ABSTRACT

The utilization of solar energy for the treatment of wastewater pollutants by photocatalysts has been considered a promising solution to address environmental problems. Herein, we have synthesized silver nanoparticle-doped strontium stannate (Ag-doped SrSnO₃) nanorods by hydrothermal method followed by ultrasonic treatment. The developed nanocomposites were applied for photocatalytic reduction of p-nitrophenol (4-NP) and methylene blue (MB) mineralization under visible light illumination. The effect of hydrothermal duration time (16–25) h, Cetyltrimethylammonium bromide (CTAB) and silver nanoparticles (Ag NPs) concentration (0.5–2.5) wt% on the crystal, surface, optical, photoluminescence as well as photocatalytic activity were studied. A well-defined crystalline cubic phase of SrSnO₃ was obtained. CTAB inhibits the crystal growth of SrSnO₃. Reduction of 4-NP and MB mineralization were used as two-model reactions for testing the effect of Ag doping concentration on the photocatalytic activities of Ag/SrSnO₃ under visible light illumination. The obtained results show that 2.0 wt% of Ag-doped SrSnO₃ exhibits efficient photocatalytic reduction of 4-NP with 98.2% conversion within 5 min of reaction time. Also, 87% of the MB sample was mineralized after 1 h of visible illumination using 2.0% Ag/SrSnO₃ in the presence of H₂O₂. Besides, we have discussed the possible photocatalytic mechanism for reduction of 4-NP and mineralization of MB using 2.0 wt% of Ag doped SrSnO₃ under visible light illumination.
1 Introduction

Environmental pollution is one of the main global challenges of the twenty-first century. Among the various resources for environmental pollution, water pollution is regarded as one of the most negative effects for the mankind and ecosystem [1, 2]. Industrial, domestic, and agricultural activities and other environmental and global changes are the main water pollution sources, which may cause serious health problems to humans [3]. Wastewater treatment and reuse for beneficial purposes is an essential requirement for a healthy lifestyle, environmental sustainability, and social equity.

Several methods have been developed for wastewater treatment. Photocatalytic degradation of pollutants is a promising technology for the efficient wastewater treatment. It is comparatively inexpensive, simple, and environment friendly [4–6]. In the past 30 years, various photocatalysts have been reported. Among of them, alkaline earth perovskite stannate (MSnO₃, M = Ca²⁺, Sr²⁺, Ba²⁺) were used as photocatalyst in recent years [7]. Perovskite SrSnO₃ is semiconductor with wide bandgap energy (~3.8–4.2 eV) [8]. Under UV illumination, its charge carriers are easily separated. These separated charge carriers are responsible for photocatalytic activity of SrSnO₃. The wide bandgap energy is the main disadvantages of SrSnO₃ photocatalyst. As consequences, SrSnO₃ absorbs UV light only from the solar spectrum. Another disadvantage of SrSnO₃ as a photocatalyst is high charge carriers’ recombination rate [9, 10].

Overcoming these challenges requires the doping of metal NPs onto perovskite. Manganese doping in CsPbCl₃ Nanocrystalline drastically enhances their optical properties due to the charge transfer of photoinduced excitons from the CsPbCl₃ host to the dopant Mn²⁺ centers [11]. Noble transition metals such as Ag NPs and their composites with semiconducting oxide have attracted increasing attention because they could induce Surface Plasmonic Resonance (SPR). The SPR was used to assist the efficiency of photocatalyst in the visible absorption range. When noble metal nanoparticles are deposited on the surface of a semiconductor, they display unique optical and catalytic capabilities that are not seen in bulk metal due to transferring photoexcited electrons from the Ag NPs to TiO₂ Conduction Band (CB), which facilitate charge separation. Gerisher has emphasized the importance of dioxygen reduction by CB electrons, which avoids the recombination of photogenerated charge carriers. Therefore, superoxide radical production could be the slowest stage in the reaction sequence leading to substrate oxidation [12, 13].

Although a wide range of alkaline earth stannate MSnO₃ (M = Sr, Ca, Ba) compounds have been synthesized and studied from a structural, magnetic, and electrical, photoluminescence, theoretical point of view [14], only a few have been attempted in studying the photocatalytic activity of pure and doped SrSnO₃ nanoparticles. For instance, Juploy et al. [15] applied Ag-doped SrSnO₃ composites for Methylene blue degradation under ultraviolet Radiation. Venkatesh et al. [16] prepared rGO- SrSnO₃ nanocomposites for degradation of aqueous methylene blue dye under UV light irradiation. The SrSnO₃/g-C₃N₄ was synthesized by a facile solid-state method and applied to visible light-mediated photocatalysis in both, wet and dry phase [17]. Subhan et al. [14] synthesized triple metal oxide from Ag/SrSnO₃ by a co-precipitation method for dye removal, antibacterial and sensing applications. However, no attempts of preparing Ag/SrSnO₃ by hybrid hydrothermal/ultrasonic method for p-nitrophenol (4-NP) reduction and methylene blue (MB) mineralization under visible light illumination can be found among literature data.

