# Photocatalytic activity of surface modified anatase $TiO_2$ with 1-(2-Pyridylazo)-2-Naphthol prepared at low temperature

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A solar light-activated $TiO_2$ photocatalyst was synthesized by the surface modification with 1-(2-Pyridylazo)-2-Naphthol (PAN) at low temperature (80 ℃). The X-ray diffraction (XRD) and scanning electron microscope (SEM) showed crystalline powder of anatase $TiO_2$ was achieved and the UV–vis absorption of $TiO_2$ modified by PAN was greatly extended to 540 nm. The modified $TiO_2$ photocatalyst exhibited much better activity than bare $TiO_2$ in the photocatalytic reactions, 70% of the CR was decomposed by $TiO_2$-PAN after 5 hours under solar light irradiation.

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*Keywords:* Modification, Photocatalyst, Photooxidation, Solar light, Titania, Anatase $TiO_2$

*Abbreviations:* PAN: 1-(2-Pyridylazo)-2-Naphthol; CR: Congo Red; XRD: X-ray diffraction; TEM: Transmission electron microscopy; SEM: Scanning electron microscope

## 1. Introduction

Titanium dioxide ($TiO_2$) as a photocatalyst for decomposing organic pollution has attracted much attention due to its appealing attributes such as non-toxicity, chemical inertness and high photocatalytic activity [1]. Nevertheless, the use of $TiO_2$ is limited by its wide band gap (3.2 eV for anatase), which requires UV light irradiation to obtain its photocatalytic activity [2]. Therefore, numerous attempts have been made to modify $TiO_2$ materials that work under visible light irradiation in order to improve the utilization of solar energy [3-5]. One approach is to prepare impurity-doped $TiO_2$, which include the doping of $TiO_2$ with transition-metal ions [6-10] and non-metal elements [11-13]. Impurity doping material would substitute the $Ti^{4+}$ ion or $O^{2-}$ ion in the $TiO_2$ lattice and form the intra band states, which could be responsible for the visible absorption of $TiO_2$. The other approach is organic modification on $TiO_2$ surface to extend the UV/vis absorption spectrum of the photocatalyst to match closely the solar emission spectrum. The most common organics used as modifiers involve dye molecules [14, 15], catechol [16], salicylic [17], binaphthol [18].

Likewise, crystalline phase of $TiO_2$ can also play important role in the photocatalytic activity. The most favorable phase for solar energy conversion and photocatalysis is the anatase $TiO_2$ [19]. It is accepted that high temperature calcination, at least at 400 °C, is required to prepared anatase $TiO_2$ [20, 21]. However, the surface area and the surface hydroxyl would decrease which was very important to the photoactivity of $TiO_2$ decreased during the high temperature treatment Process [19, 22]. Therefore, in recent years, to achieve crystalline powder of anatase $TiO_2$ at low temperature has attracted much attention [23-25].

In this work, in order to improve the photoactivity of titanium dioxide under solar irradiation, $TiO_2$ surface was modified for the first time with 1-(2-Pyridylazo)-2-Naphthol (PAN) at mild condition (80 °C). It is expected to provide a new way to utilize the $TiO_2$ composite under solar light irradiation and thereby reduce the cost for wastewater treatment. PAN is extensively used as complex indicator, with phenolic hydroxyl and π Conjugated System in the molecular structure (shown in Fig. 1). The phenolic hydroxyl of organic compound and Ti–OH on $TiO_2$ surface could form surface ligand-metal complexe through the covalent bonding or physical and chemical adsorption, which could shift the absorption edge of $TiO_2$ to the visible region [22, 26]. Furthermore, the molecule with π Conjugated System is easy to excited and $\pi^*$ orbitals of the excited ligand would promote rapid excited-state electron injection into the conduction band of $TiO_2$ [27]. Such a direct injection mechanism gives rise to a new ligand to metal charge transfer (LMCT) absorption band for the surface complexes [28].

