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Zirconium and silver co-doped TiO₂ nanoparticles as visible light catalyst for reduction of 4-nitrophenol, degradation of methyl orange and methylene blue



SPECTROCHIMICA ACTA



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HIGHLIGHTS

- Simple sol-gel synthesis of Zr and Ag co-doped TiO₂ nanoparticles is described.
- Effective photocatalysis for the reduction of nitrophenol and degradation of dyes shown.
- Recycling of photocatalyst up to 4 cycles discussed as promising industrial application.

G R A P H I C A L A B S T R A C T



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Introduction

Titanium dioxide (TiO_2) is a promising photocatalytic material due to its high stability, non-toxic nature & high performance in the mineralization of organic pollutants in air and water media and affordable cost [1–4]. However, photocatalytic processes with TiO₂ catalysts are mostly favoured under UV irradiation due to its

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ABSTRACT

Catalytic activity of Zr and Ag co-doped TiO_2 nanoparticles on the reduction of 4-nitrophenol, degradation of methylene blue and methyl orange was studied using sodium borohydride as reducing agent. The nanoparticles were characterized using X-ray diffraction, energy dispersive X-ray, high resolution transmission electron microscopy, selected area electron diffraction and UV–Vis spectroscopy. The rate of the reduction/degradation was found to increase with increasing amount of the photocatalyst which could be attributed to higher dispersity and small size of the nanoparticles. The catalytic activity of Zr and Ag co-doped TiO_2 nanoparticles showed no significant difference even after recycling the catalyst four times indicating a promising potential for industrial application of the prepared photocatalyst.

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large band gap (\sim 3.2 eV). This restricts the use of TiO₂ in practical applications because of the limited availability of UV radiation (only 5% of solar light). Hence, the focus of researchers has been on introducing dopants into TiO₂ to make the material absorb radiation visible region of the electromagnetic spectrum for its use in several applications. This approach of doping metals into TiO₂ has been proved to be a very useful in making visible light sensitive catalysts [5]. Similar approach has been reported to yield good results while two different metals were doped into ZnO or TiO₂ resulting in enhanced photocatalytic activity and unique

characteristics compared to doping of a single element [6–14]. 4-nitrophenol (4-NP), listed by the US EPA as a major pollutant, may induce blood disorders, eye, skin irritation, kidney and liver damage as well as poisoning of the central nervous system in humans and animals [15]. 4-NP has been used extensively as a raw material in chemical industry for manufacture of pesticides, herbicides, synthetic dyes, pharmaceuticals, for treatment of leather and in several military applications [16]. Several silver nanoparticle based catalysts have been reported for the reduction reaction of 4-NP. Naik et al. have reported the formation of Ag nanoparticles within the pores of mesoporous silica [17,18]. Zhang et al. have reported the preparation of tubular nanocomposites of Ag nanoparticles and silica with fairly uniform diameters in the range of 250-350 nm, by combining the single capillary electrospinning technique (for silica nanotubes as the supports) and an in situ reduction approach (for Ag nanoparticles) [19]. Liu et al. have modified halloysite (Al₂Si₂O₅(OH)₄·2H₂O,1:1 layer aluminosilicate) nanotubes by mercaptoacetic acid, ethylene glycol to encapsulate Ag nanoparticles and utilized it for the catalytic reduction of 4-NP [20].

Textile industries discharge effluents containing fairly large amounts dyes into water, some of which are mutagenic and carcinogenic to humans [21]. These effluents are characterized by their fluctuating pH with suspended particles, high oxygen demand, non-biodegradability and resistance to oxidation [22,23]. The complex structures of these dyes and their high refractoriness to degradation poses a big challenge in their decolorisation and complete mineralization. It has, therefore, become necessary to develop new promising materials for dye removal. Methylene blue (MB) causes nausea, hypertension, haemolysis and respiratory distress. To overcome the problems posed by different conventional dye removal agents, there has been a good amount of interest in inorganic composites of nano-scale dimensions. It may be seen that doping of ZnO or TiO₂ with transition elements induces crystal defects which can also change their photocatalytic properties. By electron trapping, Zr-doping possibly conquers the recombination of electrons and positive holes [24]. Furthermore, Zr is an isoelectric impurity belonging to deep energy level doping elements [25]. Methylene Blue (MB), Methyl Orange (MO), nitrobenzene and trichloroethylene have also been used as model pollutants to determine the activity of the photocatalyst [26–29].