In this report, we have focused on preparation of an efficient Ag-doped SrSnO₃ photocatalyst for degradation of common environmental pollutants in daily life as methylene blue (MB) dye and 4-nitrophenol (4-NP) under visible light illumination, and to evaluate the catalytic performance of the developed catalyst.

2 Materials and methods

2.1 Material

Strontium nitrate (Sr(NO₃)₂), Tin (IV) chloride pentahydrate, silver nitrate (AgNO₃), 4-nitrophenol (4-NP) and methylene blue (MB) were obtained from Sigma-Aldrich. Cetyltrimethylammonium bromide (CTAB) was purchased from Belami fine chemical. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were obtained from Germany Company. All
materials used were of analytical grade and were used without further purification.

### 2.2 Preparation SrSnO$_3$ nanorods

Sr(NO$_3$)$_2$ (10 mmol), SnCl$_4$·5H$_2$O (10 mmol), CTAB (1.5 mmol) and H$_2$O (30 mL) were mixed together under continuous stirring. Add 1 mol/L NaOH until the pH of the solution adjusted to 13, white suspension was obtained. Then, the suspension was transferred into a Teflon-lined stainless autoclave with about 80% degree of fill. The sealed vessel was then heated at 160 °C for 18 h, and then cooled to room temperature. The obtained precipitate was filtered and washed for several times with distilled water. The obtained powder was calcinated at 700 °C for 3 h.

### 2.3 Preparation Ag and Ag doped SrSnO$_3$

To synthesize silver nanoparticle-doped strontium stannate nanorod (Ag/SrSnO$_3$), AgNO$_3$ (0.5–2.5 wt%) was mixed with 1 g SrSnO$_3$ and 50 mL of ethylene glycol (EG, C$_2$H$_6$O$_2$) under magnetic stirring. The mixture was ultrasonically vibrated for 15 min to form dispersed and de-agglomerated brown suspension. Then the product was separated, washed several times with absolute ethanol, and dried in air at 70 °C for 24 h. Pure silver nanoparticles (Ag NP-1) were also prepared using the similar procedure using 1 mmol of silver nitrate and 50 mL of ethylene glycol (EG, C$_2$H$_6$O$_2$) under magnetic stirring. The produced silver nanoparticles (Ag NP-2) from 2 mL of 0.001 M silver nitrate were added drop wise to 30 mL of 0.002 M sodium borohydride solution that had been chilled in an ice bath.

### 2.4 Photocatalytic reduction of 4-NP

40 µL of 4-NP (0.01 M) was added to 2.8 mL deionized water and then mixed with 80 µL of freshly prepared NaBH$_4$ (0.5 M). After that, 5 mg of Ag/SrSnO$_3$ photocatalyst (0.0–2.5 wt%) was added to the above solution with stirring for 30 min to reach the adsorption/desorption equilibrium. The reaction mixture was illuminated using halogen lamp (500 W; $\lambda > 420$ nm). The above procedures were repeated under dark condition in the presence of 0.0–0.5 wt% Ag/SrSnO$_3$. Moreover, blank experiments were done in the presence of NaBH$_4$ only under dark and light condition.

### 2.5 Photocatalytic degradation of MB

20 mg of photocatalyst (0.0–2.5) weight percent (wt%) Ag/SrSnO$_3$ was added to an aqueous solution of MB (in 25 mL; 10 ppm). The reaction mixture was stirred in the dark for 30 min to reach the adsorption/desorption equilibrium. Then H$_2$O$_2$ (0.08 M) was added. Then, the halogen lamp was turned on to start the photoreaction. The decolorization of MB was followed using UV–Vis Spectrophotometer. Also, the mineralization of MB was followed using total organic carbon technique (TOC). The same experiment was done at three different pH values (3.0, 6.0, 11) in the presence of 2.0 wt% of Ag/SrSnO$_3$ under visible light illumination. A series of blank experiments for MB in the presence of H$_2$O$_2$, SrSnO$_3$ and 0.5 wt% Ag/SrSnO$_3$ in the dark were tested.

### 2.6 Characterization of the photocatalysts

The crystalline and phase structure of the materials were performed using Shimadzu 6000 X-ray diffractometer (XRD) (Cu-K radiation = 1.5406 Å) as reported in detail elsewhere. The morphology of the synthesized nanostructured were investigated by Transmission electron microscope (TEM) (200 kV, JEOL-JEM-2100, Tokyo, Japan) and scanning electron microscope (SEM) (FEI Sirion) equipped with an Energy Dispersive X-Ray (EDX) detector (S-3400 N II, Hitachi, Japan). Shimadzu UV-2450 spectrophotometer was used to measure the diffuse reflectance spectrum (UV–Vis DRS) using BaSO$_4$ as a reference sample. The photoluminescence (PL) spectra were characterized with (Shimadzu RF-5301PC) spectrofluorometer. Thermogravimetric analysis (TGA-50) and Differential thermal analysis (DTA-50) was tested in the range from 50 to 800 with Shimadzu thermogravimetric analyzer at a constant heating rate (10 min or 1) in nitrogen gas. Fourier-transform infrared spectroscopy (FTIR) was measured with KBr disks using JASCO FTIR-6800.
3 Results and discussion

