

RESEARCH PAPER

## Photocatalyst Ag@N/TiO<sub>2</sub> Nanoparticles: Fabrication, Characterization, and Investigation of the Effect of Coating on Methyl Orange Dye Degradation

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### ABSTRACT

In this research, N-doped TiO<sub>2</sub> (N/TiO<sub>2</sub>) nanoparticles have been synthesized by a sol-gel method. N/TiO<sub>2</sub> nanoparticle has been coated with Ag metal by photochemical method. Triethylamine, N(CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>, have been used as precursors of Nitrogen, titanium tetraisopropoxide (TTIP), Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>, used as precursors of titanium and Ag(NO<sub>3</sub>)<sub>2</sub> used as precursors of Silver in synthesis of these nanoparticles. The photocatalytic activity has been perused for degradation of Methyl Orange (MO) as model of natural pollutants. Synthesized nanoparticles were analyzed by X-ray diffraction spectroscopy, Fourier transform spectroscopy, scanning electron microscopy, and energy dispersive of X-ray spectroscopy and diffuse-reflectance of Ultraviolet-visible spectroscopy. Results illustrated that under both visible and ultraviolet light, N/TiO<sub>2</sub> nanoparticles had medium activity but with coating, the activity in each area efficiently improved. The presence of 1.5% Ag coated on N/TiO<sub>2</sub> (with 2:1 mole ratio) resulted to the highest activity under visible and Ultraviolet irradiation in the catalyst.

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### INTRODUCTION

Nanostructured titanium dioxide (TiO<sub>2</sub>) is widely used as a photocatalyst for the degradation of environmental pollutants in water and air. The physicochemical properties of TiO<sub>2</sub>, such as thermal and chemical stability, relatively high photocatalytic activity, low toxicity and low cost make TiO<sub>2</sub> the most interesting photocatalyst for environmental remediation [1]. The anatase phase has been applied as an excellent photocatalyst in purification [2]. This process is accomplished by activation of photocatalyst using ultraviolet or visible light to produce primarily hydroxyl and superoxide radicals which are the active sites on TiO<sub>2</sub> surfaces for oxidizing organic compounds and antibacterial to water vapor and carbon dioxide

[3]. TiO<sub>2</sub> with a wide band gap about 3.2 eV needs to UV irradiation for degradation of contaminants which constitute 4% of the sunlight [4]. Many research groups have studied the synthesis of particular TiO<sub>2</sub> that can effectively be activated by visible light, the major portion of solar light. Reports demonstrate that doping of TiO<sub>2</sub> with various transition metal and nonmetal can be shifted the optical absorption edge of TiO<sub>2</sub> from UV range to visible range [5-7]. Recently, intensive attempts have been directed to improve the photocatalytic treatment of TiO<sub>2</sub> under visible light using metal ions (such as Fe, Co, Ag, Ni) [8-10] and nonmetal elements (e.g. C, N, F, S) [11,12]. Nitrogen can be inserted into TiO<sub>2</sub> crystal lattice. Nitrogen is more attractive than all other anionic elements due to

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its closer atomic size to oxygen, small ionization energy, metastable center formation and stability [13,14]. Some investigations have shown that slightly depositing of noble metals on TiO<sub>2</sub> surface can effectively capture the photo-induced electrons or holes, omit the recombination of electron-hole pairs and also extend the light response of TiO<sub>2</sub> in the visible light region [15-17]. It is also known that loading of silver nanoparticles can boost the photocatalytic activity of TiO<sub>2</sub>. The enhancement is ascribed to the fact that the loading of silver makes the formation of Schottky barriers at each Ag@TiO<sub>2</sub> contact regions, thus promoting charge separation and preventing the recombination of electron-hole pairs and leaving holes in the valence band of TiO<sub>2</sub> [18, 19].

In this work, firstly nanocrystalline nitrogen-doped TiO<sub>2</sub> (N/TiO<sub>2</sub>) was successfully synthesized through the sol-gel method, subsequently N/TiO<sub>2</sub> has been coated with silver metal through the photochemical method. The photocatalytic activity of N/TiO<sub>2</sub> nanoparticles was plenty enhanced by decreasing the Ag@N/TiO<sub>2</sub> band gap. Then, the photocatalytic activity of the Ag@N/TiO<sub>2</sub> catalyst was tested for the removal of methyl orange dye under UV and visible light irradiation.

