

**Photocatalytic Degradation of Gaseous Acetone by
Photocatalysts with Visible Light and Their Potential
Applications in Painting**

Supplementary Materials

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2.1 Preparation of Nano-sized Synthesized Photocatalysts and Paints

A solution comprised of 5 ml tetrabutyl titanate ($\text{Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4$) and 5 ml butanol ($\text{C}_4\text{H}_{10}\text{O}$) was poured into a beaker and then mixed uniformly with a magnetic stirrer. The solution was then added drop-wise with a mixture of 5 ml butanol and 10 ml acetic acid, and turned into slurry. An amount of $\text{Fe}_2(\text{SO}_4)_3$ or AgNO_3 was dissolved in 15 ml deionized water (DI water) which was added into the slurry to achieve the desired doped concentration. The slurry was further mixed with a magnetic stirrer at 60-70°C for 0.5 h. Glasses pre-treated with hydrofluoric acid (i.e. frosted glasses; FGs) were selected as carriers which have a rough surface with a white appearance. As the slurry turned to gel, the FGs (50×50×3 mm) with rough surface were soaked into the slurry. After being drawn from the slurry, the FGs coated with TiO_2 , Fe-doped TiO_2 , or Ag-doped TiO_2 were then calcined in an oven at 500°C for 2 h. Uniform multi-layers of TiO_2 , Fe-doped TiO_2 , or Ag-doped TiO_2 photocatalysts coated on the surface of the FGs can be achieved by repeating the immersing and calcination processes as shown above.

3.1 Surface Characterization of Synthesized Photocatalysts

3.1.1. X-ray diffraction analysis

The crystalline phases of TiO_2 (i.e. anatase, rutile, and brookite) for the synthesized photocatalysts were initially analyzed with an XRD. Some researchers reported that pure brookite shows similar photocatalytic activities as anatase, stronger than rutile. However, the synthesis of pure brookite powder is technically highly difficult (Lile, et al., 2019). In general, the anatase crystalline phase is more

photocatalytically active than rutile (Amorima, et al., 2018).

As illustrated in Fig. S4 (a, b, and c), the XRD analytical results of TiO₂, Fe-doped TiO₂, and Ag-doped TiO₂ showed that most of TiO₂ coated on the FGs had the crystalline phase of anatase (Fig. S4(a)), implying high PC activity of the TiO₂ prepared by the sol-gel method in this investigation. The results concurred with previous reports that the percentages of anatase in the synthesized photocatalysts were almost 100% under calcination temperatures ranging from 200 to 650°C (Momeni, et al., 2015).

The XRD analytical results of Ag-doped TiO₂ showed that the diffraction peak of Ag was not detected (Fig. S4(b)), indicating that no crystalline transformation appeared for Ag-doped TiO₂. Moreover, 1% Ag-doped TiO₂ was found to be mostly effective on acetone degradation due to the highest intensity of anatase among four photocatalysts (i.e. TiO₂, 1%Ag-doped TiO₂, 3% Ag-doped TiO₂, and 5% Ag-doped TiO₂) (Li, et al., 2017).

As illustrated in Fig. S4(c), similar to Ag-doped TiO₂, no diffraction peak of Fe was detected for Fe-doped TiO₂. The radius of Fe³⁺ (0.64 Å) and the radius of Ti⁴⁺ (0.68 Å) were quite similar (Wen, et al., 2012; Zafar et al., 2020; Shayegan et al., 2021). As a result, Fe³⁺ could perfectly fill into the lattice of TiO₂ and replaced Ti⁴⁺ (Zafar et al., 2020). Such a structure thus possibly leads to a low detection rate of Fe with XRD (Zhou, et al., 2006; Zhang et al., 2013).

The crystallite sizes of the synthesized photocatalysts can be further estimated by the Scherrer Equation shown below,

$$d = \frac{0.94\lambda}{\beta \cos \theta} \quad (1)$$

where d is the diameter of the photocatalyst crystallite, Å; λ is the wavelength of X-ray, 1.5405 Å; β is the full width of half maxima (FWHM) of 2θ diffraction peak; and θ is the Bragg angle. The diameters of the photocatalysts estimated by Bragg angle are summarized in [Table S2](#).

3.1.2. SEM and TEM analysis

[Fig. S5](#) illustrates the SEM images of TiO₂ coated on the FGs with 75,000 and 100,000 magnifications, respectively. It was observed that the shape of TiO₂ was mostly spherical-like and uniformly distributed over the surface of the FGs. Moreover, a cluster phenomenon was commonly observed mainly due to the agglomeration of nano-sized TiO₂.

The SEM images of 1, 3, and 5% Ag-doped TiO₂ coated on the FGs with 75,000 and 100,000 magnifications are depicted in [Fig. S6 \(a, b, and c\)](#), respectively. The size of the Ag-doped TiO₂ photocatalyst increased with the amount of Ag added. The SEM images were quite consistent with the crystallite size of photocatalysts estimated by [Eq. \(1\)](#) listed in [Table S2](#). The diameter of Ag⁺ was larger than that of Ti⁴⁺, leading to the increase of the crystallite diameter with the amount of Ag doped. Similar to TiO₂, a cluster phenomenon was also observed for Ag-doped TiO₂.

The SEM images of 1, 3, and 5% Fe-doped TiO₂ coated on the FGs with 75,000 and 100,000 magnifications are illustrated in [Figs. S7 \(a, b, and c\)](#), respectively. The image of Fe-doped TiO₂ with the magnification of 75,000 showed that the shapes of the Fe-doped TiO₂ photocatalysts were mostly spherical-like. Higher shape integrity

was observed from the image of Fe-doped TiO₂ under a magnification of 100,000. Moreover, the surfaces of Fe-doped photocatalysts were more lustrous than those of Ag-doped TiO₂ photocatalysts. The diameters of the Fe-doped TiO₂ photocatalysts decreased with the amount of Fe doped, which was in accordance with the crystallite determined by the Scherrer Equation as shown in [Table S2](#). Additionally, the nano-sized photocatalysts were densely distributed over the surface of the FGs with the amount of Fe doped. Cluster phenomena were also observed from the SEM images of Fe-doped TiO₂.

The elemental contents of the synthesized TiO₂ photocatalysts were further analyzed with EDS. The molar ratios of O, Ti, and Ag or Fe in the Ag- or Fe-doped photocatalysts are summarized in [Table S3](#).

3.1.3. XPS analysis

To confirm the elemental composition and chemical states of TiO₂ and synthesized TiO₂, XPS measurements of TiO₂, Ag-, and Fe-doped TiO₂ were further performed. The XPS spectra of Ti, Ag-, and Fe-doped photocatalysts are illustrated in [Figs. S8 \(a, b, c, and d\)](#).

As shown in [Figs. S8\(a\) and \(c\)](#), two peaks of Ti2p_{1/2} and Ti2p_{3/2} in the XPS spectra of Ti2p binding energy were observed. The slitting energy between Ti2p_{1/2} and Ti2p_{3/2} was 5.6 eV, indicating a state of Ti⁴⁺ in the form of anatase TiO₂ ([Harifi and Montazer, 2014](#)). It can be further seen in [Fig. S8\(a\)](#) that the peak responding to Ti2p_{3/2} (458.9 eV) shifted to 459.4 and 459.2 eV for 3% and 5% Ag-doped TiO₂, respectively. This phenomenon revealed that the deposition of Ag⁺ on the surface of

TiO₂ led to the change of electron cloud density and binding energy shift. Therefore, Ag doped on the surface of TiO₂ could capture electrons and thus retard the recombination of electron and electron hole pairs. Two peaks in the XPS spectra of Ag3d binding energy (Fig. S8(b)) at 368.8 and 374.8 eV corresponded to Ag3d_{5/2} and Ag3d_{3/2}, indicating the successful deposition of Ag nanoparticles on the surface of TiO₂ (Harifi and Montazer, 2014). The peak responding to Ti2p_{3/2} (458.9 eV for bare TiO₂) in Fig. S8(c) shifted to 460.9 and 459.8 eV for 3 and 5% Fe-doped TiO₂, respectively, indicating that the electron capturing capability of Fe-doped TiO₂ could be enhanced by Fe³⁺ (Wen et al., 2012; Yu and Zhou, 2009). Fig. S8(d) illustrates the spectra of Fe2p for 3 and 5% Fe-doped TiO₂. Although no evident peaks of Fe2p were observed by XPS, the EDS results apparently demonstrated the existence of Fe in TiO₂ (Table S3). Similar XPS spectra have been reported by previous studies (Wen et al., 2012; Yu and Zhou, 2009), who found that doping Fe could significantly affect the surface electronic structure of TiO₂ and thus lowered the recombination rate of photoinduced electron and electron hole pairs, which may increase the probability of the interfacial transfer of photoinduced electrons and holes. Thus, it implied that Fe³⁺ could be filled into the lattice of TiO₂. Owing to the high band energy of the synthesized TiO₂ photocatalysts, the use of Ag- and Fe-doped TiO₂ was expected to be more effective than TiO₂ on the photocatalytic degradation of acetone.