3.1 XRD

The effect of hydrothermal time at 160 °C on the crystal structure of as-synthesized SrSnO₃ in the absence and presence of CTAB was studied by XRD analysis. The XRD patterns are shown in Fig. 1a (I). The observed diffraction peaks of hexagonal phase SrSn(OH)₆ matched well with precursor (JCPDS-ICDD card No.090086) [20]. However, up on hydrothermal treatment at 160 °C for different duration times in absence and presence of CTAB, a well-defined crystalline cubic phase of SrSnO₃ was obtained (JCPDS-ICDD card No. 22–1442) [21], Fig. 1a (II–VII). The diffraction peaks located at 21.54, 30.8, 44.47, 55.66, 64.96, 73.86 are related to (200), (202), (400), (440), (442), (620) crystallographic planes. The observed data of the prepared photocatalysts are summarized in Table 1. In the absence of CTAB, as the hydrothermal duration increase the full width at half maximum (FWHM) of SrSnO₃ decreases (Table 1). In addition, an increase in the lattice parameter values was observed, reflecting that heat treatment can appreciably influence SrSnO₃ crystallinity. However, on the presence of CTAB, SrSnO₃ exhibited a reverse behavior suggesting that the presence of CTAB during preparation inhibits the crystallization of SrSnO₃. Figure 1b shows the XRD pattern of SrSnO₃ at different Ag loading content wt%. The results XRD spectral pattern exhibited XRD peaks belonging to SrSnO₃, in addition to a minor phase of Ag NPs (2θ = 38.12° and 44.2°) was observed at higher concentrations of Ag NPs (2.0 and 2.5 wt%) (JCPDS Card 04–0783), Fig. 1c shows XRD patterns of pure Ag NP-1 and Ag NP-2 [22]. Doping of Ag NPs on the surface of SrSnO₃ may be due to the reduction Ag⁺ by EG during ultra-sonication step. As Ag NPs concentration increase, the intensity of the main diffraction peak of Ag/SrSnO₃ at (202) was...
gradually decreased. This phenomenon is likely due to Ag NPs can inhibit the growth of SrSnO₃ crystal (Table 2). In addition, it was observed that the main diffraction peak was shifted to lower angle as a function of Ag NPs concentration. Also, it is observed that the lattice parameter decreased by increasing Ag NPs loading content in the Ag/SrSnO₃, Fig. 1d. This is due to growing of small size of Ag NPs (10–40 nm) on the surface of micro scale SrSnO₃ rods, which minimize the total surface energy of Ag/SrSnO₃ system.

Figure 1e shows the FTIR spectrum of the SrSn(OH)₆ precursor, SrSnO₃ and 2 wt% Ag NPs-doped SrSnO₃ NPs. SrSn(OH)₆ exhibits peak at 850 cm⁻¹ due to bending mode of the hydroxyl group. This peak disappears after formation of SrSnO₃ NPs. SrSn(OH)₆ shows broad peaks at 3500 and 1441 cm⁻¹ due to adsorbed water molecules [22]. However, SrSnO₃ and 2 wt% Ag/SrSnO₃ exhibit peak in the range of 521–660 cm⁻¹ which is attributed to vibration of the O–Sn–O bridging [23]. The FTIR spectrum of 2 wt% Ag/SrSnO₃ nanocomposite shows small shift in the absorption peaks, due to the charge transfer interaction between Ag NPs and oxygen atoms in the SrSnO₃ NPs. Furthermore, the peak intensity at 1440 cm⁻¹ was increased due to presence of the OH groups on the surface. Therefore, Ag NPs attached on the surface of SrSnO₃ can improve its surface state and generate more hydroxyl groups on the surface.

The TG-DTA analysis were performed to determine the temperature and weight change for decomposition of the precursor SrSn(OH)₆ into SrSnO₃ phase. Figure 1f displays the TGA thermogram with three different steps, which showed ~18% total weight loss on the temperature range 25–800 °C. The first step from 25 to 200 °C with the weight loss ~3.5% due to the evaporation of water and ethanol physically adsorbed on surfaces of the precursors. At 200–350 °C, the faster weight loss (12%) corresponding to the dehydroxylation and dihydroxylation processes of the Sr–Sn–O–H precursor. The third step 530–800 °C showed complete release of H₂O molecules from their grains, with the formation of SrSnO₃. The observed phase change of SrSn(OH)₆ precursors into SrSnO₃ at 700 °C via three endothermic peaks (37, 275, 563 °C) in the DTA thermogram shows similar behavior throughout the decomposition process to produce SrSnO₃ [24].