Recovery of the catalyst is an important step in heterogeneous catalysis and to facilitate this, metal nanoparticles are usually dispersed onto solid matrices while preparing the heterogeneous catalysts. The supporting matrices used include carbon nanotubes, silica, titania, ceria and alumina [30–32]. Shi et al. [33,34] have synthesized stable gold nanoparticles using natural materials such as tannin or collagen. However, TiO_2 is still one of the most favorable supports for metal nanoparticles due to its thermal and chemical stability, non-toxic nature and relatively low cost. The present study reports the synthesis of Zr and Ag co-doped TiO₂ nanoparticles and their application as photocatalyst for the reduction of 4-NP, degradation of MB and MO using NaBH₄ as the reducing agent.

Materials and methods

Materials

Titanium (IV) isopropoxide from Sigma Aldrich, commercial azo dyes methylene blue, methyl orange, 4-nitrophenol and sodium borohydride (NaBH₄) from SD-Fine chemicals, hydrazine hydrate and zirconyl nitrate [ZrO(NO₃)₂] from SRL chemicals, tween 20 from Himedia were used in the present study. Milli-Q water was used in all the experiments.

Synthesis of Zr and Ag co-doped TiO₂ nanoparticles

A mixture of 5 mL of titanium (IV) isopropoxide in 50 mL isopropanol was added drop wise to 200 mL of distilled water maintained at pH 1.5 while the solution was continuously stirred. To this solution, required amount of aqueous solutions of AgNO₃ and ZrO(NO₃)₂ (0.2–0.8 mol%) were added drop wise and stirring continued for an additional 45 min. Then, a small aliquot of distilled water and 0.05 M hydrazine hydrate were added to it followed by 5 mL of tween 20 (capping agent to prevent agglomeration of particles) and the stirring was continued for an additional 30 min. The resultant sol was sonicated at 80 MHz for 90 min and then dried at 100 °C in a hot air oven for 24 h to get the dry gel. The gel was then calcinated at 450 °C to obtain required nanoparticle powder.

Characterization of co-doped TiO₂ nanoparticles

Powder XRD pattern was recorded using X-ray BRUKER D8 Advance X-ray diffractometer with Cu K α source (λ = 1.5406 Å). The crystalline phase of the nanoparticles was identified by comparing the major peak positions with standard JCPDS files. JEOL JEM 2100 high resolution transmission electron microscope (HRTEM) was used for imaging, SAED pattern and energy dispersive X-ray with an accelerating voltage of 200 kV at different magnifications. Diffuse reflectance spectra were recorded using JASCO V-670 UV–Vis spectrophotometer. Specific surface area of the sample was arrived at through nitrogen adsorption at 77 K using BET, Micromeritics ASAP2020 V4.01 (V4.01 H).

Catalysis

Reduction of 4-NP, degradation of MB and MO catalyzed by Zr and Ag co-doped TiO₂ nanoparticles was carried out at room temperature (30 °C). The reduction process was initiated by adding the 0.01 g doped nanoparticles to a solution containing 50 mL of 4-NP (0.1 mmol L⁻¹) and 5 mL of freshly prepared 0.05 M NABH₄ in a beaker while constantly stirring. The resultant suspension was irradiated with a 200 W Philips tungsten filament lamp ($\lambda > 400$ nm) which was placed at a distance of 5 cm from the suspension.

The catalytic degradation of MB and MO was carried out by adding1 mL of 0.01 M NABH₄ solution to 30 mL of 10^{-3} M MB and MO solutions respectively while stirring. After 5 min, 0.01 g of catalyst powder was added and the stirring continued. The kinetics of degradation of dyes was studied by taking a small aliquot of the sample and measuring the absorbance at specific λ_{max} at regular time intervals. Degradation was visualized by the disappearance of color of the dye solutions. In the case of MB, the blue color which was initially seen in an oxidizing environment turned colorless in the presence of reducing agent (NaBH₄) indicating the degradation of MB to leuco MB (LMB) [35].

The catalytic activity was verified by varying the amount of catalyst (0.01, 0.05 and 0.1 g) while monitoring the degradation processes through absorbance measurements on the UV–Vis spectrophotometer.