Congo red is a compound that contains azo groups (–N=N–) (shown in Fig. 2). In view of its high stability, Congo red is commonly used as titration indicator and staining agent. Hence, it was chosen as a model pollutant in this study.

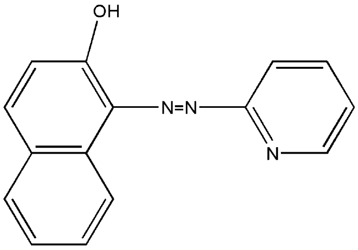

*Fig. 1. The structure of 1-(2-Pyridylazo)-2-Naphthol.*

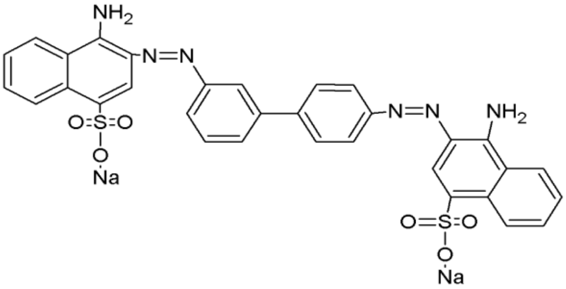

*Fig. 2. The structure of Congo Red (CR).*

## 2. Experimental

### 2.1 The preparation of $TiO_2$-PAN

PAN (0.1g) was mixed with 100 ml anhydrous ethanol, 10 ml butyl titanate was slowly introduced into the solution under violent stirring, and then 13 ml distilled water was slowly added to form suspension. Nitric acid was added to maintain a low pH (pH =6). The suspension was heated at 80 $^oC$ (under reflux) for 8 hours, cooled down to the room temperature, and filtered. The obtained powder was washed with anhydrous ethanol and water several times, and then dried in an oven at 80 $^oC$ for 2 h. The finally obtained powder was thus PAN modified $TiO_2$ photocatalyst (labeled as $TiO_2$-PAN). The bare $TiO_2$ was prepared by the same method without adding PAN.

### 2.2 Characterization of photocatalyst

The crystalline phase of samples was determined by X-ray diffraction (XRD; Cu K$\alpha$, 35 kV, 125 mA, DX1000 CSC). The particle morphology was characterized by an environmental scanning electron microscope (ESEM, Philips S4800) at an accelerating voltage of 5 kV. UV–vis diffuse reflectance spectra (DRS) were obtained for the dry-pressed disk samples using a Scan UV–vis–NIR spectrophotometer (Varian Cary 500) equipped with an integrating sphere assembly, using $BaSO_4$ as reflectance sample.

### 2.3 Photocatalytic experiment

Photocatalytic experiment was carried out by adding 0.15 g photocatalyst into a 200 ml glass tube reactor containing 150 ml target pollutant solution (the initial concentration of CR was 20 mg/l. photocatalytic reactions were conducted with stirring under UV light irradiation ( $\lambda \approx 360nm$ , UV-340), visible irradiation ($\lambda \geq 420nm$ 300W Xenon lamp with a glass filter, PLS-SXE300), solar light. The solar experiments were performed under direct sunlight from 10:00 to 15:00 on clear days of August 2009 (Yibin, latitude 28°47′ N, longitude 104°36′ W). During this time the UV-A intensity ranged between 25 and 30 W $m^{-2}$ measured by an UV irradiance meter at 375-475 nm (UV-A, Beijing). At given intervals of illumination, reaction solution (about 4.0 ml) was sampled and the suspensions were then centrifuged at 4000 rpm for 20 min to remove the catalysts and analyzed by UV–vis spectrophotometer (UV-2401PC) at wavelength of 498 nm to determine the residue concentration of target pollutant (CR). The degradation ratio of CR was calculated from follow equation:

$$\text{Adsorption ratio (\%)} = \left[(C_0 - C_a)/C_0\right] \times 100$$
$$\text{Degradation ratio (\%)} = \left[(C_a - C_t)/C_a\right] \times 100$$

Where $C_0$ is the initial concentration; $C_a$ is the CR concentration after adsorption by catalysts; $C_t$ is the remaining concentration after irradiation.

