Removal of 4-Nitrophenol from Water Using Ag–N–P-Tridoped TiO₂ by Photocatalytic Oxidation Technique

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ABSTRACT: Photocatalytic oxidation using semiconductor nanoparticles is an efficient, eco-friendly, and cost-effective process for the removal of organic pollutants, such as dyes, pesticides, phenols, and their derivatives in water. In the present study, nanosize Ag–N–P-tridoped titanium(IV) oxide (TiO₂) was prepared by using sol–gel-synthesized Ag-doped TiO₂ and soybean (*Glycine max*) or chickpea (*Cicer arietinum*) seeds as nonmetallic bioprecursors. As-synthesized photocatalysts were characterized using X-ray diffraction, Fourier transform infrared, and ultra violet (UV)–visible spectroscopic techniques. Average crystallite size of the studied photocatalysts was within 39–46 nm. Whereas doped Ag in TiO₂ minimized the photogenerated electron–hole recombination, doped N and P extended its photoabsorption edge to visible region. Tridoping of Ag, N, and P in TiO₂ exhibited synergetic effect toward enhancing its photocatalytic degradation of 4-nitrophenol (4-NP), separately, under UV and visible irradiations. At three hours, degradations of 4-NP over Ag–N–P-tridoped TiO₂ under UV and visible radiations were 73.8 and 98.1%, respectively.

KEYWORDS: photocatalytic, degradation, 4-nitrophenol, tridoping, TiO₂

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Introduction

Organic compounds, such as dyes and phenols, released through industrial effluents are responsible for severe contamination of soil and surface water. These chemicals are carcinogenic and exhibit high toxicity and/or mutagenicity for living organisms, either directly or through some of their metabolites.¹ Nitrophenols, used as intermediates in the synthesis of pesticides, synthetic dyes, and other chemicals,² are priority environmental pollutants listed by the US EPA. The usual chemical, biological, microfiltration, and adsorption techniques adopted for the removal of organic pollutants from water are either inefficient or produce a large amount of sludge as a secondary pollutant.

In recent years, photocatalytic removal of organic pollutants from contaminated water, using semiconductors, such as titanium(IV) oxide (TiO₂) and ZnO, as photocatalysts, has emerged as an efficient, clean, and cost-effective alternative.^{3–7} Photogenerated electrons and holes (h⁺) at the semiconductor produce highly reactive hydroxyl (·OH) radicals in aqueous solution, which can degrade the organic compounds to their nontoxic end products, such as CO₂ and H₂O.

An ideal photocatalyst should be photoactive, chemically inert, resistant to photocorrosion, nontoxic, and of low cost. TiO₂ is known to possess all these characteristics. It possesses high ultra violet (UV) absorption capacity and stability, which make it suitable for different applications, such as electronics, ceramics, glass, and in photocatalytic degradation

of chemicals in water and air. However, because of the wide band-gap (3.2 eV) of TiO₂, it requires UV light for its use in photocatalytic applications. Due to the high cost of UV source, the use of TiO₂ as a photocatalyst for the large-scale treatment of polluted water is not cost effective. Moreover, as the UV component of the sunlight is only 3–5%, the photocatalytic efficiency of TiO₂ under solar radiation is poor.

In order to harness the visible range of the sunlight spectrum, several attempts have, earlier, been made to reduce the band gap of TiO₂ by different means and thus to increase its efficiency using solar energy. Such attempts include doping of metals and/or nonmetals^{6,8,9} and compositing high band photocatalysts with a low band gap photocatalyst.¹⁰ The simultaneous doping of metals and nonmetals into TiO₂ has attracted considerable interest since it could result in special characteristics and higher photocatalytic activity compared with single element doping in TiO₂.^{11–13}

Earlier, we have observed that codoping of Ag and N in TiO₂ exhibits synergetic effect in improving the photocatalytic degradation of methyl orange dye.⁶ In continuance of our studies in this area, we have tried here to investigate the effect of tridoping Ag–N–P in TiO₂ on its photocatalytic efficiency for the degradation of 4-nitrophenol (4-NP) in aqueous solution, separately, under UV and visible irradiations. 4-NP is used to manufacture drugs, fungicides, insecticides, and dyes. Its presence in water bodies through industrial effluents is a serious environmental concern. According to the US

Environmental Protection Agency (EPA), nitrophenols have toxic effects, such as irritation and inflammations of eyes, skin, and respiratory tract, which potentially cause cyanosis, confusion, unconsciousness, abdominal pain, and vomiting, when ingested. Therefore, developing an efficient and cost-effective technique for the removal of nitrophenols from contaminated water has attracted interest of the scientific community.