Results and discussion

Optical properties

Fig. 1(a) shows the UV–Vis absorption spectra of pure TiO₂, Ag doped TiO₂ & Zr and Ag co-doped TiO₂. A definite band edge in the UV region at 300–350 nm seen in the spectra which could be assigned to photo excitation from valence band to conduction



Fig. 1. (a) UV–Vis absorption spectra of nanoparticles and (b) optical energy gap (E_g) of nanoparticles.

band. It is interesting to note that the sample doped with silver (Ag doped TiO_2) has shown lower shift compared to Zr and Ag codoped TiO_2 (0.8 mol%), which has shown a significant red shift to higher wave length. This shift was observed to increase with increasing levels of Zr and Ag, indicating enhancement in the optical activity of the samples. The energy gap (E_g) was calculated from the equation [36]

$$(\alpha h \upsilon)^2 = A(h\upsilon - E_g)$$

where α is the absorption coefficient, *A* is a constant, and n = 2 for direct transition; n = 1/2 for indirect transition. The optical energy gap (E_g) was arrived at by extrapolation of Kubelka Munk plot of hv vs. $(\alpha hv)^2$ as shown in Fig. 1(b).

The energy gap values of the pure TiO₂, Ag doped TiO₂ & Zr and Ag co-doped TiO₂ nanoparticles were calculated to be approximately 3.21 eV, 2.87 eV and 2.71 eV respectively. Doping TiO₂ with transition metals (zirconium and silver) is usually accompanied with a decrease in band energy and increase in the wave length value (red shift). These results indicate that both Zr and Ag co-doped in the TiO₂ nanoparticles probably make the material exhibit a high photocatalytic activity in the visible region.

X-ray diffraction

Fig. 2 shows the X-ray diffraction pattern of the doped nanoparticles. In all the samples, anatase phase of the TiO₂ was confirmed by the 2θ peaks at 25.3°, 37.9°, 47.9°, 55.0° and 62.8°, while phases related to Ag and Zr were not identified in any of the samples due



Fig. 2. X-ray diffraction pattern of Zr and Ag co-doped TiO₂ nanoparticles.

to their low concentration levels. Doping of Ag and Zr did not result in significant changes in crystallinity. A slight shift in the d-spacing with discernible change in cell volume indicated the incorporation of dopants into TiO_2 . Since Ag and Zr have not shown any phase change, aggregates may have been formed on crystal borders and on the surface of the photocatalyst, thus facilitating visible light absorption as discussed earlier.

TEM and EDX analysis

The morphologies of the nanocrystals were analyzed using TEM. Fig. S1(a) and (b) (Supplementary data) show highly uniform nanocrystalline microstructure images of Zr and Ag co-doped TiO₂ nanoparticles confirming uniform grain sizes as estimated by XRD. Uniform distribution of particles ranging from 8 to 20 nm, with irregular sized spherical morphologies and slight agglomeration can also be seen from the images. The SAED pattern of the sample, shown in Fig. S1(c), has dark rings on the right corresponding to the standard polycrystalline diffraction rings for the anatase phase (indexed). In spite of great care, no sign of diffraction rings related to other phases were observed. EDX mapping (Fig. S1(d)) of the photocatalyst showed uniform dispersion of the doped metals onto the support, which is in agreement with the XRD results. HRTEM shown in Fig. S1(b) was used to obtain more discernible microstructure information to enable analyze the single grains and grain boundaries accurately. The BET (Brunauer-Emmet-Teller) surface area of the Zr and Ag co-doped TiO₂ has been measured as $309.2 \text{ m}^2/\text{g}$.

Catalysis

Catalytic reduction of 4-nitrophenol

The reduction of 4-NP using the metal nanocomposites in the presence of NaBH₄ was previously investigated by researchers for the efficient production of 4-aminophenol (4-AP) [37–40]. In addition, in the present study, this reaction was used as a model reaction to examine the effect of visible light on the catalytic activity of Zr and Ag co-doped TiO₂. From the results, it is clear that the prepared catalysts have efficiently assisted the reduction of 4-NP. Furthermore, no reduction of 4-NP was observed without the catalyst. After addition of NaBH₄ to 4-NP, intense yellow color was observed due to the formation of highly stable 4-nitrophenolate intermediate. Interestingly, after the addition of photocatalyst to the solution, there was a continuous decrease in the intensity of color till it finally turned colorless. This phenomenon was confirmed by the decrease in intensity of the absorption at 400 nm,



Fig. 3. UV–Vis absorption spectra for the reduction of 4-nitro phenol by NaBH₄ in the presence of (a) 0.01 g of photocatalyst and (d) plot of C_t/C_0 vs. time.

which is characteristic of 4-nitrophenolate (Figs. 3(a) and S2(b) and (c)). Also, appearance of two new absorbance peaks at 295 and 230 nm which showed increase with progress of time indicated the increase in concentration of 4-AP. It was noticed that, intensity of the 4-AP peak was not proportional to decrease in the 4-NP concentration, probably due to the difference in the molar extinction co-efficient of 4-nitrophenolate and 4-AP [41].