## MATERIALS AND METHODS

All the chemicals were purchased from Merck and were used without any further purification. Tetraisopropyl orthotitanate (TTIP, C<sub>12</sub>H<sub>28</sub>O<sub>4</sub>Ti, MW=284.25 g/mole, d=0.96 g/mL) was used as TiO<sub>2</sub> source, Triethylamine (N(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>, MW=101.19 g/mole, d=0.7255 g/mL) was used as Nitrogen precursor and Silver nitrate (AgNO<sub>3</sub> Mw=169.87 g/mole, d=4.35 g/mL) was used as Silver precursor. Deionized water was obtained from ultra-pure water system (type smart-2-pure TKA, Germany). Methyl Orange (MO, M.W. = 695.58 g mole<sup>-1</sup>) dye was provided by Alvan Co., Iran.

### Physical measurements

XRD patterns have been recorded from a diffractometer of Philips Company with X'pert pro filtered by Cu K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ). The diffractograms have been recorded in the 2 $\theta$  range of 10-80°. The morphology and size of nanoparticles have been characterized using scanning electron microscope (SEM) (Philips XL-30ESM) equipped with an energy dispersive X-ray (EDX). The diffuse reflectance UV-Vis spectra (DRS) of the samples have been recorded by an Ava

Spec-2048TEC spectrometer. FT-IR spectra of the samples have been recorded on a Nicolet Magna IR 550 spectrometer. The extent of MO degradation was monitored using UV-Vis spectrophotometer (Perkin Elmer Lambda2S).

### Synthesis procedure

The mole ratio of N/TiO<sub>2</sub> in preparation of Ag@N/TiO<sub>2</sub> was 2:1 for N/TiO<sub>2</sub>. The N/TiO<sub>2</sub> prepared by sol-gel method. The products were synthesized using TTIP as TiO<sub>2</sub> source and triethylamine as N sources. The preparation process was as follow: TTIP, ethanol and acetic acid with the mole ratio of 1:2:2 were mixed together and the mixed solution was stirred for 3 h. After that, the nitrogen source, deionized water and PVP with the molar ratio of 2:10:1 were mixed together then added to the first mixed solution. The resultant solution was kept under continuous stirring for 2 h and then under irradiation with a high intensity ultrasonic of 20 kHz in a sonication cell for 15 min, result is the formation of a transparent solution of TiO<sub>2</sub> sol. The prepared solution was kept for 24 h in the dark for nucleation process. After this period, the gel was dried at 100 °C, and subsequently the catalyst was deformed into fine powder and calcined in a muffle furnace at 500 °C for 2 h. This precursor has been dispersed in deionized water by ultrasonic irradiation. Then, Required amount of Ag salt (for covering of N/TiO<sub>2</sub>) have been added to solution and stirred for 30 min and for prevent of oxidation of metals the solutions have been deoxygenated and irradiated for 18 h by UV light. The result solution has been dried in oven on 120 °C.

### Photocatalytic decomposition of methyl orange

Photocatalytic activity of N/TiO<sub>2</sub> and Ag@N/TiO<sub>2</sub> nanoparticles was evaluated by the decomposition of MO solution under UV and visible light irradiation. The degradation reaction was performed in a quartz photocatalytic reactor. The photocatalytic degradation was carried out with 100 mL aqueous MO solution (10 mg L<sup>-1</sup>) containing 100 mg of catalyst nanoparticles. This mixture was aerated for 30 min to reach adsorption equivalency. Then, the mixture was placed inside the photoreactor in which the vessel was 40 cm away from the UV and 25 cm away from visible lamps. The quartz vessel and light source were placed inside a black box equipped with a fan to prevent UV leakage. The experiments were accomplished at room temperature and the pH of

MO solution was adjusted to 2-3 [20]. Aliquots of the mixture were taken at periodic pauses during the irradiation and after centrifugation they were analyzed with the UV-Vis spectrometer.