3.1.4. UV-Vis spectroscopic analysis

The UV-Vis spectra of TiO₂ and its synthesized photocatalysts were measured with a spectrometer. The UV-Vis diffuse reflectance spectra of TiO₂, Ag-doped TiO₂,

and Fe-doped TiO₂ are illustrated in [Figs. S9 \(a and b\)](#). It can be seen from [Fig. S9\(a\)](#) that the doping of Ag to TiO₂ resulted in a significant increase of the absorbance in the UV light wavelength region. A red-shift phenomenon was observed for Ag-doped TiO₂ photocatalysts, showing that the absorbance in the visible light wavelength region increased with the amount of Ag⁺ doped. The results concurred with previous studies that Ag-doped TiO₂ played as an electron trap which could effectively retard the recombination of electron and electron hole pairs ([Amzam, 2014](#)). illustrates that the Fe-doped TiO₂ photocatalysts extended a shift of the absorption wavelength and increased the absorbance in the visible range. The absorbance of visible light increased with the amount of Fe³⁺ doped for the wavelengths ranging from 400 to 800 nm, which was in the wavelength region of visible light. The results revealed that Fe-doped TiO₂ had smaller band gap energy than TiO₂ ([Isari et al.,2018](#)).

Overall, the Ag- and Fe-doped TiO₂ shifted an electron (e⁻) in the d orbit of the valence band to the conduction band, which could lead to a lattice defect or deformation. Thus, a lower energy of visible light could be absorbed to excite e⁻ from the valence band to the conduction band with two states. Either a donor level above the original valence band or an acceptor level below the original conduction band was created to make the tested synthesized photocatalysts, particularly the Fe-doped TiO₂, efficiently respond to visible light. As a result, the absorption wavelength could be shifted to the visible light wavelength region, which is known as the red-shift phenomenon ([Wen et al., 2012](#)).

3.1.5. BET specific surface area analysis

Specific surface area (SSA) is one of the major physical properties that influence the PC reactions occurred on the surface of the photocatalysts. Normally, higher SSA of photocatalysts tends to enhance the degradation efficiency of reactants. The SSA and the average pore diameter of TiO₂ and synthesized photocatalysts are listed in Table S4.

As shown in Table S4, the SSA of Ag- and Fe-doped photocatalysts decreased with the amount of Ag and Fe doped to TiO₂, which was mainly attributed to the effects of aggregation phenomena (see Fig. S5-S7). The maximum SSA was obtained for 1% Fe-doped TiO₂, and followed by 3% Fe-doped TiO₂, 1% Ag-doped TiO₂, and TiO₂. It implied that the photocatalytic activities of 1% Fe-doped TiO₂, 3% Fe-doped TiO₂, and 1% Ag-doped TiO₂ could be higher than that of bare TiO₂.

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Table Caption

Table S1 Model of the analytical instruments used for detecting the characteristics of the photocatalysts.

Table S2 Crystallite sizes of Ag- and Fe-doped TiO₂ determined by Scherrer Equation.

Table S3 Results of EDS analysis for TiO₂ and synthesized photocatalysts.

Table S4 The SSA and the average pore diameter of the nano-sized TiO₂ and synthesized photocatalysts.

Table S1 Model of the Analytical Instruments

Analytical Instrument	Model	Notes
XRD	Bruker, D8 Advance	Excitation Voltage: 40,000 V; Current: 30 mA; Diffraction Angles: 20-75°.
FE-SEM	JEOL, JSM-6330 TF	
EDS	FEI, Quanta 200	
XPS	Thermo Scientific, Escalab 250	The binding energy of 284.8 eV for carbon 1s line was employed to calibrate the binding-energy scale of the XPS.
UV-Vis spectrometer	JASCO, V-670	Equipped with an integrating sphere. BaSO ₄ was used as a reference to estimate the band gap of semi-conductors.
Specific Surface Area Analyzer (SSAA)	Micromeritics, ASAP 2020	

Table S2 Crystallite sizes of Ag- and Fe-doped TiO₂ determined by Scherrer Equation.

Photocatalysts	Crystalline phases	Diffraction angles (2θ)	FWHM	Crystallite sizes (nm)
TiO ₂	Anatase	25.342	0.981	8.35
1% Ag-dopedTiO ₂	Anatase	25.502	0.928	8.78
3% Ag-doped TiO ₂	Anatase	25.349	0.905	9.00
5% Ag-doped TiO ₂	Anatase	25.473	0.880	9.23
1% Fe-doped TiO ₂	Anatase	25.444	0.801	10.23
3% Fe-doped TiO ₂	Anatase	25.437	0.887	9.18
5% Fe-doped TiO ₂	Anatase	25.421	0.996	8.36

Table S3 Results of EDS analysis for TiO₂ and synthesized photocatalysts.

Photocatalysts	Molar ratios of different elements in phtocatalysts (%)				
	O	Ti	Ti:O	Ag	Fe
TiO ₂	67.66	32.34	1:2.1	-	-
1% Ag-doped TiO ₂	67.33	31.36	1:2.1	1.31	-
3% Ag-doped TiO ₂	65.54	31.48	1:2.1	2.98	-
5% Ag-doped TiO ₂	64.18	30.59	1:2.1	5.23	-
1% Fe-doped TiO ₂	74.23	24.85	1:3.0	-	0.92
3% Fe-doped TiO ₂	73.36	23.87	1:3.1	-	2.77
5% Fe-doped TiO ₂	70.79	24.35	1:2.9	-	4.86

Table S4 The SSA and the average pore diameter of the nano-sized TiO₂ and synthesized photocatalysts.

Photocatalysts	SSA (m ² /g)	Average pore diameter (nm)
TiO ₂	139.35	5.58
1% Ag-doped TiO ₂	145.32	4.99
3% Ag-doped TiO ₂	126.66	6.63
5% Ag-doped TiO ₂	119.35	9.71
1% Fe-doped TiO ₂	160.58	4.72
3% Fe-doped TiO ₂	153.39	4.84
5% Fe-doped TiO ₂	120.94	7.18

Figure Caption

Fig. S1 Spectrum of fluorescent lamps used in this study.

Fig. S2 Adsorption of acetone in the batch PC reactor.

Fig. S3 Photolysis and catalysis (without visible light) of acetone in the batch PC reactor.

Fig. S4 X-ray diffraction patterns of (a) TiO_2 , (b) Ag-doped TiO_2 , and (c) Fe-doped TiO_2 calcined at 500 °C.

Fig. S5 FE-SEM images of TiO_2 calcined at 500 °C with the magnifications of 75,000 and 100,000.

Fig. S6 FE-SEM images of 1-5% Ag-doped TiO_2 calcined at 500 °C with the magnifications of 75,000 and 100,000.

Fig. S7 FE-SEM images of 1-5% Fe-doped TiO_2 calcined at 500 °C with the magnifications of 75,000 and 100,000.

