



# Synthesis of blue anatase TiO<sub>2</sub> nanoplates with {001} facets and *in situ* noble metal anchoring



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## ABSTRACT

Fe<sup>2+</sup> and Ti<sup>3+</sup> co-doped anatase TiO<sub>2</sub> nanocrystallites with ca. 50% exposed {001} facets have been successfully synthesized by a facile hydrothermal method. The transition metal dopant induces the stability of Ti<sup>3+</sup> ions in the structure. As-prepared anatase TiO<sub>2</sub> exhibits a broad absorbance in the visible light region, which shows blue colour. Furthermore, these Ti<sup>3+</sup> ions can *in situ* reduce the noble metal cations to neutral atoms, which form homogeneously nanoclusters on the TiO<sub>2</sub> surface. The noble metal anchored samples show enhanced photocatalysis compared to the original Fe,Co-doped TiO<sub>2</sub> sample under ultraviolet light. Among the noble metal anchored samples, Pd@Fe<sub>3</sub>-TiO<sub>2</sub> can completely oxidize CO at the mild temperature above 250 °C.

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## 1. Introduction

Anatase TiO<sub>2</sub> has attracted extensive research interests owing to its widespread applications, such as hydrogen generation by water splitting, dye-sensitized solar cells, pigments, and photocatalytic degradation of organic pollutants [1–4]. The photoactivity of anatase is greatly hindered by its low quantum efficiency in photocatalytic processes, which results from its rapid recombination of photogenerated electron–hole pairs and wide band gap (3.0–3.2 eV). Both theoretical and experimental studies show that the {001} facets of crystalline anatase are more reactive than {010} and {101} facets [5–7]. An important breakthrough was made by Lu and co-workers, who successfully synthesized micro-sized anatase TiO<sub>2</sub> sheets with high percentage of reactive {001} facets [8].

Many efforts have been made to modify the electronic structure to enable low energy photo excitation and increase the lifetime of photogenerated electron–hole pairs, such as coupling TiO<sub>2</sub> with a narrow band gap semiconductor, dye sensitization, metal or nonmetal doping, noble metal deposition, and defect disorder [9–16]. Recent studies have revealed that the physical and chemical

properties of TiO<sub>2</sub> can be modulated by sufficient Ti<sup>3+</sup> self-doping, often referred to as reduced or n-type doped TiO<sub>2</sub> [17,18]. For example, using Zn and H<sub>2</sub> as reductants, the formation of defects create donor levels in the electronic structure to narrow the band gap, which can enhance the visible light absorption and photocatalysis [16,19]. The transition metal doping can weaken oxygen bonds to make the oxygen vacancies, thus stable the Ti<sup>3+</sup> species [20,21].

Anchoring noble metal nanoclusters (Au and Ag) on the surface of TiO<sub>2</sub> particles was an effective strategy to develop the catalysts for multiple applications, such as photocatalysis, CO oxidation, and anti-bacterial, etc. The incorporation of noble metals with a large work function significantly enhances the charge separation efficiency via interfacial electron transfer (ET) from the conduction band (CB) of semiconductors to noble metals [22,23]. On the other hand, TiO<sub>2</sub> is an active support for promoting the catalytic performance of noble metal. Oxide supported noble metal nanoclusters (<5 nm) exhibit exceptional catalytic activity for several reactions, including low-temperature CO oxidation [24–26]. To improve their performance, it is necessary to have a homogeneous distribution of noble-metal NPs on the oxide surface as well as a good Schottky contact between the metal particles/clusters and oxide supports. Beside the classical methods, such as impregnation, the deposition-precipitation, the photo-deposition, and the sol–gel methods, *in*

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*situ* anchoring method was recently suggested a better way of tuning these factors [27]. In this strategy, UV light was used to generate unstable  $Ti^{3+}$  ions on the surface of anatase  $TiO_2$  under gaseous  $N_2$  protection. Subsequently a noble metal salt is directly added in the  $TiO_2$  suspension to deposit the noble metal particles on  $TiO_2$  particles through an *in situ* redox reaction.

Our work focuses on the development of the functional pigments [28,29]. Here we report the metal iron assisted method to hydrothermally synthesize the reduced  $TiO_2$  nanocrystallites with exposed {001} facets and *in situ* noble metal anchoring. This method was capable to produce blue  $TiO_2$  nanoplates for a large scale commercial production due to its low-costly condition, one-step process, and easy handled. The reaction of Fe with  $Ti^{4+}$  in the reaction can lead to the formation of  $Fe^{2+}$  and  $Ti^{3+}$  centers in the structure of  $TiO_2$  nanoparticles in this hydrothermal condition [20]. The noble metal salts is directly added in the  $TiO_2$  suspension to deposit the noble metal nanoclusters (Ag, Au, Pd) on  $Fe_3-TiO_2$  nanoparticles through *in situ* redox reaction. Photocatalysis and CO oxidation activities of the noble metal anchored catalysts were evaluated.

## 2. Experimental

**Caution!** Handling of  $TiCl_4$  and HF must be carefully performed and requires eye and skin protection.

### 2.1. Synthetic procedures

All chemicals were analytical grade and used as received without further purification. Titanium tetrachloride was dropped slowly into the ice water bath alcohol under vigorous stirring to prepare an aqueous  $TiCl_4$  alcohol solution.