The results of the visible light photocatalytic reduction of 4-NP in aqueous solution showed that doping of Zr and Ag greatly improved the efficiency of TiO_2 nanocrystallites. The improvement of visible light photocatalytic activity could be due to the modification of TiO_2 with Ag and Zr, which could increase the separation efficiency of photogenerated electrons and holes in TiO_2 , and the improvement of photo stability of TiO_2 is attributed to a considerable decrease in the surface defect sites of TiO_2 after doping of Zr and Ag.

The effect of the amount of Zr and Ag co-doped TiO₂ nanoparticles on the rate of reduction of 4-NP to 4-AP was investigated using different amounts of the catalyst ranging from 0.01 to 0.1 g, while keeping the other parameters unchanged. Fig. 3(d) shows plot C_t/C_0 vs. time for different amounts of catalyst used for reduction of 4-NP in the presence of NaBH₄ at room temperature. As expected, the catalytic efficiency and reduction percentage (Fig. S5(a), in Supplementary data) of the photocatalyst have been observed to increase with increasing amount of the catalyst. When the catalyst added was 0.01 g, the reduction time was observed to be 28 min for conversion of 4-NP to 4-AP and the same got shortened to 16 min and 8 min when 0.05 g and 0.1 g of photocatalyst was used.

Catalytic degradation of methyl orange

Today, environmental protection has become extremely important for human beings and some toxic and stable dye molecules like MO show potential danger to the environment [42]. Hence, the present study attempts to use Zr and Ag co-doped TiO₂ nanoparticles for catalytic degradation of MO. Figs. 4(a) and S3(b) and (c) show the visible light catalytic degradation of MO. From the graphs, it can be seen that the MO absorption band at 463 nm disappeared and a new absorption band appeared at 247 nm because of formation of hydrazine derivative [43]. Maximum absorbance at 463 nm gradually has been observed to decrease with respect to time and the solution finally became colorless, indicating complete degradation of the dye. However when the same experiment was performed in the absence of photocatalyst, only 7% degradation was observed even after irradiation with tungsten lamp for 5 h. In the presence of Zr and Ag co-doped TiO₂ nanoparticles, but in the absence of NaBH₄, 18% degradation was observed after 5 h, which could be due to the adsorption of dye on the surface of doped nanoparticles. This observation confirmed that both catalyst and visible light are essential for effective degradation of dye.

To study the effect of amount of catalyst loading on the photodegradation of MO, experiments were carried out by varying its amount from 0.01 to 0.1 g for a fixed concentration of the dye. It was observed that time to degrade MO has decreased with increase in amount of catalyst from 0.01 to 0.1 g and when the amount of catalyst was 0.01 g, total degradation of MO has been seen in 30 min while 0.05 g and 0.1 g of photocatalyst have been able to complete the degradation in 12 min and 7 min respectively. Fig. 4(d) shows the plot of C_t/C_0 vs. time for different amounts of catalyst used during the reduction of MO. It can be seen that the



Fig. 4. UV–Vis absorption spectra for the degradation of methyl orange by NaBH₄ in the presence of (a) 0.01 g of photocatalyst and (d) plot of C_t/C_0 vs. time.

efficiency of the photocatalyst increased with increase in catalyst loading (Fig. S5(b), see Supplementary data). The increase in rate constant with increase in amount of photocatalyst could be attributed to an increase in number of active sites on photocatalyst surface which resulted in an increase in generation of hydroxyl radicals and thus led to an increase in the number of dye molecules degraded.