Fig. S8 XPS spectra of (a) $\text{Ti}2p$ for TiO_2 , 3% and 5% Ag-doped TiO_2 ; (b) $\text{Ag}3d$ for 3% and 5% Ag-doped TiO_2 ; (c) $\text{Ti}2p$ for 3% and 5% Fe-doped TiO_2 ; (d) $\text{Fe}2p$ for 3% and 5% Fe-doped TiO_2 .

Fig. S9 UV-Vis spectra of (a) Ag-doped TiO_2 and (b) Fe-doped TiO_2 calcined at 500°C.

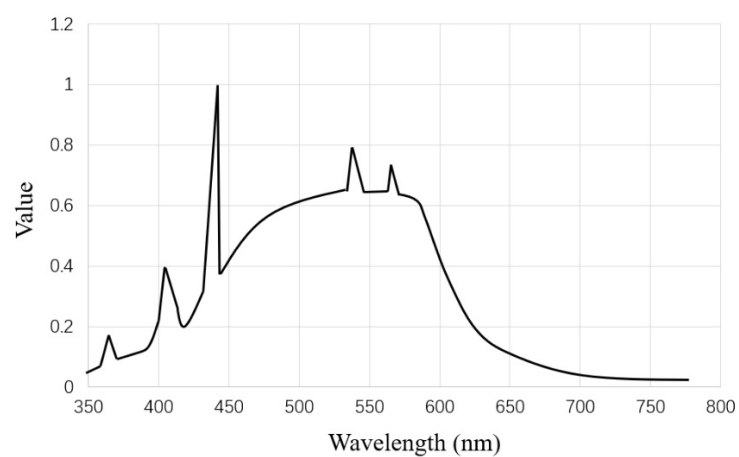


Fig. S1 Spectrum of fluorescent lamps used in this study.

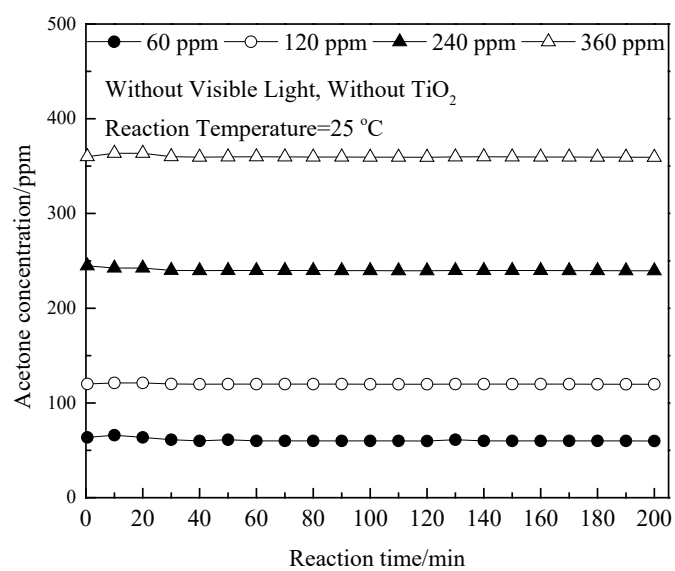


Fig. S2 Adsorption of acetone in the batch PC reactor.

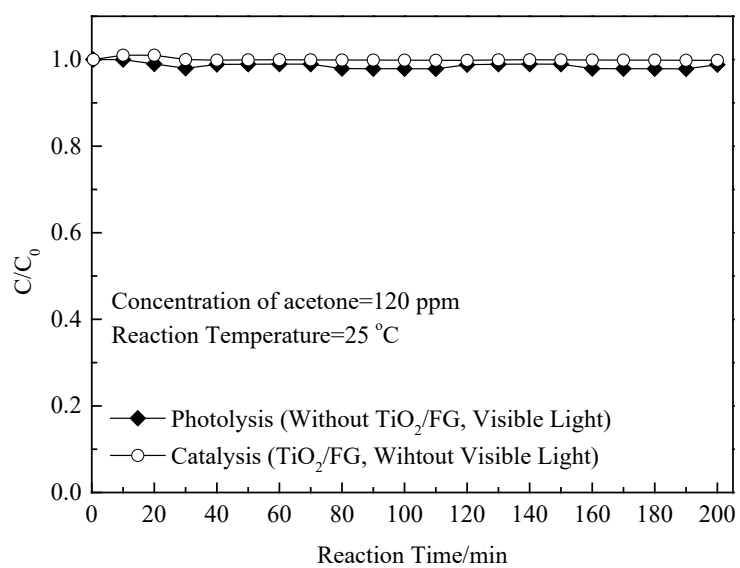
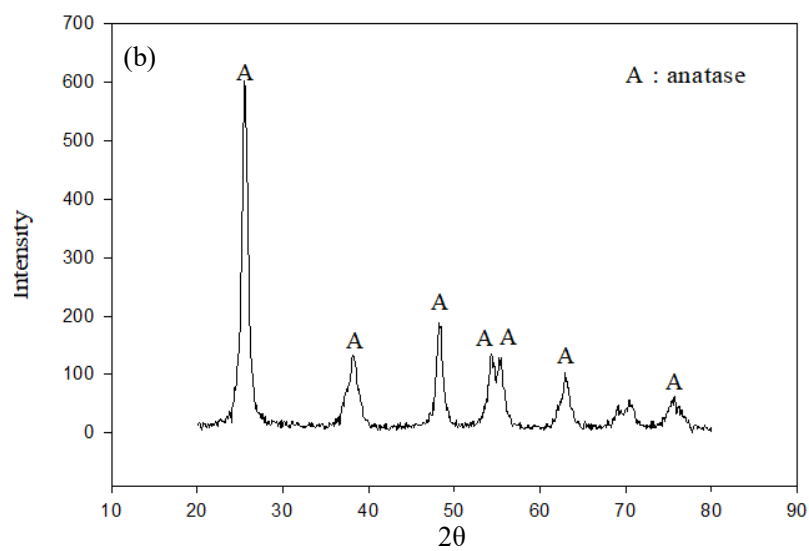
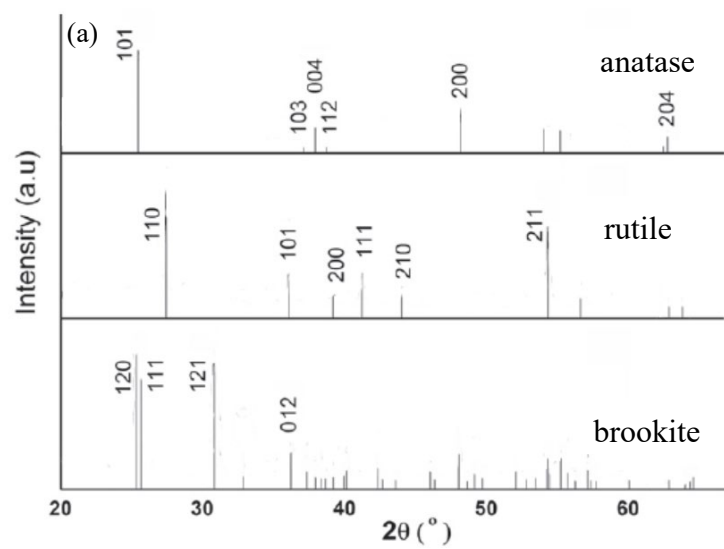


Fig. S3 Photolysis and catalysis (without visible light) of acetone in the batch PC reactor.