## 3. Results and discussion

### 3.1 Crystal phase and morphography of $TiO_2$-PAN

The properties of $TiO_2$ are significantly dependent on the crystalline phase, i.e., anatase, rutile, or brookite. Because of its high photoactivity, anatase is the most favorable phase for solar energy conversion and photocatalysis [19]. The powder XRD patterns of the $TiO_2$-PAN photocatalysts is shown in Fig. 3. The $TiO_2$-PAN powder sample appeared to be crystallinity and showed obvious diffraction peaks of anatase (major peaks: 25.34°, 38.1°, 47.8°, 54.6°, 63.2°) [29]. It was also observed that the XRD patterns of $TiO_2$ -PAN was identical with that of bare $TiO_2$ (not shown here), indicating that the surface PAN modification to $TiO_2$ had no effect on the crystalline phase. The inset in Fig. 3 showed that the phase of $TiO_2$ prepared at 20 $^oC$ was amorphous. Therefore, the above results suggested that higher hydrolysis temperature (80 $^oC$) could promote the phase transition and crystallization of amorphous $TiO_2$ at low temperature. The crystallite sizes of anatase according to the Scherrer's equation were about 3.64 nm. Morphologies of PAN modified $TiO_2$ revealed by SEM micrograph was shown in Fig. 4. The $TiO_2$-PAN powder aggregates consisting of smaller particles to larger particles with a high tendency for crystallisation. In this work, anatase nanocrystalline $TiO_2$-PAN particle was prepared at 80 $^oC$ without further treatments. Low temperature synthesis is helpful for obtaining anatase $TiO_2$ and saving of energy.