Materials and Methods

Chemicals. TiO_2 [molecular weight (MW): 79.87 g/mol, commercial], silver nitrate (AgNO_3 ; MW: 169.87 g/mol, 99.9% BLULUX), hydrochloric acid (HCl ; MW: 36.5 g/mol), sodium hydroxide (MW: 40 g/mol, BDH), chickpea (*Cicer arietinum* L.) and soybean (*Glycine max*) seeds, and 4-NP ($\text{C}_6\text{H}_5\text{NO}_3$; MW: 139.11 g/mol) were used in this study. The structure of 4-NP is given in Figure 1.

Methods.

Preparation of Ag-doped TiO_2 . Commercial TiO_2 (30 g) was mixed with 20 mL of 0.1 M AgNO_3 aqueous solution in a crucible, dried at 110°C for 30 minutes, and calcined at 400°C for four hours. The product was cooled to room temperature and ground to get a fine powder.

Preparation of Ag-N-P-tridoped TiO_2 . Chickpea (*C. arietinum* L.) or soybean (*G. max*) seeds (15 g) were cleaned with distilled water. The coatless seeds were treated with 100 mL of 5% HCl (v/v) solution for 12 hours to get rid of K^+ , Ca^{2+} , and S^{2-} ions and then washed with distilled water. As-prepared Ag-doped TiO_2 was separately mixed with the above-treated seeds, dried at 80°C for 24 hours, and calcined at 500°C for three hours.¹⁴

X-ray diffraction (XRD) analysis. XRD patterns of as-synthesized photocatalysts were obtained using an X-ray diffractometer (Bruker D8 Advance XRD) equipped with a Cu target generating a CuK_α radiation ($\lambda = 1.5406 \text{ \AA}$). The instrument was operated using an accelerating voltage, 40 kV, and an applied current, 30 mA, and the diffraction pattern was recorded over 2θ range $4\text{--}64^\circ$.

UV-visible absorption study. Photocatalyst powder (100 mg) was added to 100 mL of distilled water and vigorously stirred to get a homogeneous dispersion. Absorption spectra were recorded over 200–800 nm using a UV-visible spectrophotometer (SANYO, SP65, GALANAKAMP).

Fourier transform infrared (FTIR) study. FTIR spectrometer (SHIMADZU) was used for obtaining the FTIR spectra

of as-synthesized photocatalysts. In a typical run, powdered sample (10 mg), premixed with a drop of paraffin, was sandwiched between two parallel KBr plates, and the spectra were recorded over $400\text{--}4000 \text{ cm}^{-1}$.

Photocatalytic degradation study. Photocatalytic activities of synthesized nanomaterial were tested, separately, under UV and visible radiations using the degradation of 4-NP as a probe. A batch-type photocatalytic reactor (Fig. 2) consisting of a quartz tube provided with an inlet tube for purging air into the reaction mixture and an outlet tube for collecting the samples of reaction mixture at regular intervals was used. A UV lamp (PHILIPS) (11 W) and a tungsten filament lamp (100 W) each fixed at 10 cm above the reactor tube were used as ultraviolet and visible light sources, respectively.

The substrate (4-NP) solution (100 mL) at a specified concentration and a known amount of photocatalyst powder were mixed in the reactor tube. Before irradiation, the reaction mixture was allowed for sorbate-sorbent equilibrium in the dark for one hour. The reaction mixture was magnetically stirred with simultaneous air purging at a regular flow rate. Samples of reaction mixture, 5 mL each, were collected at regular intervals and centrifuged at 4000 rpm. The clear supernatant liquid was spectrophotometrically analyzed for the substrate (dye) content, and the absorbance values were recorded at 485 nm.

Percentage degradation of the substrate (4-NP) was calculated using the relation

$$\% \text{ Degradation} = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

where A_0 and A_t are the absorbance values at initial stage of reaction and at time t , respectively.

Figure 2. Components of batch-type photocatalytic reactor: (A) reactor tube made of Pyrex glass, (B) inlet tube for air purging, (C) outlet for collecting the reaction mixture, (D) radiation source, and (E) magnetic stirrer.

Figure 1. Structural formula of 4-nitrophenol.