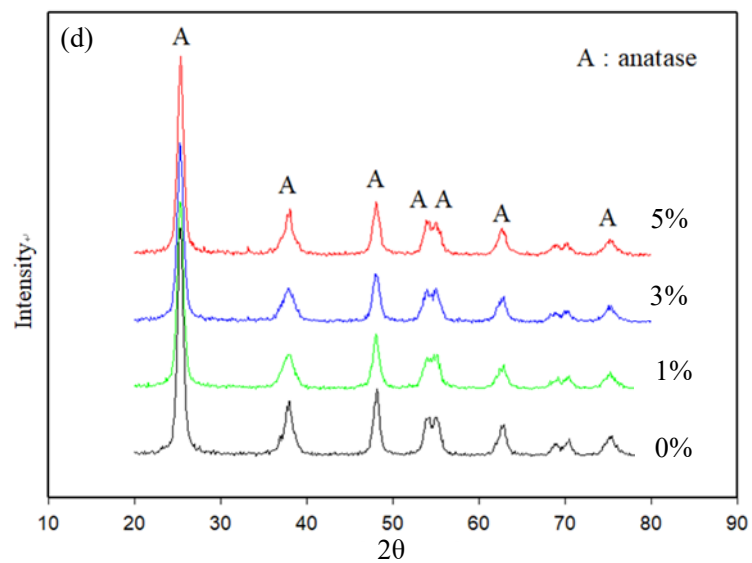
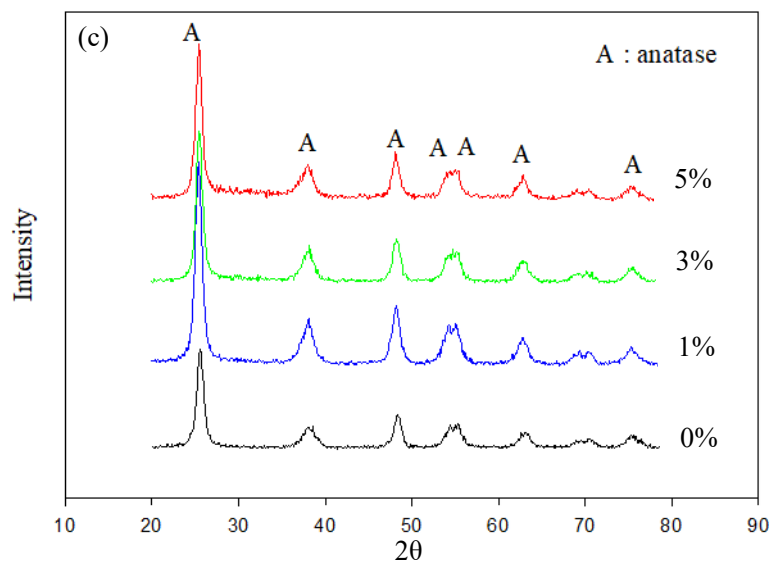


Fig. S4 X-ray diffraction patterns of (a) standard card pattern of TiO₂ anatase (JCPDS card no. 21-1272); rutile (JCPDS card no. 21-1276); brookite (JCPDS card no. 29-1360) (b) TiO₂, (c) Ag-doped TiO₂, and (d) Fe-doped TiO₂ calcined at 500°C.