Figure 2 shows SEM images of SrSnO₃ at different hydrothermal times in the absence and presence of CTAB. In the absence of CTAB, the irregular shape from SrSnO₃ converted to rod-like shape by increasing hydrothermal time, Fig. 2a–c. The average diameter and length of rods are 700 μm and 5 μm, respectively. Presence of CTAB during preparation allows the formation of rod shape at different hydrothermal duration times, Fig. 2d–f. The rod diameter decreases from 1–2 μm to 200–300 nm as hydrothermal time are increased from 16 to 25 h at same CTAB concentration. The rod length is also

| Conditions | Reaction time/h | 2θ (°) | Lattice parameter, a (nm) | FWHW (202) |
|------------|----------------|-------|--------------------------|-------------|
| Without CTAB | 16            | 30.90 | 8.0315                   | 0.2735      |
|            | 20            | 30.79 | 8.1729                   | 0.2725      |
|            | 25            | 30.87 | 8.2012                   | 0.2660      |
| With CTAB  | 16            | 31.27 | 8.1163                   | 0.2765      |
|            | 20            | 30.57 | 8.1050                   | 0.2816      |
|            | 25            | 31.30 | 8.1060                   | 0.2885      |

Table 2 The crystal parameters of SrSnO₃ at different wt% content of Ag NPs (SrSnO₃ prepared by hydrothermal method at 160 °C for 25 h in the presence of CTAB)

| Ag wt% | 2θ (°) | Lattice parameter, a (nm) | FWHW (202) | Band ap (eV) |
|--------|-------|--------------------------|-------------|--------------|
| 0.0    | 31.30 | 8.1060                   | 0.2885      | 3.80         |
| 0.5    | 30.82 | 8.0889                   | 0.2886      | 3.71         |
| 1.0    | 30.86 | 8.0888                   | 0.2889      | 3.63         |
| 1.5    | 30.78 | 8.0680                   | 0.2912      | 3.60         |
| 2.0    | 30.70 | 8.0428                   | 0.2923      | 3.53         |
| 2.5    | 30.50 | 8.0315                   | 0.2963      | 3.52         |
reduced by addition of CTAB. Additionally, CTAB and hydrothermal reaction time have significant effect on the morphology and size of the SrSnO₃.

No changes in the morphology of SnSrO₃ after Ag NPs loading are observed, Fig. 2g–i. SEM and TEM showed the uniform loading of Ag NPs on the surface of SnSrO₃. Nevertheless, some Ag NPs has little aggregation on the surface. The SEM–EDS spectrum of Ag/SrSnO₃, Fig. 2j displays the presence of Sr, Sn, O and Ag elements.

Figure 3a depicts the UV–Visible (UV–Vis) absorption spectra of SrSnO₃ on the absence and presence of different concentrations of Ag NPs. As shown on Fig. 3a, SrSnO₃ shows a broad absorption band at 285 nm due to intrinsic exciton absorption, [25, 26]. Ag/SrSnO₃ rod shows an additional absorption band in the visible region (427 nm), Fig. 3a. The intensity of this band increases by increasing the content of Ag NPs loading, which is due to the characteristic plasmon surface resonance (SPR) phenomenon of free electron in Ag NPs conduction bands [27, 28]. This confirms the presence of Ag NPs on the surface of SrSnO₃, as shown in Fig. 3b.

![SEM images of SrSnO₃ at hydrothermally treated at 16, 20, 25 h (a, b, c) without CTAB; and in the presence of CTAB at 16, 20, 25 h (d, e, f), respectively, scale bar 1 μm. TEM images g of SnSrO₃ nanorod, The SEM and TEM images h, i of 2 wt% Ag/SnSrO₃ Nanorods, and j EDX of 2 wt% Ag/SnSrO₃ Nanorods](image-url)
The bandgap energy values of Ag/SrSnO₃ at different Ag NPs loading concentrations were determined using the following Wood and Tauc Eq. (1) [29]:

\[ a h \nu = C (h \nu - E_g)^n \]  

(1)

where \( a \) is the absorbance, \( h \nu \) is the photon energy and \( C \) is a band tailoring constant. The nature of the optical transition in the semiconductor is indicated by the exponent “\( n \)”. The values of \( n \) are 2 and \( \frac{1}{2} \) for allowed indirect and direct optical transitions, respectively [30]. Plotting \((a h \nu)^{1/2}\) versus \(h \nu\) according to relationship (1) leads to the evaluation of the bandgap energy \( (E_g) \) by extracting the linear portion of curves to \((a h \nu)^{1/2} = 0\), Fig. 3c. The calculated bandgap energy values of Ag/SrSnO₃ NPs are summarized in Table 2. As can be seen from Table 2, values of \( E_g \) decrease with increasing content of Ag loading, and the observed \( E_g \) values are relatively lower than some reported literature values (4.1–3.9 eV) [31]. Figure 3c show a high absorption peak at 2.9 eV, which is ascribed to the surface deposition of Ag NPs.

Figure 3d shows the photoluminescence (PL) emission spectra of SrSnO₃ at different Ag NPs concentrations (\( \lambda_{ex} = 275 \) nm). Notably, the PL emission of SrSnO₃ results from indirect transition of the excited electron from the conduction band to valance band. However, the PL of Ag/SrSnO₃ rods were quenched as Ag loading increased. This quenching is because the doped Ag NPs on the surface of SrSnO₃ acts as electron trapping under UV excitation, in which, Ag NPs can trap the SrSnO₃ excited electrons on the conduction band. We assume that Ag NPs retard the electron–hole recombination in the SrSnO₃ rods, which, increases the photocatalytic efficiency of the Ag/SrSnO₃ under UV excitation [32].