#### 2.1.1. Preparation of blue $TiO_2$

Synthesize transition metal doped  $TiO_2$  nanocrystallites: Blue polycrystalline powders of  $Fe^{2+}, Ti^{3+}$ -co-doped  $TiO_2$  were synthesized by a mild hydrothermal method.  $TiCl_4$  (0.45 mol/L, 20 mL), Fe (a given amount of Fe powder with different Fe/Ti molar ratios,  $r_{FT} = 1:4, 3:8$  and  $1:2$ , respectively) and HF (33 mol/L, 0.5 mL) as starting materials were mixed to form a transparent solution. The mixture was added into 16 mL distilled water and then sealed in an autoclave with a Teflon liner (25 mL). The autoclave was heated up to 180 °C and kept for 12 h, followed by cooling to room temperature by switching off the furnace. After reaction, the products were collected by centrifugation and washed with distilled water several times until the pH reached 7 and was dried in air. The yield of the final collected products is 90%. As-prepared sample with Fe/Ti molar ratio  $r_{FT} = 1:4, r_{FT} = 3:8$ , and  $r_{FT} = 1:2$  referred to as  $Fe_1-TiO_2, Fe_2-TiO_2$ , and  $Fe_3-TiO_2$  respectively.  $Zn-TiO_2$  stands for the as-prepared sample with Zn/Ti molar ratio  $r_{ZT} = 1:2$ . Pure  $TiO_2$  was obtained by the method using  $TiCl_4$  and alcohol with and without addition of HF.

#### 2.1.2. Noble-metal *in situ* loading

In a typical process of preparing  $Au@TiO_2$  (1 wt% of Au),  $HAuCl_4 \cdot 4H_2O$  aqueous solution (0.01 mol/L, 2 mL) was slowly injected into the blue water solution with  $Fe_3-TiO_2$  suspension in the dark. After stirring for 12 h, the color of the suspension changed from blue to auburn. The  $Au@Fe_3-TiO_2$  sample in the reactor was collected and washed with water several times, and dried at 60 °C for characterization.  $Ag@Fe_3-TiO_2$  and  $Pd@Fe_3-TiO_2$  samples were synthesized using the same procedure except that  $HAuCl_4 \cdot 4H_2O$  was replaced with  $AgNO_3$  and  $PdCl_2$ , respectively.

### 2.2. Characterization method

The powder products were directly used for the characterizations. The powder XRD patterns of products were collected on a PANalytical Empyrean diffractometer with  $Cu K\alpha$  radiation ( $\lambda = 0.15418$  nm) of 40 KV and 40 mA at room temperature by step scanning in an angle range of  $10^\circ \leq 2\theta \leq 80^\circ$  and increments of  $0.0263^\circ$  were employed. Scanning electron microscope (SEM) was performed using HITACHI-SU8020. Transmission electron microscopy (TEM) was performed on a FEI Titan electron microscope operated at 300 kV. X-ray photoemission spectroscopy (XPS, Thermo ESCALAB250) experiment was performed using monochromatic Al  $K\alpha$  radiation (1486.6 eV).

### 2.3. Photocatalytic activity

Photocatalytic activity is evaluated by the degradation of methylene orange (MO) under UV light irradiation using a 125 W high-pressure Hg lamp and main output 313 nm. Experiments are carried out at ambient temperature as follows: the catalysts (20 mg) are suspended in MO solution (20 mg/L, 50 mL). Before illumination, the aqueous suspension is mechanically stirred for 30 min in the dark to ensure the establishment of an adsorption-desorption equilibrium between photocatalyst and MO. Then, the suspension is exposed to UV irradiation under continuous stirring. During irradiation, the reactant solution is withdrawn at regular intervals. The residual dye concentration is monitored by measuring the absorbance of the solution with a UV-2450 UV-Visible spectrophotometer.

### 2.4. Catalytic oxidation of CO

The catalytic activity was evaluated with a fixed-bed flow reactor. The weight of catalyst used was 50 mg, and the reaction gas consisting of 1% (v/v) CO, 20% (v/v)  $O_2$ , and 79% Ar was fed at a rate of 50 mL/min. The composition of the effluent gas was detected with an AgilentGC6890N gas chromatograph. The conversion of CO was calculated from the difference in CO concentrations between the inlet and outlet gases.

## 3. Results and discussion

### 3.1. Synthesis, XRD, and UV-vis spectrum

Besides Fe powder, Zn powder was also successful to prepare the blue anatase powder with pure phase. Meanwhile, Fe dopant and F dopant promote the formation and stabilization of  $Ti^{3+}$  on the surface of  $TiO_2$ . It is known that the Zn doping favours the stability of  $Ti^{3+}$  in the  $TiO_2$  structure [19]. It seems that the Fe plays the same role as Zn in dyeing the anatase  $TiO_2$ . Meanwhile, the air stability of blue sample implies that the  $Ti^{3+}$  ions exist in both surface and bulk.

The powder X-ray diffraction patterns of the samples demonstrated the as-prepared anatase phase of high purity, as shown in Fig. 1a. All the diffractions can be well indexed to anatase phase structure, which indicate the purity of the samples. The peak width at half height of the white  $TiO_2$  prepared without HF show more broaden compared to that of the  $TiO_2$  prepared with HF and the intensity of the (004) diffraction peak of HF treated  $TiO_2$  was suppressed. It implies that the oriented growth of the HF treated sample. This result proves that HF plays a decisive role in the crystallization of phase-pure anatase nanocrystallites with {001} facets in hydrothermal treatment [30]. Normally transition metal doping could promote the transformation from anatase to rutile phase by increasing the oxygen vacancy concentration [20].  $F^-$  ions

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