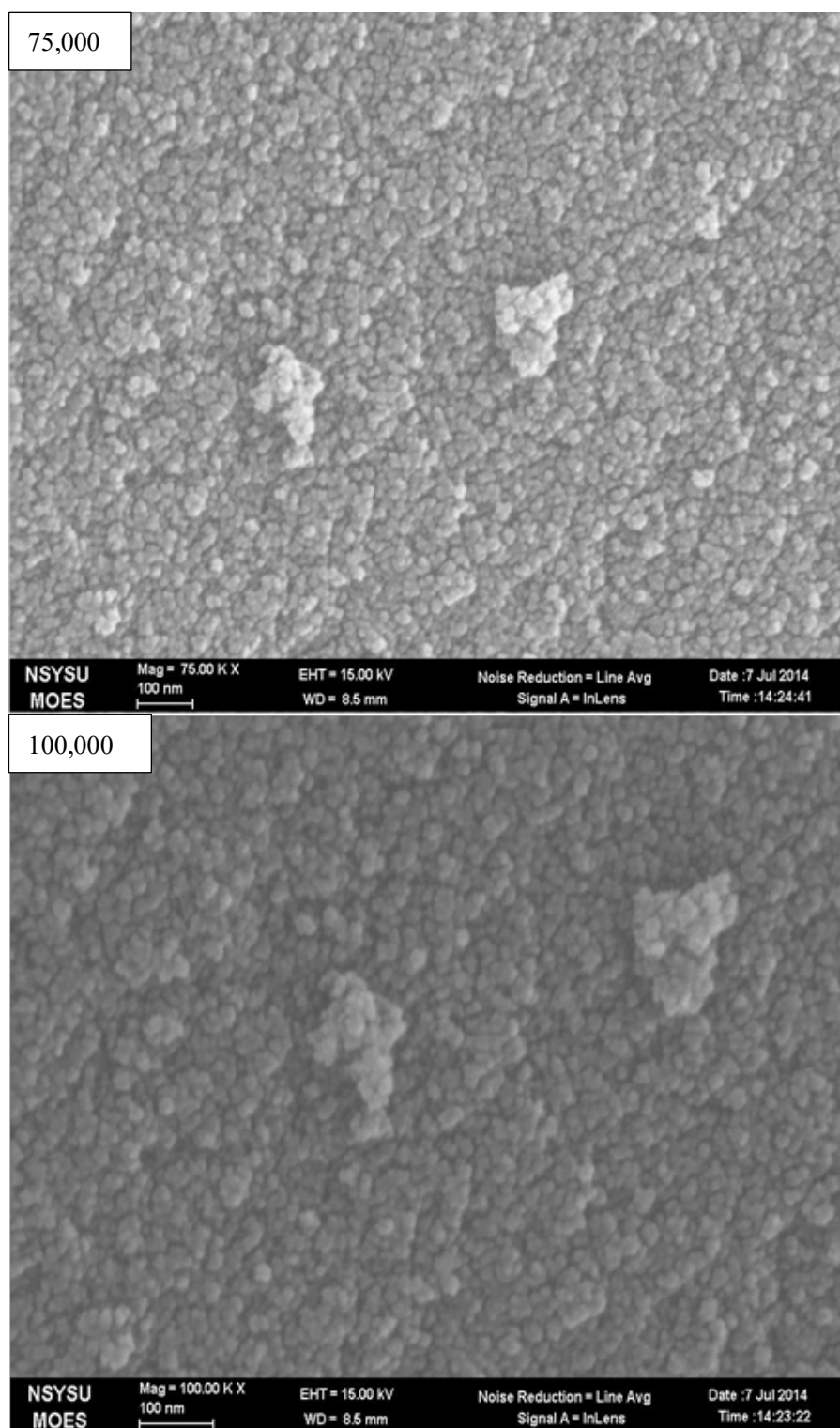
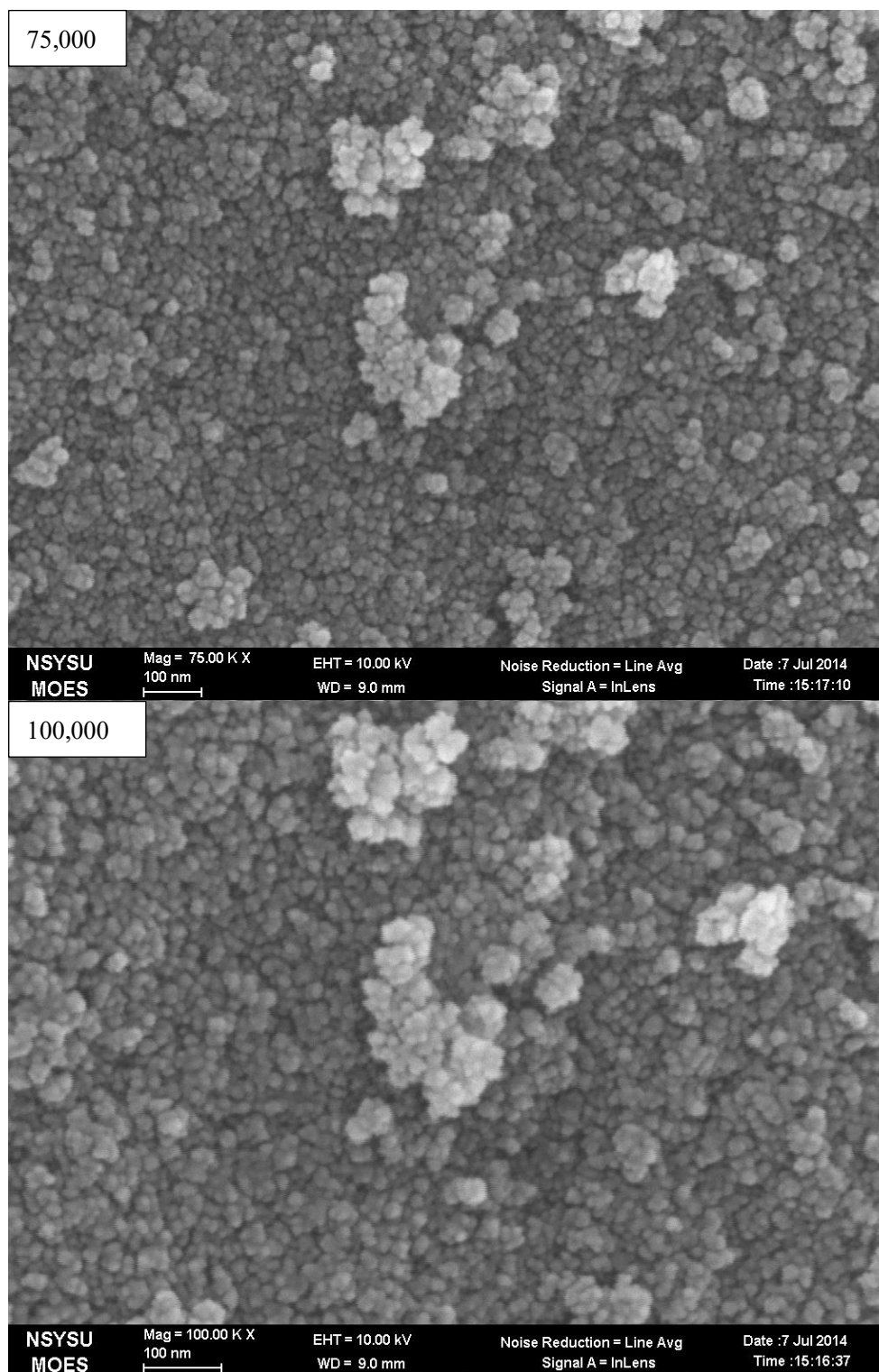
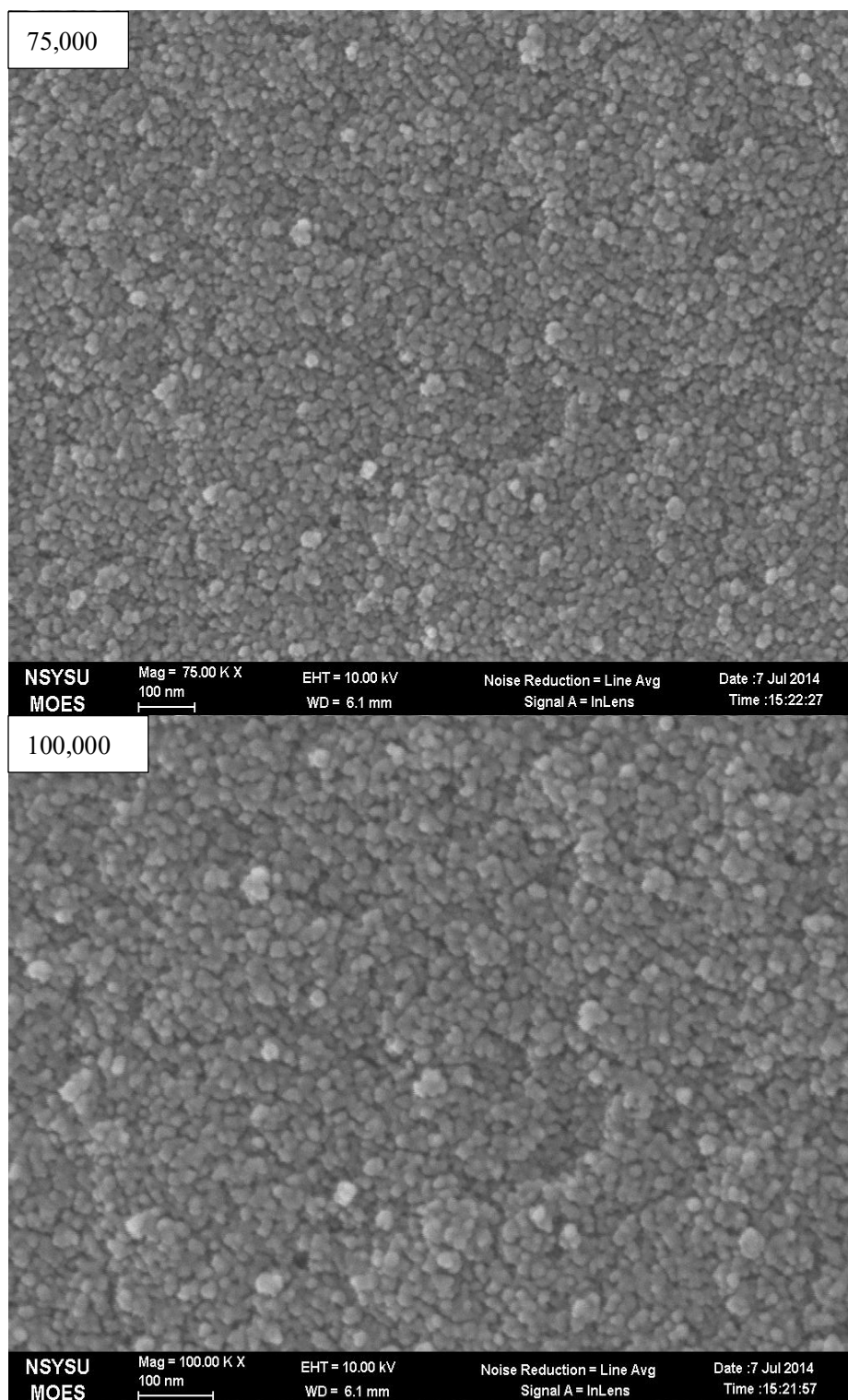