The observed \( \zeta \)-potential values (Fig. 3e) of SrSnO₃, Ag/SrSnO₃, Ag NP-1 and Ag NP-2 suspension in water are \(-27.4\) mV, \(-39\) mV, \(-15\) mV and 0 mV, respectively. These high negative charges suggesting the electrical stability of the Ag/SrSnO₃ is higher than that of SrSnO₃ and Ag NP 1–2, i.e., resist aggregation. [33, 34]. The effect of pH on the \( \zeta \)-potential of SrSnO₃ and Ag/SrSnO₃ rods on the pH range 1–12 is shown in Fig. 3e. The estimated isoelectric points of SrSnO₃ and optimized Ag/SrSnO₃ are at pH values of 3.8 and 4.2, respectively. The observed negative \( \zeta \)-potential values suggesting enhanced adsorption of MB (cationic dye) on the surface of photocatalyst at these pH values [35]. This is because the photo-generated holes after irradiation...
and excitation of electrons from the valence to the conduction band either directly oxidize the dye to reactive intermediates or react with hydroxyl ions (OH\textsuperscript{−}) leading to the formation of highly oxidative hydroxyl radicals (OH) and further complete the degradation of the dye.

3.2 Photocatalytic applications

3.2.1 Photocatalytic reduction of 4-nitrophenol

Figure 4a, b show effect of NaBH\textsubscript{4} on 4-NP in dark and visible light illumination was tested. Also, the photocatalytic activity of SrSnO\textsubscript{3} on 4-NP was performed in dark and visible light illumination as shown in Fig. 4c, d. The obtained results show a very small change in the absorption spectrum of 4-NP in the presence of only SrSnO\textsubscript{3} or NaBH\textsubscript{4}. In all experiments, the adsorption/desorption equilibrium was performed by adding 5 mg of photocatalyst to 4-NP under stirring for 30 min in dark. as shown in Fig. 4e, weak adsorption of 4-NP was observed on the photocatalyst surface. As shown in Fig. 4, the absorption spectrum of 4-NP changed insignificantly in the presence of only Ag NP (1, 2) in the dark (f, g). However, in the presence of Ag NP (1, 2) and NaBH\textsubscript{4}, a small change in the absorption spectrum of 4-NP was observed under visible light. This is because the negative charges of Ag NP-1 (−12 mV) and Ag-2 (−2 mV) adsorbed weakly with the negative charge of

![Fig. 4 Absorption spectra of 4-NP in the presence of NaBH\textsubscript{4} in dark (a) and under visible light illumination (b). Absorption spectra of 4-NP in the presence SrSnO\textsubscript{3} in dark, c and under visible light illumination (d). The adsorption % of prepared photocatalysts for 4-NP under different reaction conditions (e), and f, g absorption spectra of 4-NP in dark in the presence Ag NP-1 (f) and Ag NP-2 (g). Absorption spectra of 4-NP in the dark and under visible light in the presence Ag NP-1/NaBH\textsubscript{4} (h) and Ag NP-2/NaBH\textsubscript{4} (i).]
nitrophenol, resulting in a reduction in reduction efficiencies [33].

Figure 5a shows the UV–Vis absorption spectra of blank in the dark, NaBH₄ (a) as well as under visible light illumination with Ag NPs content: b 0.5 wt%, c 0.10 wt%, d 1.5 wt%, e 2.5 wt%, f 2.0 wt% Ag/SrSnO₃. Plots of A/A₀ (g) and ln(A/A₀) (h) versus reaction time for the catalytic reduction of 4-NP to 4-AP using (0–2.5) Ag/SrSnO₃ with different conditions Ag/SrSnO₃ photocatalyst compared with AgNP-1, 2 only.

The rate constant of the reaction can be evaluated by the pseudo first-order kinetics according to the following Eq. (2) [37]:

\[
\ln \left( \frac{A}{A_0} \right) = -k_{app}t
\]

where \( A_0 \) and \( A \) are the absorption intensity before illumination and at different times of illumination, respectively. \( k_{app} \) is an apparent rate constant. The relationships between ln(\( A/A_0 \)) against t over Ag/SrSnO₃ catalysts are shown in Fig. 5g and h. The photocatalytic reduction of 4-NP follows the pseudo
first-order kinetics. The degradation kinetic parameters of Ag/SrSnO₃ catalysts are summarized in Table 3. The rate constant values increase with increasing Ag NPs content, until reaching maximum at 2 wt% of Ag NPs and then decrease after adding 2.5 wt%. Compared to other reported candidates (Table 4), the as-prepared Ag-doped SrSnO₃ photocatalyst exhibit relatively higher photocatalytic reduction rate, suggesting that the prepared photocatalyst is promising material for water treatment.

The measured pH IEP value of 2.0% Ag/SrSnO₃ is 4.2, which is lower than the pkₐ value of 7.2 for 4-NP [38]. This indicates that under neutral condition (pH = 7.0), the surface of 2.0% Ag/SrSnO₃ and 4-NP have a negative charge, which means that in dark, the adsorption factor has less effect on the reaction rate (Figs. 3e, 4e and Table 3) [36, 39–42]. Also, the hydrolysis rate of borohydride ions increases by decreasing the pH of the medium [43, 44]. However, the measured rate of reaction for blank experiment without 2.0% Ag/SrSnO₃ photocatalyst, is very low, which enhances significantly in the presence of 2.0% Ag/SrSnO₃ and NaBH₄ in visible light.