## RESULTS AND DISCUSSION

### XRD analysis

Fig. 1 shows the X-ray diffraction patterns of the Ag@N/TiO<sub>2</sub> with different weight percentages of Ag. In these patterns have not been observed any peaks of Ag and all of diffraction peaks have been closed to TiO<sub>2</sub> nanocrystals which shows that Ag ions uniformly have been dispersed among the anatase crystallites. The nanocrystalline anatase structure was confirmed by (1 0 1), (0 0 4), (2 0 0), (1 0 5) and (2 1 1) diffraction peaks [20]. Characteristic peaks of anatase were observed at 2θ values 25.62°, 38.1°, 48.33°, 54.20°, 55.33°, 62.03°, 69.1°, 70.59°, and 75.41° that illustrate the structure of supplied doped-TiO<sub>2</sub> was anatase (JCPDS no. 36-1451). The crystallite size measurements were done using the Scherrer equation:  $D_c = 0.9\lambda / \beta \cos\theta$  where β is the width at half maximum intensity of the observed diffraction peak, and λ is the X-ray wavelength (Cu Kα radiation, 0.154 nm) [21]. The estimated crystallite size is about 37 nm.

### FT-IR spectra

The FT-IR spectra of 1.5 weight percentage (Wt%) of Ag covered N/TiO<sub>2</sub> (1.5%Ag@N/TiO<sub>2</sub>)

have been illustrated in Fig. 2. The broad intense band below 1200 cm<sup>-1</sup> is due to Ti-O-Ti vibrations. Two absorption peaks in this spectrum have been corresponded to stretching vibrations of the O-H and bending vibrations of the adsorbed water molecules around 3350-3450 cm<sup>-1</sup> and 1620-1635 cm<sup>-1</sup>, respectively. In synthesis procedure for preparation of TiO<sub>2</sub> a lot of deionized water has been applied to enhance the nucleophilic attack to Ti precursors and caused to a super-fast condensation and preparing of TiO<sub>2</sub>. On the other hand, presence of remained alkoxy groups could be decreased the rate of formation of less dense anatase phase [7].

### SEM and EDS analysis

Fig. 3 shows SEM image of 1.5% Wt Ag coated on N/TiO<sub>2</sub> catalyst. It is clear that 1.5% Wt Ag coated on N/TiO<sub>2</sub> is composed of big particles which are aggregation of small and relatively uniform particles with diameter from 40 to 80 nm.

The EDS data of 1.5% Wt Ag coated on N/TiO<sub>2</sub> sample (Fig. 4) shows a peak around 0.4 and 0.5 keV and another intense peak appears at 4.5 and 4.9 keV for Ti. The peaks due to nitrogen, oxygen and silver are clearly distinct at 0.3, 0.6 and 4 keV, respectively. These results confirm the existence of Ti, O, N, and Ag atoms in the catalyst structure.

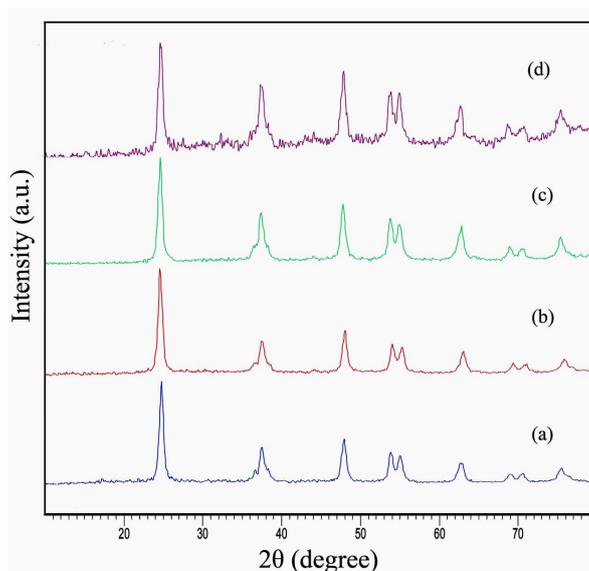


Fig. 1. XRD patterns of covered N-doped TiO<sub>2</sub> with (a) 0.5 % (b) 1% (c) 1.5% (d) 2% weight percentage of Ag