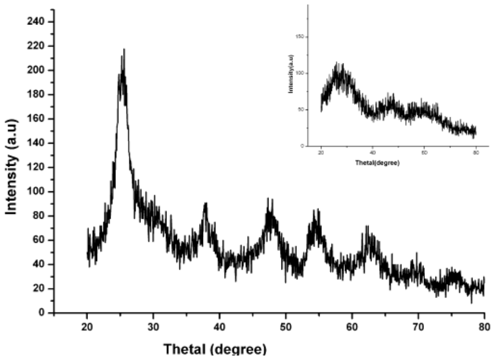

*Fig. 3. XRD of powder pattern of $TiO_2$-PAN particle.*

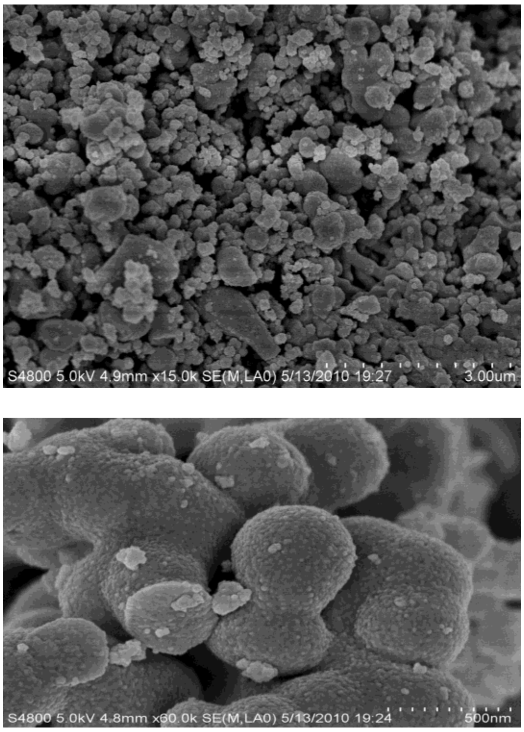

*Fig. 4. SEM of powder pattern of $TiO_2$-PAN particle.*

### 3.2 UV–vis absorption

The UV–vis DRS spectra of $TiO_2$, $TiO_2$-PAN and the UV–vis absorption spectrum of PAN are shown in Fig. 5. PAN has a maximum absorption at 462 nm. $TiO_2$ itself has an upper absorption edge at about 400 nm. The absorption of $TiO_2$-PAN is greatly extended to 540 nm. It was reported that the Ti–OH on $TiO_2$ surface could react with phenolic hydroxyl of organic compound to form surface complexes through a phenolate linkage [30, 31], which could shift the absorption edge of $TiO_2$ to the visible region. Furthermore, PAN structure was a typical electron donor type conjugated structure, and Ti was the electron acceptor due to the electron-deficient of d-orbital. Consequently, the photo-induced electron might easily transfer from PAN to $TiO_2$ (ligand-to-metal) [32]. This donor-acceptor chemical structure led to the extension of conjugation and decrease of the electron-transition energy [33]. Thus, such a direct injection mechanism gives rise to a new ligand to metal charge transfer (LMCT) absorption band for the surface complexes. As a result, the PAN modified $TiO_2$ exhibits a red shift.

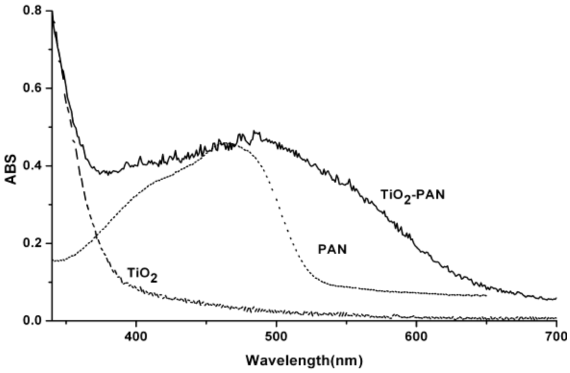

*Fig. 6. UV-vis DRS spectra of $TiO_2$, $TiO_2$-PAN and UV-vis absorption spectrum of PAN.*

### 3.3 The performance of $TiO_2$-PAN photocatalyst

Prior to irradiation, the suspension was magnetically stirred in the dark for 2 h to ensure the establishment of an adsorption–desorption equilibrium of Congo Red (CR) on the surface of photocatalyst. The degradation due to the adsorptions of CR on the surface of $TiO_2$-PAN and $TiO_2$ were 5.5% and 1.75% respectively, which was showed in the Fig. 6a and Fig. 6b (reaction time at 0h).

In UV illumination, as showed in the Fig. 6a, similar degradation ratios (7.4%) of CR was observed in the presence of PAN and absence of sensitizers after 2h. It indicated that PAN showed almost no photocatalytic activity. The modified catalyst $TiO_2$-PAN showed higher catalytic activity than bare $TiO_2$. About 60% of CR was photodecomposed by $TiO_2$-PAN while that by bare was only 46% for 2 hours. Under visible light irradiation, the case was different. As showed in Fig. 6b, 40% of the CR was decomposed by $TiO_2$-PAN after 5h. In contrast, No significant CR loss was observed in the presence bare $TiO_2$ except adsorption. CR itself did not undergo direct photo with visible light. As showed in the Fig. 6C, 70% of the CR was destroyed with particle $TiO_2$-PAN after 5 hours of solar light irradiation but $TiO_2$ showed inconspicuous Photocatalytic activity under the same conditions.