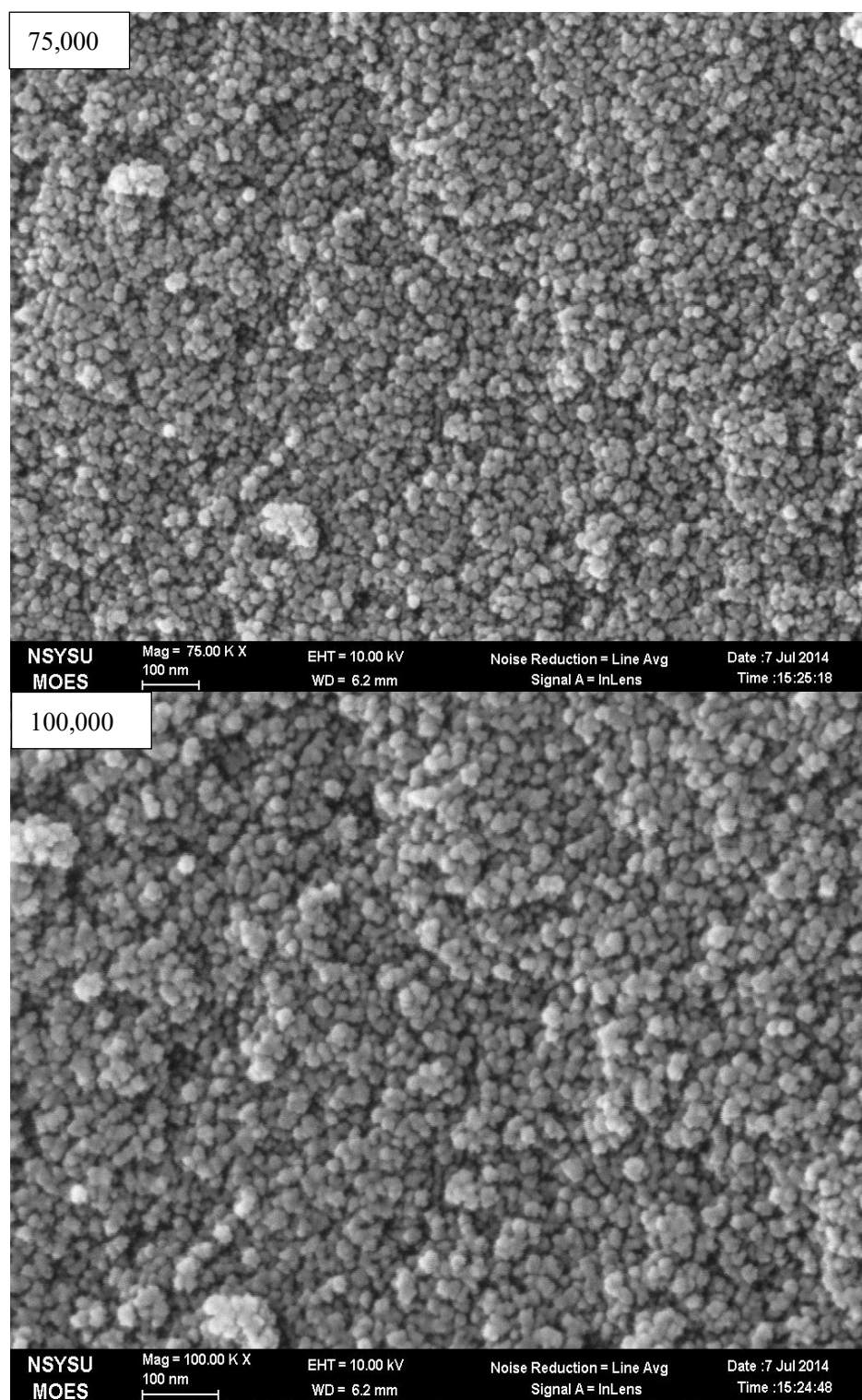
Fig. S5 FE-SEM images of TiO₂ calcined at 500°C with the magnifications of 75,000 and 100,000.