Results and Discussion

XRD analysis. XRD patterns of the studied photocatalyst powders are presented in Figure 3. The observed diffraction peaks at $2\theta = 25.4, 37.7, 48.0, 54.4, 55.2,$ and 63.0° are from the crystal planes (101), (004), (200), (105), (211), and (118), respectively, of the anatase phase of TiO₂ (JCPDS Card Nos. 21-1272; JCPDS 84-1286).^{15–17} The broad and intense diffraction peaks suggest the small crystallite size of TiO₂.

The average crystallite size of each photocatalyst powder was calculated using Scherrer's formula:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (2)$$

where 0.9 is the shape factor, λ is the X-ray wavelength (0.154 nm) for CuK α , β is the full width at half maxima (in radians) for the diffraction peak observed at $2\theta = 25.4^\circ$ due to crystal plane (101), and θ is Bragg's angle.

The average crystallite size of the studied photocatalysts is presented in Table 1 and is in the range 39–46 nm. A decrease in particle size is observed upon doping the metal as well as the nonmetal.¹⁸ It may be due to the restriction of growth of TiO₂ on the doping metal (Ag). Such a decrease in the size of the photocatalyst upon doping a metal has also been observed by other workers. For example, doped Mo in TiO₂ restricted the size of the latter.¹⁹ In some cases, metal doping also causes intercrystalline cracking, resulting in the decrease of particle size. The observed XRD patterns of Ag-doped TiO₂ and Ag–N–P-tridoped TiO₂ are similar but broader compared to that of TiO₂. This suggests that doped Ag, N, and P are incorporated into the TiO₂ lattice.

Figure 3. XRD patterns: (A) TiO₂ (commercial), (B) Ag-doped TiO₂, (C) soybean-mediated Ag–N–P-tridoped TiO₂, and (D) chickpea-mediated Ag–N–P-tridoped TiO₂.

Table 1. Average crystallite size (D) of the studied photocatalysts obtained from XRD data using Scherrer's formula.

PHOTOCATALYST	2θ (DEGREE)	β (RADIAN)	D (nm)
TiO ₂ (commercial)	25.3	0.180	46
Ag-doped TiO ₂	25.3	0.209	39
Ag–N–P-tridoped TiO ₂ (Soybean-mediated)	25.5	0.182	41
Ag–N–P-tridoped TiO ₂ (Chickpea-mediated)	25.5	0.188	40

UV/visible diffuse absorption study. UV–visible absorption spectra of 0.1% (w/v) aqueous dispersion of the studied photocatalyst powders are presented in Figure 4. Absorption edges for TiO₂ (commercial), Ag-doped TiO₂, soybean-mediated Ag–N–P-tridoped TiO₂, and chickpea-mediated Ag–N–P-tridoped TiO₂ are 412, 440, 484, and 512 nm, respectively. The observed redshift in photoabsorption upon doping Ag, N, and P may be attributed to the creation of additional electronic levels by these elements between valence band (VB) and conduction band (CB) of the photocatalyst (TiO₂), by the doped elements.

Band gap energy of photocatalysts was calculated using the relation.²⁰

$$E_g = \frac{1240}{\lambda} \quad (3)$$

where E_g is the band gap energy in electron volt (eV) and λ is the wavelength (nm) corresponding to the absorption edge. Band gap energy values of the above photocatalysts thus obtained were 3.0, 2.8, 2.6, and 2.4 eV, respectively.

FTIR analysis of photocatalysts. FTIR spectra of Ag-doped TiO₂, soybean-mediated Ag–N–P-tridoped TiO₂, and chickpea-mediated Ag–N–P-tridoped TiO₂ photocatalysts are presented in Figure 5. The broad band over 3704–3000 cm^{–1} observed in all samples may be due to the vibrational mode of OH group of water,²¹ indicating the existence of small amount of water absorbed by the photocatalysts. Absorption bands observed at 680, 694, and 691 cm^{–1} are assigned to the stretching vibrations of Ti–O. Absorption peaks at 1695, 1638, and 1659 cm^{–1} are attributed to symmetric C–H stretching of alkanes in paraffin oil used as a dispersant. The weak absorptions at 1384 and 1129 cm^{–1} in case of Ag–N–P-tridoped photocatalysts are assigned to N–O bond stretch²² and P–O bond stretch,²³ respectively.