### 3.2.2 Photocatalytic degradation of methylene blue

The photodegradation efficiency of MB dye was studied using Ag/SrSnO₃/H₂O₂ photocatalyst. The change in UV–Vis absorption maximum at λ_max = 664 nm was employed to monitor the entire photodegradation process. Also, the effect of H₂O₂ addition on the photocatalytic degradation of MB dye was also investigated in dark and under visible light illumination, as shown in Fig. 6a, b. Remarkable very slow degradation of the dye was observed in the dark under visible light illumination. However, a small change in the absorption spectrum of MB was observed in presence of SrSnO₃ and 0.5 wt% Ag/SrSnO₃ in dark, Fig. 6c, d.

Moreover, the SrSnO₃ shows a small change in the absorption spectrum of MB under visible light illumination, Fig. 6e. This is due to the high bandgap energy of SrSnO₃ (3.8 eV), which activated with UV illumination more than visible light as shown in Fig. 6e, weak adsorption of MB was observed on the photocatalyst surface under different condition, as shown in Fig. 6f. Furthermore, weak adsorption was observed in the dark, where oxidation of MB under visible light was observed in the presence and absence of Ag NP 1, 2, (g–i). As a positive-charged cationic dye, MB can reduce the adsorption of low-value negatively charged Ag NP-1 and AgNP-2 on the surface, lowering degradation efficiencies [33]. It is well known that MB can be present in aqueous solution as the cationic species (MB⁺) and undissociated molecules (MB₀). Also, the (MB⁺) is only species present at pH > 6 [45]. At experimental pH condition, both forms are present. Although, the photocatalyst carrying a negative charge (IEP at pH = 4.2), the presence of undissociated molecules (MB₀) decreases the adsorption efficiency of MB on the photocatalyst surface. Ag/SrSnO₃ shows higher decolorization efficiency under visible light illumination, Fig. 7a. This due to presence of Ag NP lowering the bandgap energy and acts as a sensitizer for SrSnO₃. To accelerate the reaction rate, H₂O₂ was used in combination with Ag/SrSnO₃. Figure 7b shows that the addition of H₂O₂ enhances the decolorization efficiency of 0.5 wt% Ag/SrSnO₃ under visible illumination. Figure 7b–f show that less

### Table 3 Kinetic parameters for the photocatalytic activity of different photocatalysts for reduction of 4-NP

| Photocatalysts | Rate (k) min⁻¹ | Reaction time (min) |
|---------------|----------------|---------------------|
| 0.5% Ag/SrSnO₃ (dark) | 0.017 | 70 |
| 0.5% Ag/SrSnO₃ (light) | 0.035 | 18 |
| 1.0% Ag/SrSnO₃ (light) | 0.047 | 16 |
| 1.5% Ag/SrSnO₃ (light) | 0.082 | 10 |
| 2.0% Ag/SrSnO₃ (light) | 0.171 | 5.0 |
| 2.5% Ag/SrSnO₃ (light) | 0.082 | 11 |

### Table 4 Comparison of the characteristic data from literature

| Photocatalyst | Time (min) | Decomposition (%) | Ref. |
|---------------|------------|-------------------|------|
| 6%Au@g-C₃N₄ | 8 | 100 | [39] |
| 5%Ag (10 nm)/g-C₃N₄ | 210 | 100 | [40] |
| MIL-125/Ag@g-C₃N₄ | 30 | 82 | [41] |
| 1.5 Ag@g-C₃N₄/V₂O₅ | 8 | 100 | [42] |
| 2% Ag/SrSnO₃ | 5 | 98.2 | This work |
time was needed for complete disappearance of the intense blue color (MB) to colorless leucomethylene blue (LMB) by increasing concentration of loading Ag NPs until reached to optimum concentration 2 wt%. The Ag NPs concentrations of 0.5, 1.0, 1.5, 2.0 and 2.5 produce complete decolorization within 70, 64, 60, 40 and 50 min, respectively. The linear plot of \((A/\Lambda_0)\) vs time \((t)\) are shown in Fig. 7g. The degradation rate constants were determined from the linear plot of \(\ln(A_t/\Lambda_0)\) vs time \((t)\), (Fig. 7h) and the results are summarized in Table 5. All experiments were performed at pH = 5.5 using 0.08 mol of \(\text{H}_2\text{O}_2\) in the presence of 20 mg (0–2.5) wt% of Ag/SrSnO\(_3\).

