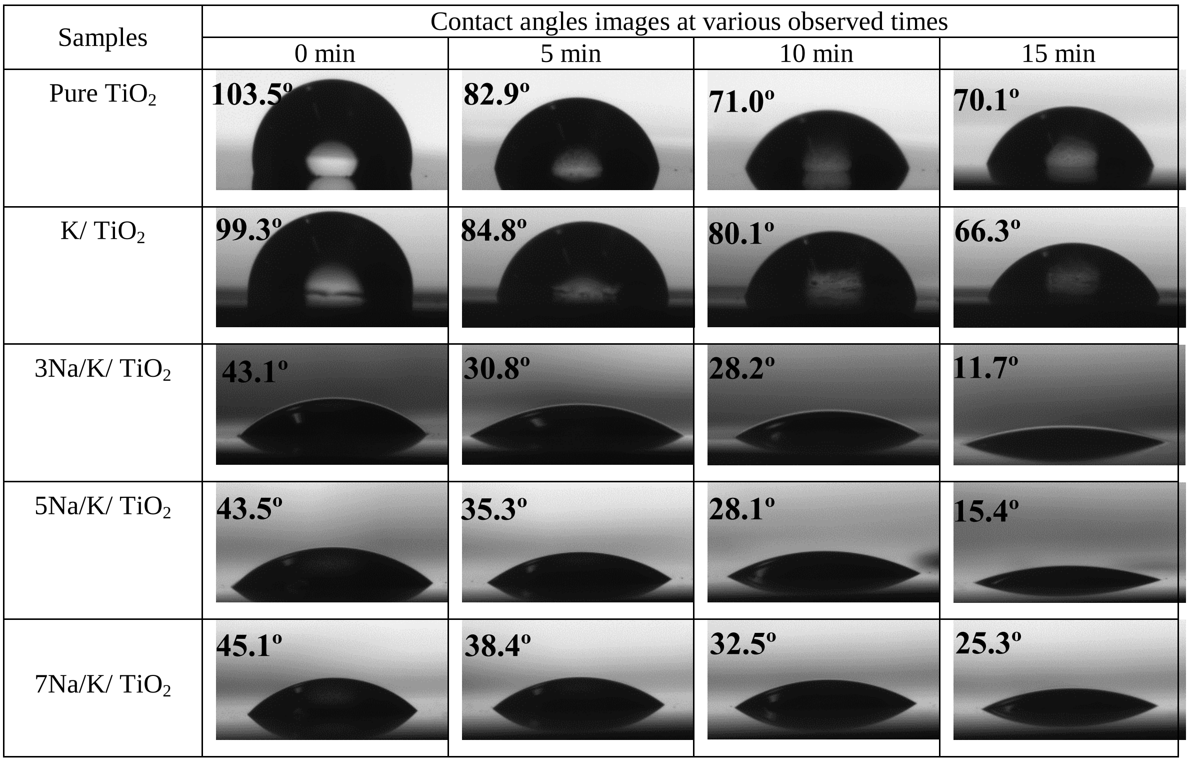


*Fig. 6. Water contact angles and their images of pure $TiO_2$ and Na/K/$TiO_2$ composite films observed at 0, 5, 10 and 15 min.*

### 3.3 Photocatalytic activity and hydrophobic property

The photocatalytic activities of pure $TiO_2$ and Na doped K/$TiO_2$ thin films were measured by the degradation of MB, with an initial concentration of $1\times10^{-5}$, under visible light for various irradiation times. Fig. 5 shows the fraction of MB remaining vs. irradiation time, which equals current concentration relative to initial concentration, $C/C_0$. The 3Na/K/$TiO_2$ thin film has optimal photoactivity across the range of compositions tested. According to prior reports, various factors affect the photoactivity of $TiO_2$ photocatalysts, including crystallinity, grain size, specific surface area, surface morphology and surface state (surface OH radicals). These factors are dependent but closely related to each other [7].

Wettability of the substrates was evaluated by contact angle measurement. The contact angle seemed to depend on the photocatalytic activity of the film. It can be noted that the hydrophilicity in terms of contact angle correlates to the photocatalytic activity of the film. The smaller contact angle is responsible for more hydrophilicity, which agrees well with the finding of Guan [8]. Contact angles and their images of films were done at room temperature as a function of treatment time as shown in Fig. 6. It was found that contact angles decreased with an increase in time and those for 15 min tended to be small. The contact angle of Na doped K/$TiO_2$ thin films was significantly larger than that of pure $TiO_2$ and K/$TiO_2$ films. This is due to the photocatalytic effect of $TiO_2$ films. K doping has a significant effect on lowering the contact angle of water droplet due to their enhancement of photocatalytic activity, leading to a high hydrophilic property of the film compared to that of the pure $TiO_2$ film. The Na doped films of 3 mol % have smaller contact angle than the pure $TiO_2$ film with higher Na dosage. However, the super hydrophilicity (contact angle <15 degree) of 3Na/K/$TiO_2$ film was found at 15 min.

## 4. Conclusions

Various doped $TiO_2$ thin film coatings were successfully synthesized and deposited on Ti substrates, via sol–gel and dip-coating methods. The coated glasses were calcined at 400°C for 1 h at a heating rate of 10°C/min. The 3Na/K/$TiO_2$ composite film was near optimal across the compositions tested, having super-hydrophilicity properties of 3Na/K/$TiO_2$ composite films and the highest photocatalytic activity on the degradation of methylene blue. Further studies on 3Na/K/$TiO_2$ composite films have a real interest in such films considering the applications to surfaces with enhanced cleanability.

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