Photocatalytic degradation study. Plots of percentage degradation of 4-NP as a function of time under UV and visible irradiations are given in Figures 6 and 7, respectively. Ag-doped TiO₂ exhibited higher photocatalytic activity compared to undoped TiO₂ under both UV and visible radiations. It may be due to the minimization of electron–hole recombination due to the trapping of photoexcited electron by the doped Ag⁺ ions. Furthermore, the photocatalytic activity of

Figure 4. UV–visible absorption spectra: (A) commercial TiO_2 (absorption edge 412 nm), (B) Ag-doped TiO_2 (absorption edge 440 nm), (C) soybean-mediated Ag–N–P-tridoped TiO_2 (absorption edge 484 nm), and (D) chickpea-mediated Ag–N–P-tridoped TiO_2 (absorption edge 512 nm).

Figure 5. FTIR spectra of as-synthesized photocatalysts: (A) Ag-doped TiO_2 , (B) soybean-mediated Ag–N–P-tridoped TiO_2 , and (C) chickpea-mediated Ag–N–P-tridoped TiO_2 .

Figure 6. Plots of percentage degradation of 4-nitrophenol as a function of time under UV radiation using different photocatalysts.

Abbreviations: Tc, commercial TiO₂; AT, Ag-doped TiO₂; chickpea (ANPT), chickpea-mediated Ag–N–P-tridoped TiO₂; soybean (ANPT), soybean-mediated Ag–N–P-tridoped TiO₂.

Ag–N–P-tridoped TiO₂ was higher than that of Ag-doped TiO₂. This may be because doping of N and P in the photocatalyst (TiO₂) causes redshift of photoabsorption resulting in the harvesting of more photons in the visible region. Maximum photocatalytic degradations of 4-NP under UV and visible radiations over Ag–N–P-tridoped TiO₂ were 73.8 and 98.1%, respectively. Photocatalytic degradations of 4-NP over chickpea-mediated Ag–N–P-tridoped TiO₂ were marginally higher compared to those of soybean-mediated Ag–N–P-tridoped TiO₂. This could be due to the slightly lower particle size of the former. The observed highest degradation of 4-NP over Ag–N–P tridoped among the studied photocatalysts can be attributed to the cumulative effect of (a) minimization of

Figure 7. Plots of percentage degradation of 4-nitrophenol as a function of time under visible radiation using different photocatalysts.

Abbreviations: Tc, commercial TiO₂; AT, Ag-doped TiO₂; chickpea (ANPT), chickpea-mediated Ag–N–P-tridoped TiO₂; soybean (ANPT), soybean-mediated Ag–N–P-tridoped TiO₂.

electron–hole recombination by the doped silver and (b) extension of the photoabsorption in the visible region by doped N and P. Both these processes contribute, positively, in enhancing the photocatalytic degradation of the substrate (4-NP).

Mechanism of photocatalytic degradation of 4-Nitrophenol.

Photocatalytic degradation of 4-NP in aqueous solution is initiated by the absorption of a photon by a semiconductor (TiO₂) particle causing excitation of an electron from the VB to CB leaving behind a positively charged hole (h⁺) (step I). The hole at the valence bond (h⁺_{VB}), with a high oxidation potential, can directly oxidize the substrate (4-NP) to form the intermediate 4-NP⁺ that, subsequently, degenerates non-toxic simple products such as CO₂ and H₂O (step II). Alternatively, the hole (h⁺_{VB}) can combine with H₂O or hydroxyl (OH[−]) ion to generate hydroxyl radical (·OH) (steps III and IV). The hydroxyl radical being an extremely strong and non-selective oxidant ($E_0 = +3.06$ V)²⁴ causes the degradation of the substrate (4-NP) (step V).

Conclusion

Nanosize Ag–N–P-tridoped TiO₂ was prepared using sol–gel-synthesized Ag-doped TiO₂ and soybean (*G. max*) or chickpea (*C. arietinum*) seeds as nonmetallic bioprecursors. The synthesized material was characterized using XRD, FTIR, and UV–visible spectroscopic techniques. Tridoping of Ag, N, and P in TiO₂ exhibited synergetic effect for enhancing the photocatalytic activity of TiO₂ and hence an increase in the degradation of 4-NP. Degradations of 4-NP over Ag–N–P-tridoped TiO₂ under UV and visible radiations at three hours were 73.8 and 98.1%, respectively.

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Author Contributions

Conceived and designed the experiments: OPY. Analyzed the data: TA. Wrote the first draft of the article: OPY. Contributed to the writing of the article: OPY. Agreed with the article results and conclusion: OPY and TA. Jointly developed the structure and arguments for the article: OPY and TA. Made the critical revisions and approved the final version: OPY. All authors reviewed and approved the final article.

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