Figure 8a–c show the effect of pH on the photocatalytic activity of 2.0 wt% Ag NPs content of Ag/SrSnO\(_3\) for degradation of MB in the presence of \(\text{H}_2\text{O}_2\). As shown in Table 5, the decolorization of MB using Ag/SrSnO\(_3\) is depending on pH value. Complete decolorization occurs within 26 min at pH = 11. The values of the decolorization rate constants were 0.025, 0.058 and 0.107 at pH values of 3.0, 6.0 and 11, respectively, Fig. 8d, e and in Table 5. The gradual increase in the photocatalytic activity was mainly due to the predominant cationic MB\(^+\) species at pH > 6. Also, the negative charge of the surface of Ag/SrSnO\(_3\) increases by increasing the pH of the solution. The
electrostatic attraction between the cationic form of MB and the negative photocatalyst surface improve the adsorption ability and consequently the photocatalytic activity.

Additionally, the photodegradation efficiency of MB was investigated using the highly active nanoparticles (2.0% Ag/SrSnO₃ in the presence of H₂O₂) under visible light illumination. The obtained results show that the TOC value reduced from 100 mg/l (TOC₀) to 13 mg/l (TOC) after 1 h of visible light illumination. This implies

**Table 5** Kinetic parameters for the MB catalytic degradation activity using different photocatalysts under dark and light conditions

| Photocatalysts                  | Rate (k) min⁻¹ | Reaction time (min) |
|---------------------------------|----------------|--------------------|
| SrSnO₃ (dark)                   | 0.0090         | 70                 |
| SrSnO₃ (light)                  | 0.012          | 70                 |
| 0.5% Ag/SrSnO₃ (dark)           | 0.016          | 70                 |
| 0.5% Ag/SrSnO₃ (light)          | 0.017          | 70                 |
| 0.5% Ag/SrSnO₃/H₂O₂ (light)     | 0.026          | 70                 |
| 1.0% Ag/SrSnO₃/H₂O₂ (light)     | 0.032          | 64                 |
| 1.5% Ag/SrSnO₃/H₂O₂ (light)     | 0.047          | 60                 |
| 2.0% Ag/SrSnO₃/H₂O₂ (light) pH = 6 | 0.058          | 40                 |
| 2.0% Ag/SrSnO₃/H₂O₂ (light) pH = 3 | 0.025          | 70                 |
| 2.0% Ag/SrSnO₃/H₂O₂ (light) pH = 11 | 0.107          | 26                 |

Fig. 7 Absorption spectra of MB in the presence of Ag/SrSnO₃ under visible light illumination: (a), in the absence of H₂O₂ and 0.5 wt% Ag NPs content, (b) presence of H₂O₂/0.5 wt% Ag NPs content, (c) presence H₂O₂/0.10% wt Ag NPs content, (d) presence of H₂O₂/1.5 wt% Ag NPs content, (e) presence of H₂O₂/2.5 wt% Ag NPs content and (f) presence of O₃/2.0 wt% Ag. Plots of (g) A/A₀ and (h) ln(A/A₀) versus reaction time for the photocatalytic degradation of MB.
that 87% of the sample was completely decomposed after 1 h (Fig. 9a).

SrSnO₃ absorption was difficult in the presence of direct light as a result of its large bandgap (3.8 eV), which greatly diminished its usage as a photocatalyst under visible light, Scheme 1. To improve the photocatalytic process, plasmonic noble metals such as Ag NPs were doped SrSnO₃ to increase visible light absorption. Degradation of organic pollutants is dominated by photo generated electron–hole pairs. As a result, the method was used to calculate the Conduction Band (CB) and VB (Valence Band) potentials for catalysts by the following Eqs. (3,4) to study the photocatalytic process [46],

\[ E_{CB} = \chi - E^e - 0.5E_g \]  
\[ E_{VB} = E_{CB} + E_g \]  

The potential energies of the conduction and valence bands are \( E_{CB} \) and \( E_{VB} \), respectively, while \( E^e \) is the energy of free electrons against a normal hydrogen electrode (4.5 eV). The resulting electronegativity of different individual semiconductors is given by the following Eq. (5) [47]

\[ \chi = \left[ \frac{x(A)^a x(B)^b x(C)^c}{(a+b+c)^{1/2}} \right] \]  

where \( a, b, \) and \( c \) are the number of atoms in semiconductors. The measured CB and VB potentials of SrSnO₃ were -0.996 and 2.81 eV, respectively. As shown in Scheme 1, the surface plasmon resonance (SPR) phenomenon occurs on the surface Ag NPs under irradiation of Ag/SrSnO₃ with visible light. This leads to movement of electrons on surface Ag NPs to the other side. Then the interfacial electron flow from Ag NPs to CB of SrSnO₃ produces a positive charge on the Ag NPs [45]. SrSnO₃ was responsible for trapping electrons, charge separation and slow down the rate of recombination photogenerated charge carriers [12, 13, 48]. However, the reaction of H₂O₂ with electrons on the CB of SrSnO₃ produces highly reactive hydroxyl radicals that oxidize MB. SrSnO₃’s CB position has more negative than the possibility for oxidize MB decrease (−0.33 eV vs NHE). At the same time, \( h^+ \) on surface Ag NPs interacted immediately with H₂O to produce \( \text{OH}^- \) then MB was oxidized (MB-OX), creating water and carbon dioxide that is good for the environment [36, 49, 50].