It was obvious that PAN modification enhanced the catalytic activity of $TiO_2$. Due to the far more intense absorbance in visible region and higher adsorption capacity (shown in Fig. 5) of $TiO_2$-PAN catalysts than that of bare $TiO_2$, it was reasonable that $TiO_2$-PAN catalysts showed much better photocatalytic activity than bare $TiO_2$ under visible light irradiation. Visible-light induced photodegradation of dissolved organic contaminants on $TiO_2$ was thought to proceed through a sensitizing mechanism initiated by excitation of the surface complex by visible light followed by electron injection into the conduction band of $TiO_2$ [31]. Solar light contains continuous pump wavelengths and UV light accounts for a small fraction (~5%) of the sun rays on the surface of the earth [36]. Thus solar light could use as the excitation source. Under UV irradiation, the electron-hole created in the $TiO_2$, followed by competition between recombination and interfacial charge transfer to adequate acceptors. As electron donor, PAN attached to $TiO_2$ is an essential requisite for direct hole transfer from $TiO_2$ to CR. PAN facilitated the charge transfer between the $TiO_2$ valence band and the CR molecules. At the same time, the recombination of electron and hole could be inhibited. As showed in Fig. 5, $TiO_2$-PAN has an intense absorption at 360-600 nm, which match the solar emission spectrum well. As a result, $TiO_2$-PAN photocatalyst exhibited higher reactivity than bare $TiO_2$ under solar light. Since the artificial lamp device is particularly expensive, the solar photocatalytic degradation technology developed may be available for water treatment.

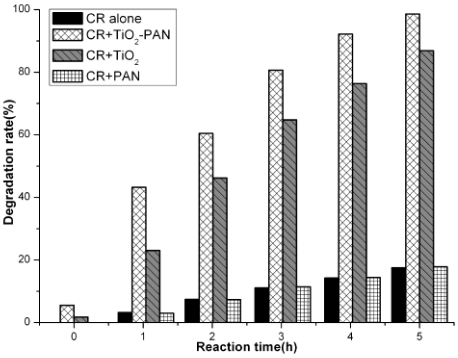

*Fig. 6a. Performance of catalysts under UV light irradiation.*

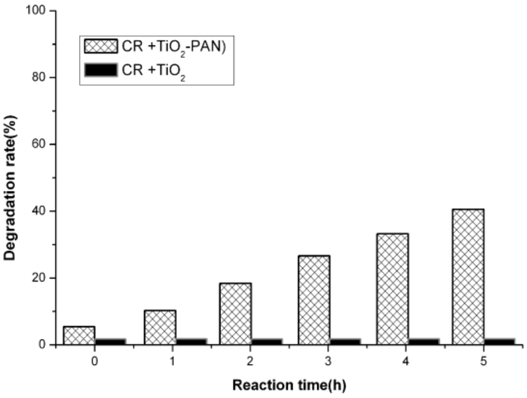

*Fig. 6b. Performance of catalysts under visible light irradiation.*

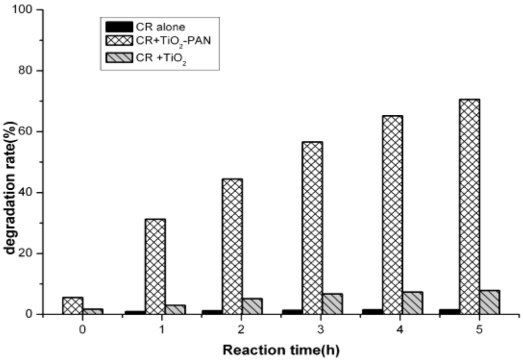

*Fig. 6c. Performance of catalysts under solar light irradiation.*

## 4. Conclusions

1-(2-Pyridylazo)-2-Naphthol modified anatase phase $TiO_2$ were successfully synthesized under mild condition. The modified $TiO_2$ exhibited enhanced photocatalytic properties under UV, visible and solar light irradiation compared to the bare $TiO_2$. In a word, the photocatalytic activity of $TiO_2$ has been greatly improved by PAN modification. This method represents a feasible option for the remediation of contaminants water using modified $TiO_2$ photocatalyst under solar irradiation. In order to better understand the mechanism of photocatalytic activity of PAN modified $TiO_2$, Further studies along this line are now under way.

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