(a) 1% Ag/TiO₂

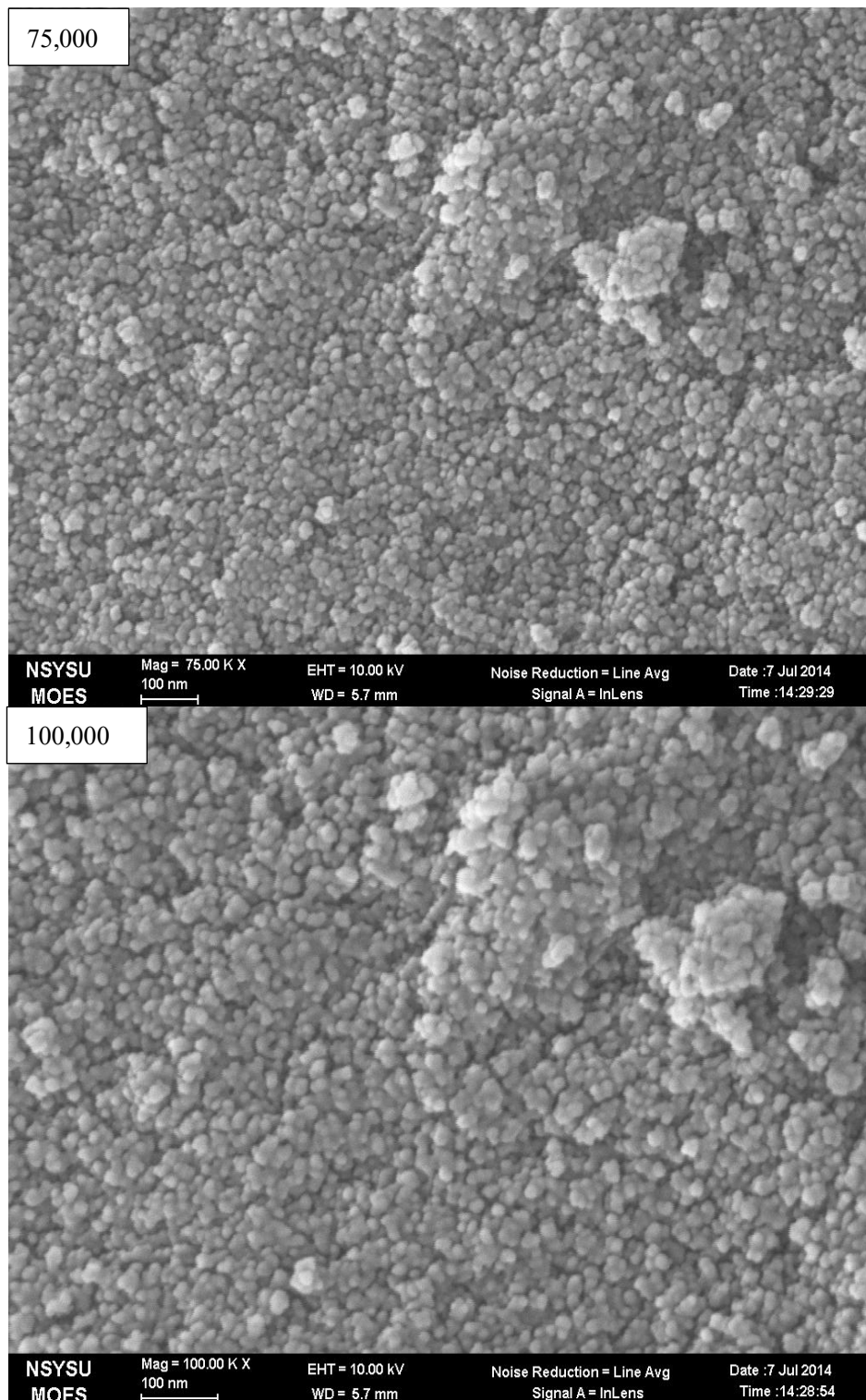


(b) 3% Ag/TiO₂

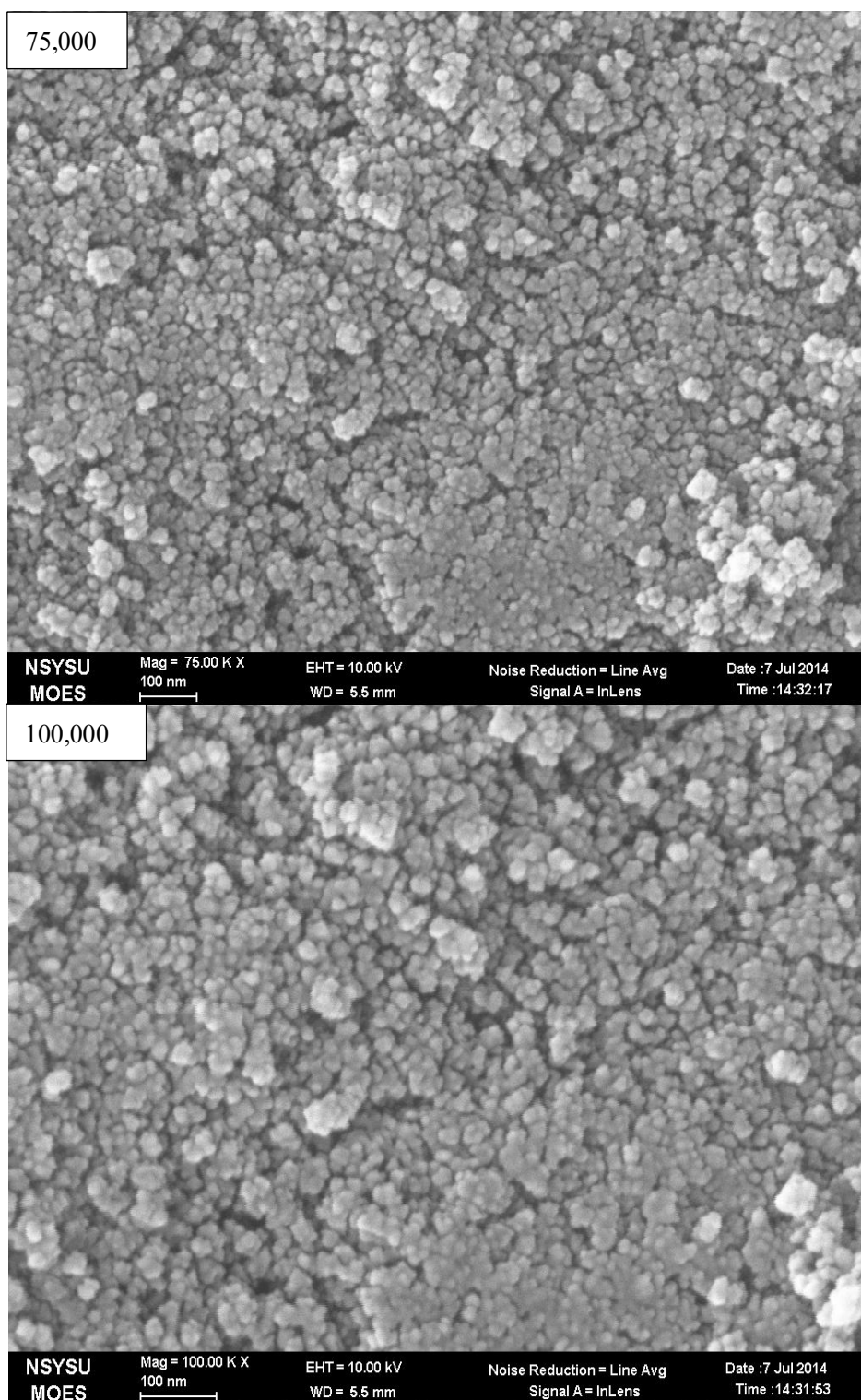


(c) 5% Ag/TiO₂

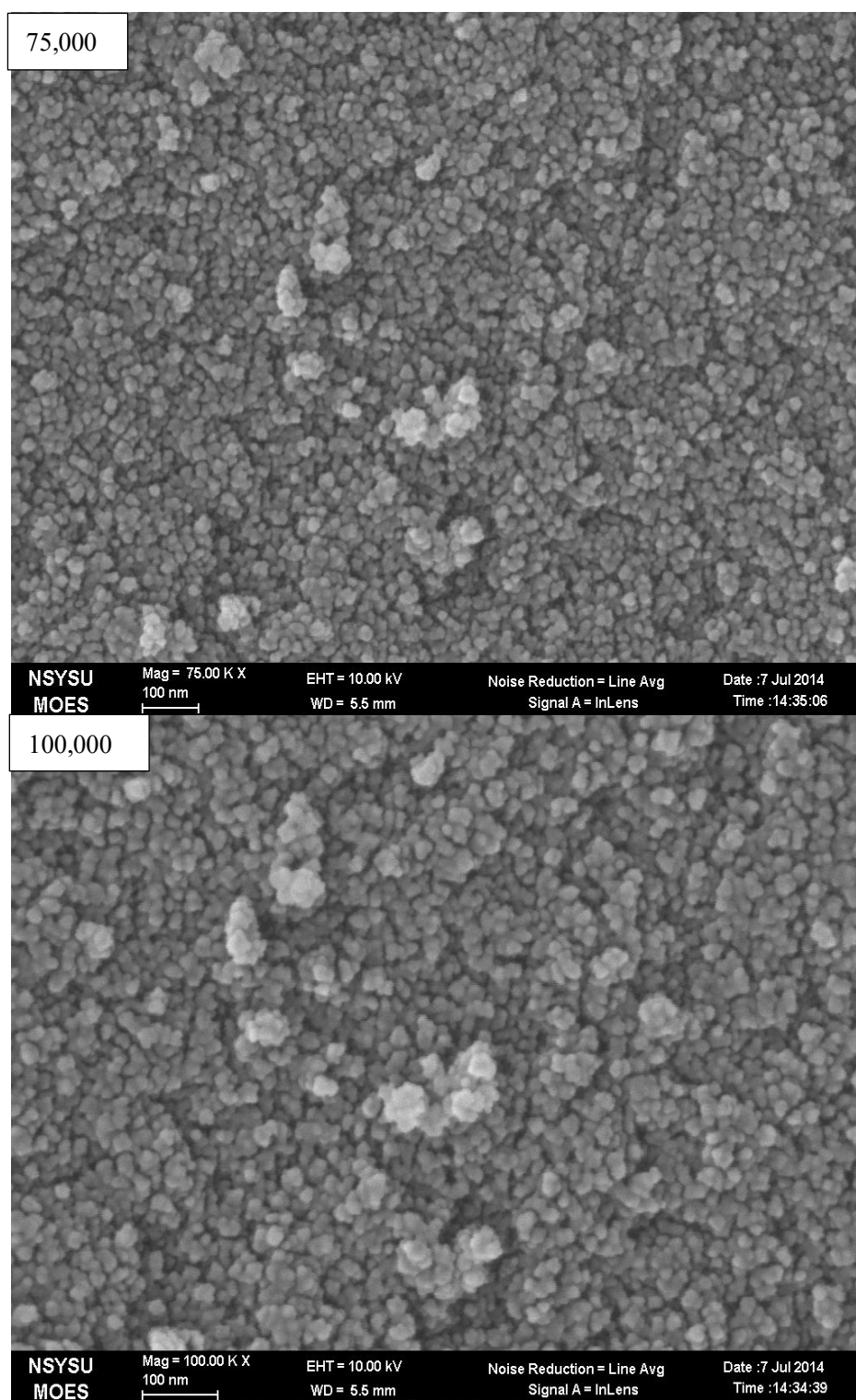
Fig. S6 FE-SEM images of 1-5% Ag-doped TiO₂ calcined at 500°C with the magnifications of 75,000 and 100,000.



(a) 1% Fe/TiO₂

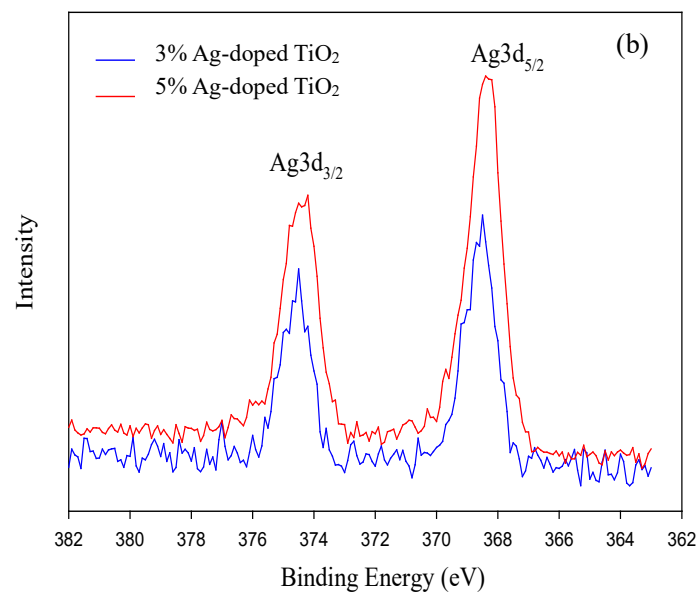
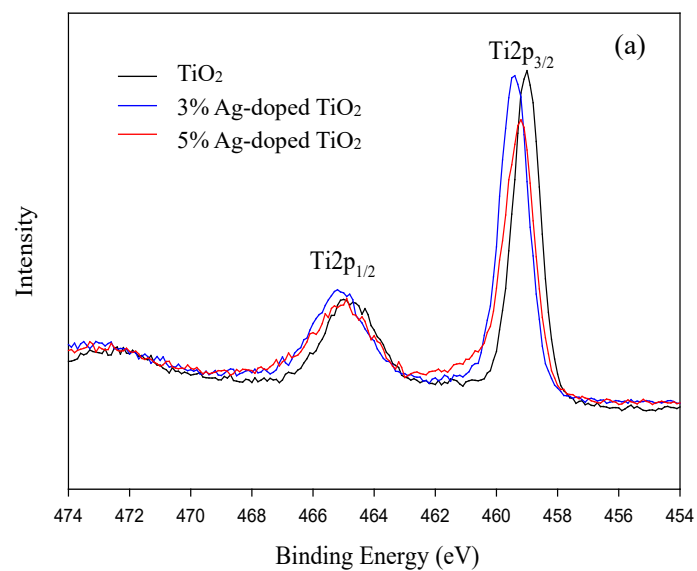


(b) 3% Fe/TiO₂



(c) 5%Fe/TiO₂

Fig. S7 FE-SEM images of 1-5% Fe-doped TiO₂ calcined at 500°C with the magnifications of 75,000 and 100,000.