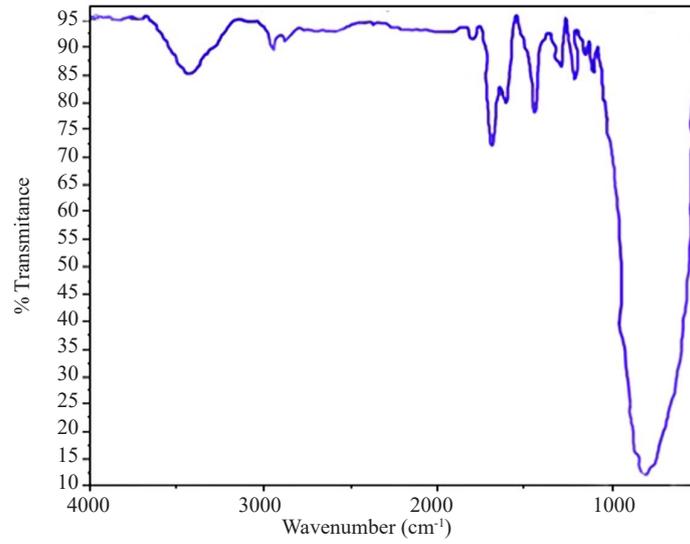


Fig. 2. FTIR spectra of covered N-doped TiO<sub>2</sub> with 1/5% of Ag

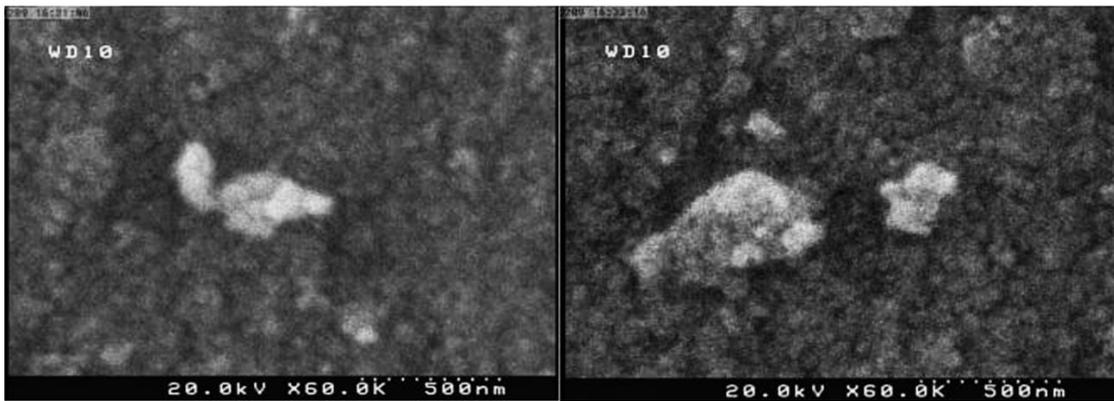


Fig. 3. SEM images of 1.5% Wt Ag@N/TiO<sub>2</sub>

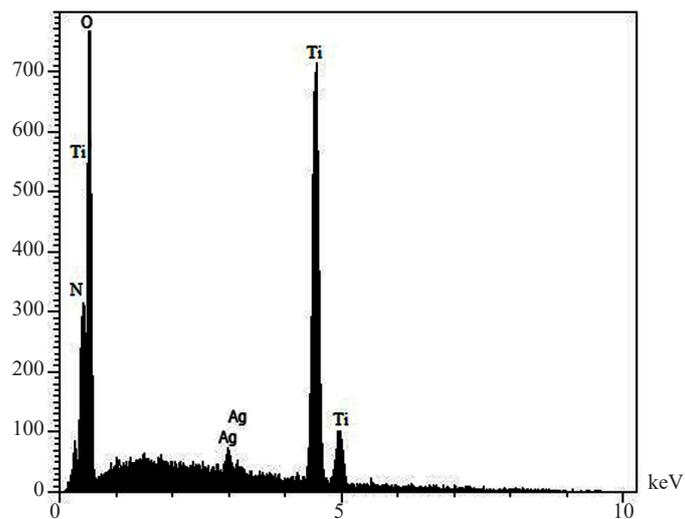


Fig. 4. EDS spectrum of 1.5% Wt Ag@N/TiO<sub>2</sub>

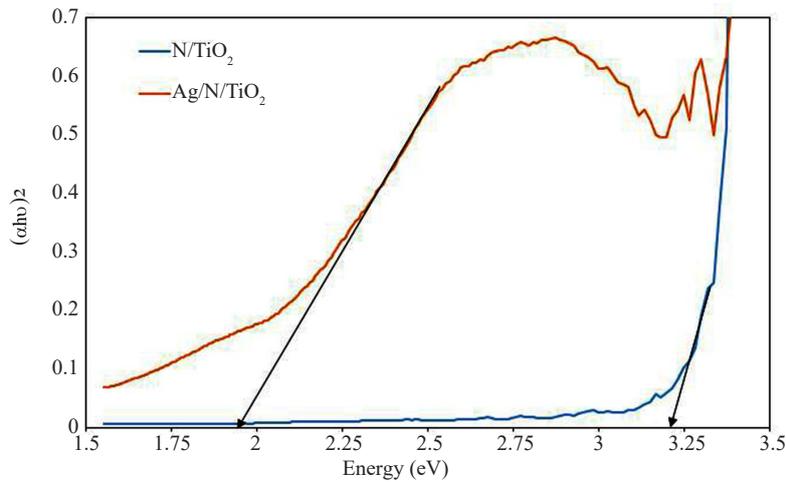


Fig. 5. DRS spectra of covered N-doped TiO<sub>2</sub> with 0%, 0.5 %, 1%, 1/5% and 2% weight percentage of Ag

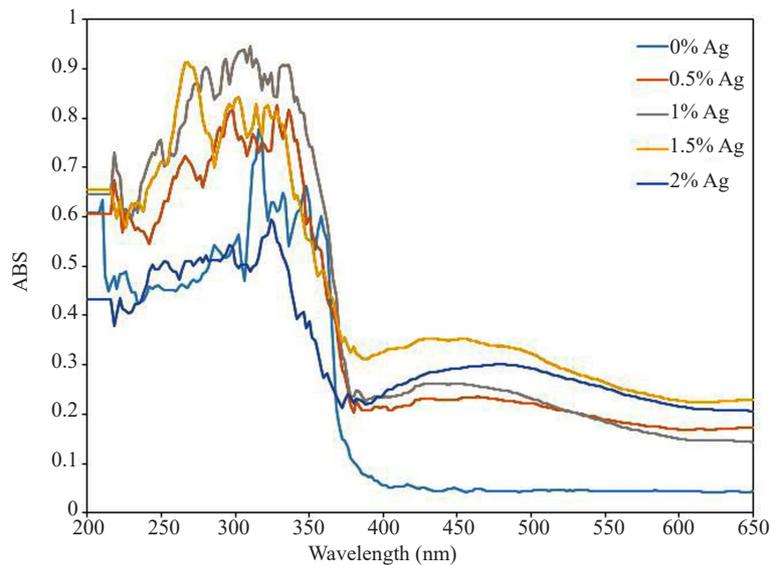


Fig. 6. The band gap for samples N-doped TiO<sub>2</sub> and 1.5% Wt Ag@N-doped TiO<sub>2</sub>

#### UV-Vis Diffuse Reflectance Spectroscopy (DRS)

The electronic bands of the different titania samples were studied and corresponding spectra are provided in Fig. 5. The absorption spectrum of TiO<sub>2</sub> consists of a single broad intense absorption around 400 nm due to the charge-transfer from the valence band to the conduction band [22]. As shown in Fig. 6, covering of N/TiO<sub>2</sub> by different amount of Ag causes the red shift of the absorption peaks to higher wavelength (visible region). The band gap of Ag@N/TiO<sub>2</sub> has changed from 3.24 eV in N/TiO<sub>2</sub> to 1.9 eV for 1.5%Ag@N/TiO<sub>2</sub> sample that shown in Fig. 6.

#### Photocatalytic degradation

Degradation of MO under UV and visible irradiation has been followed by UV-Vis spectroscopy and the results have been represented in Fig. 7 and Fig. 8. The degradation of methyl orange under visible and UV light by N/TiO<sub>2</sub> nanoparticles shows 74% degradation after 240 min and 86.3% after 30 min, respectively. Fig. 7 and Fig. 8 has been shown the photocatalytic behavior of Ag covered to N/TiO<sub>2</sub> with different percentage of Ag. After covering of N/TiO<sub>2</sub> with metal the recombination of electron and hole-pair has been reduced and the photocatalytic behavior has meliorated. The