Catalytic degradation of methylene blue

The oxidized and reduced forms of MB have different absorption bands in the UV-Vis spectrum. Hence, the progress of decoloration or reduction reaction from MB to leuco MB (LMB) can be monitored by measuring the decrease in absorption of MB on UV–Visible spectrum at a λ_{max} of 664 nm. The time dependent electronic absorption spectrum of MB during visible light photo irradiation is presented in Figs. 5(a) and S4(b) and (c). After 30 min of irradiation under visible light in the presence of Zr and Ag codoped TiO₂ suspension, more than 95% of dye got degraded and the solution became colorless. Also, no new bands appeared in the UV-Vis spectrum, confirming the absence of reaction intermediates during the degradation process. The effect of amount of photocatalyst on degradation of MB was also studied. In the presence of mixed photocatalyst and visible radiation, more than 95% of dye got degraded after 30 min of irradiation while only 32% degradation was observed in the presence of photocatalyst without irradiation and only 11% degradation of the dye was observed in the absence of photocatalyst even after 3 h of irradiation. These experiments demonstrate that both visible light and a photocatalyst are essential for effective degradation of MB. This could be attributed to the fact that when Zr and Ag co-doped TiO₂ nanoparticles are



Fig. 5. UV–Visible absorption spectra for the degradation of methylene blue by NaBH₄ in the presence of (a) 0.01 g of photocatalyst and (d) plot of C_t/C_0 vs. time.

irradiated with the visible light, electrons get promoted from the valence band to the conduction band of the semiconducting oxide to give electron–hole pairs. The potential of the valence band (h_{VB}) is positive enough to generate hydroxyl radicals at the surface and the potential of the conduction band (e_{CB}) is negative enough to reduce molecular oxygen. The hydroxyl radical is a powerful oxidizing agent and attacks organic pollutants present at or near the surface of photocatalyst (Zr and Ag co-doped TiO₂).

In order to determine the effect of amount of photocatalyst on photodegradation of MB, experiments were performed by varying the amount of catalyst from 0.01 to 0.1 g. The rate of degradation was observed to increase as the amount of catalyst was increased from 0.01 to 0.1 g (Fig. S5(c), see Supplementary data). This could be due to increase in the number of photons with increase in the number of Zr and Ag co-doped TiO₂ nanoparticles which the dye molecules absorb. Fig. 5(d) shows the plot of C_t/C_0 vs. time for 0.1 g of catalyst. It can be seen that rate of degradation increased with increase in catalyst loading. The time for complete degradation of MB was observed to come down from 30 min to 9 min with increase in amount of catalyst from 0.01 to 0.1 g.

Recovery and reuse of catalyst in catalytic processes is of major importance for industry, since the use of catalytic process significantly contributes to lowering the operational cost and wastewater treatment cost. To explore the advantage of Zr and Ag-doped TiO₂ photocatalyst and the applicability and reuse of catalysts was verified for the reduction of 4-NP, degradation of MO and MB (Fig. S6, see Supplementary data). Experiments were performed where the photocatalyst was recovered (0.1 g) and reused by keeping all other parameters constant. The results revealed that Zr and Ag co-doped TiO₂ photocatalyst has shown very good activity for four successive catalytic runs without any significant loss in catalytic activity. The yield for the conversion 4-NP, MO and MB was 94%, 93% and 95% respectively for the four runs respectively. It could be concluded that Zr and Ag co-doped TiO₂ nanoparticles have good stability and they can be reused for at least 4 runs, thus showing a promising potential for practical applications.

Possible degradation mechanism of pollutants

Based on the above results and the available literature, the possible mechanism of photocatalytic degradation of three organic pollutants by Zr and Ag co-doped TiO₂ is shown in Fig. S7 (see Supplementary data). When the semiconductor is irradiated by visible light, an electron from valance band (VB) goes to conduction band (CB) leaving a hole in valance band. Generally, these electron-holes recombine to reduce the photocatalytic activity of semiconductors. But 'Ag' and 'Zr' present in the material, trap the electron from CB of TiO₂ which inhibits the electron-hole recombination. It is well established that 'Ag' traps the electrons from CB of TiO₂. The 'Zr' doping also suppresses the electron-hole recombination by electron trapping [24,44]. The electrons trapped by Ag and Zr produce more number of superoxide radical anions and at the same time VB holes of TiO₂ react with water to produce highly reactive hydroxyl (OH) radical. The superoxide radical anion and hydroxyl radical facilitate the degradation of dye.

Conclusion

In this work, Zr and Ag co-doped TiO_2 nanoparticles prepared through sol-gel process were used as effective photocatalyst for reduction of 4-NP, degradation of MO and MB under visible light irradiation. The effective loading of Zr and Ag decreased the optical band gap of TiO_2 significantly, making them suitable for visible light photocatalysis resulting in the better utilization of a much broader spectrum of solar radiation. The results confirm that both the catalyst and visible light are essential for effective reduction/ degradation of the organic pollutants. The experimental data prove that the amount of photocatalyst plays an important role in the catalytic reduction 4-NP and degradation of MO and MB.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2014.07.070.

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