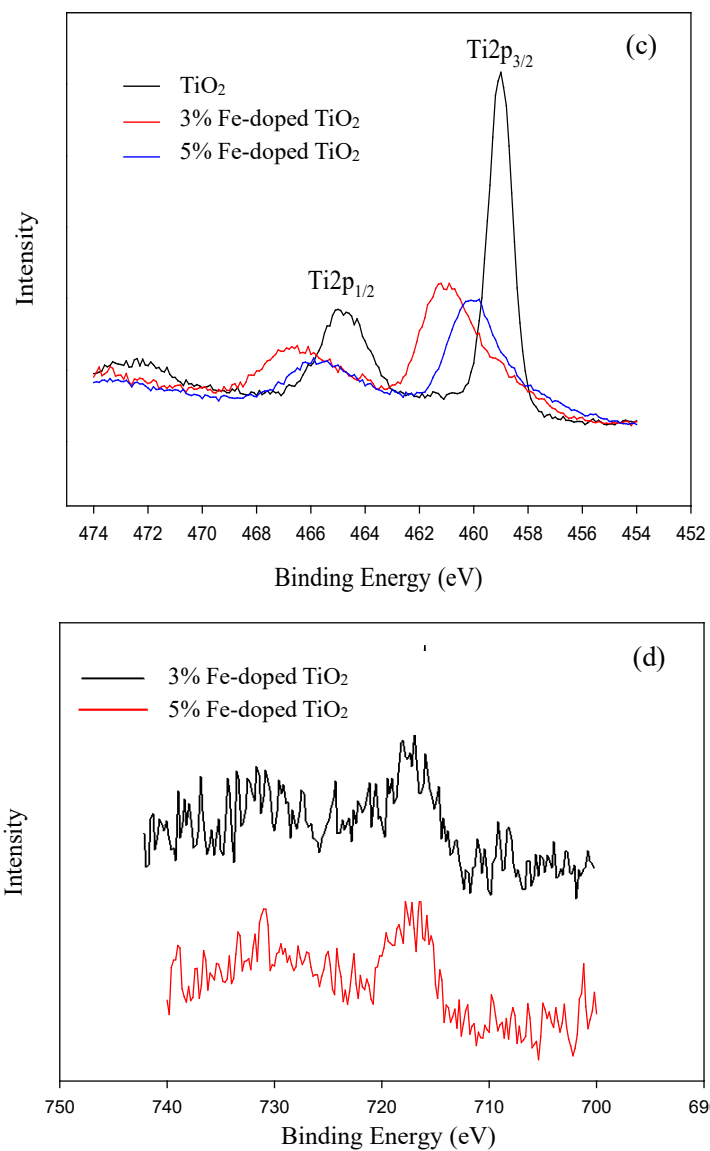


Fig. S8 XPS spectra of (a) Ti2p for TiO₂, 3% and 5% Ag-doped TiO₂; (b) Ag3d for 3% and 5% Ag-doped TiO₂; (c) Ti2p for 3% and 5% Fe-doped TiO₂; (d) Fe2p for 3% and 5% Fe-doped TiO₂.

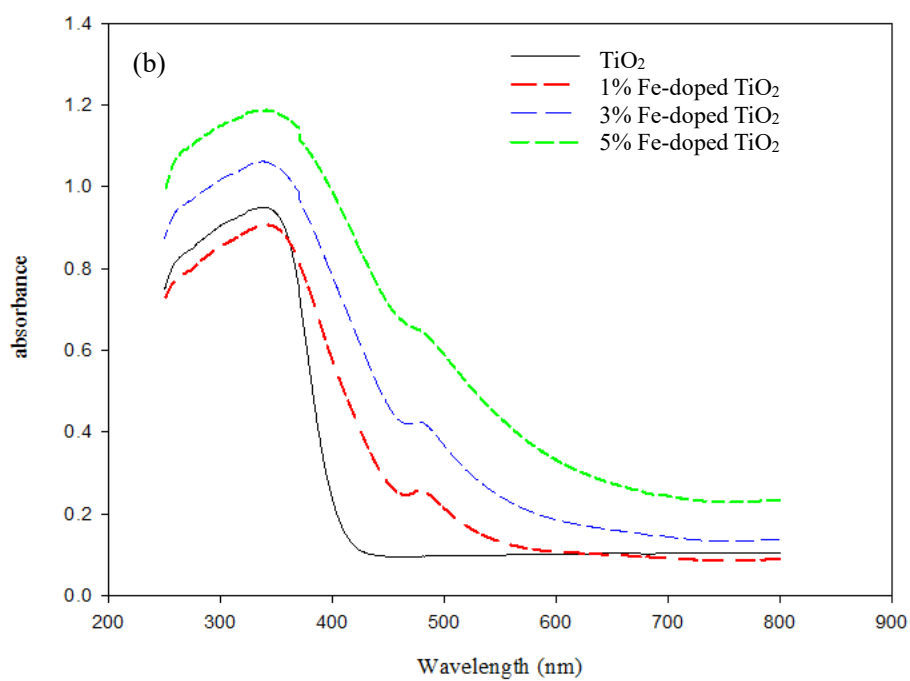
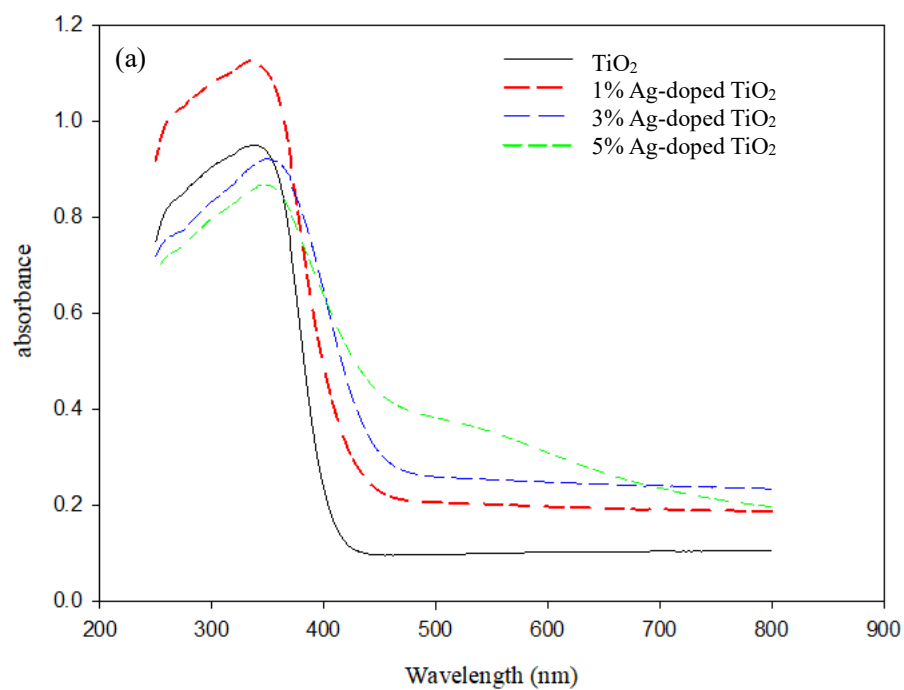


Fig. S9 UV-Vis spectra of (a) Ag-doped TiO_2 and (b) Fe-doped TiO_2 calcined at 500 °C.