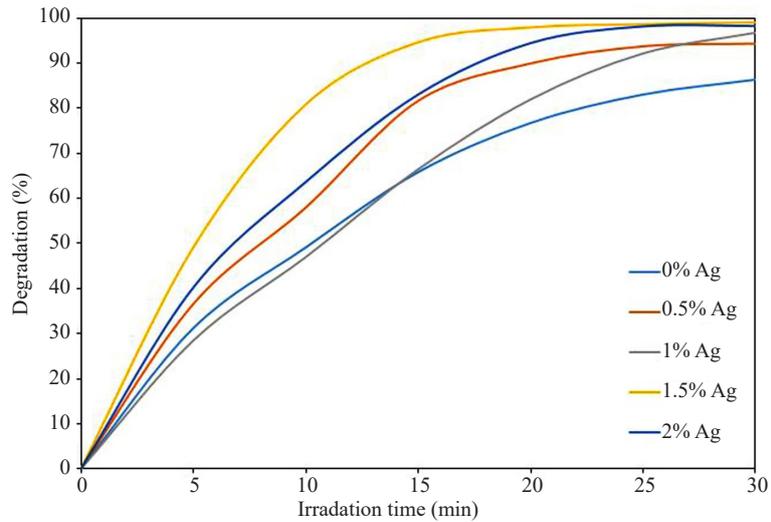


Fig. 7. Photocatalytic activity of covered N-doped TiO<sub>2</sub> with 0%, 0.5 %, 1%, 1/5% and 2% weight percentage of Ag under UV light

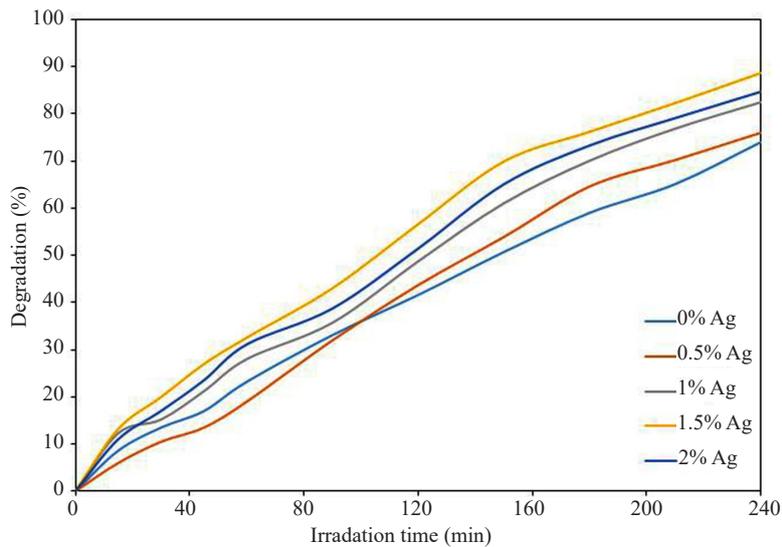


Fig. 8. Photocatalytic activity of covered N-doped TiO<sub>2</sub> with 0%, 0.5 %, 1%, 1/5% and 2% weight percentage of Ag under visible light

photocatalytic behavior in covering all percentage have been increased. but, the best photocatalytic activity has been observed for 1.5% of Ag that shows 89% degradation after 240 min of visible light irradiation and 99% after 30 min of UV light irradiation.

## CONCLUSIONS

N/TiO<sub>2</sub> and Ag@N/TiO<sub>2</sub> nanoparticles were prepared by the sol-gel and photochemical method, respectively. From all of the samples

only anatase phase was confirmed from the XRD results. From the XRD, SEM-EDX, UV-Vis and FT-IR results, it was confirmed that the incorporation of Ag in N/TiO<sub>2</sub> decreases the grain size, shifts the absorption peaks to higher wavelengths (red shift) and lowers the surface area due to agglomeration of the particles. The photocatalytic degradation of MO under UV and visible irradiation revealed higher activity in the presence of the Ag coated on N/TiO<sub>2</sub> than the N/TiO<sub>2</sub>. Among the Ag coated on N/TiO<sub>2</sub> samples,

the 1.5% Ag@N/TiO<sub>2</sub> catalyst exhibited the highest photocatalytic activity, while under visible and UV irradiation.

#### CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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