The proposed mechanism for 4-NP reduction using the Ag/SrSnO₃ catalyst in the presence of NaBH₄ is shown in Scheme 2. The experimental results show that the reduction rate in the presence of NaBH₄ alone is very slow but enhanced significantly in the presence of Ag NPs on the surface of photocatalyst. Under irradiation of Ag/SrSnO₃ with Visible light, the surface plasmon resonance (SPR) phenomenon occurs on the surface of Ag NPs. This leads to movement of electrons on surface Ag NPs to the other side. Then the interfacial electron transfer from Ag NPs to SrSnO₃ induces a positive charge on the Ag NPs (Scheme 2). Consequently, this enhances the adsorption ability of \( \text{BH}_4^- \) and the 4-NP onto the surface of positively charged Ag NPs compared with Ag NP only. Then the reaction starts by hydrolysis of the borohydride ions. The \( \text{BO}_2^- \) is one of the borohydride ion hydrolysis products. \( \text{BO}_2^- \) deprotonates 4-nitrophenols form 4-nitrophenolate ions (4-NP\( \bar{a}t \)).
on the photocatalyst surface (Scheme 2b) [51]. Also, borohydride ions react with the Ag NPs and produce hydrogen gas as a source of an active hydrogen species on it (Ag-H). These hydrogen species are unstable and have a negative charge in the metal–hydrogen structure. As consequences, it can easily attack the positively charged nitrogen in the nitro group of nitrophenols to produce nitroso group (Scheme 2c). This is followed by the reductive addition of two hydrogen atoms to form hydroxylamine (Scheme 2d). Finally, the hydroxylamine is further reduced to the 4-AP (Scheme 2e) [43, 52].

Figure 9b shows trapping experiment to confirm the suggested mechanism by addition of different scavengers. We utilized p-benzoquinone PBQ (0.1 mmol), isopropanol IPA (0.1 mol L\(^{-1}\)), silver nitrate AgNO\(_3\) (0.1 mmol), and sodium oxalate Na\(_2\)C\(_2\)O\(_4\) (0.1 mmol) as \(\cdot\)OH, electron, and h\(^+\) scavengers, respectively. These results indicate that photogenerated electrons play a significant role in the removal of organic compound, while OH and h playing a secondary function.

From an economic point of view, the chemical stability of the photocatalyst is the main issue. Therefore, we performed the stability of Ag/SrSnO\(_3\)
under five cycles of photocatalytic degradation of MB as shown in Fig. 9c, d. The five cycles degradation of MB and 4-NPs were performed under the same condition in the presence of H2O2 and NaBH4. It is apparent that the degradation efficiency of Ag/SrSnO3 was not significantly decreased after three-time photocatalytic cycles. The degradation efficiency of MB only decreases from 96.5 to 93.4% and reduction efficiency of 4-NPs decreased slightly from 98.2 to 95.5%. The decrease in the photocatalytic efficiency related to the decreasing of concentration Ag NPs. The ICP results showed a slight decrease of Ag NPs concentration from 2.0 to 1.88% [35]. Whereas After 1 cycle the degradation efficiency of MB and reduction efficiency 4-NPs by Ag/SrSnO3 in absence H2O2 and NaBH4 decreased from 96.5–10% to 98.2–5%, respectively indicating H2O2 and NaBH4 has synergistic effect with Ag/SrSnO3.

4 Conclusions

Silver-doped perovskite strontium stannate with different wt% (Ag/SrSnO3) was prepared by hydrothermal method followed by ultrasonic treatment. The effect of hydrothermal time, CTAB and Ag NPs loading were studied. All samples exhibited a well-defined crystalline cubic phase of SrSnO3 with rod like morphology. CTAB inhibits the crystal growth of SrSnO3. The UV–Vis absorption measurements confirm the formation of Ag doped on the surface of SrSnO3 via appearance of high intense surface plasmon resonance absorption band of Ag NP. The high \( \zeta \)-potential value of Ag/SrSnO3 suspension (\(-39\) mV) refers to its electrical stability. The prepared photocatalysts were applied for the reduction of 4-nitrophenol (4-NP) and degradation of MB under visible light. The obtained results show that 2 wt% of Ag/SrSnO3 is highly active sample. 2.0 wt% Ag/SrSnO3 photocatalyst reduces 4-NP with 100% conversion within 5 min of reaction time. Also, 87% of the MB sample was mineralized after 1 h of visible illumination using 2.0% Ag/SrSnO3 in the presence of H2O2.

Acknowledgements

The study was financially supported by the Institute of Nanoscience and Nanotechnology, Kafrelsheikh University, Egypt.

Author contributions

ZG: experiments, analyzed data and original draft, RK and HM: data acquisition, conceptualization, reviewing, MS and HH: supervision, conceptualization, reviewing, ME-K: supervision, conceptualization, editing & review, and funding acquisition.
Funding

Open access funding provided by The Science, Technology & Innovation Funding Authority (STDF) in cooperation with The Egyptian Knowledge Bank (EKB).

Data availability

All data generated or analyzed during this study are included in this published article.

Declarations

Conflict of interest  The authors have no conflict of interest to declare that are relevant to the content of this article.

Ethical approval  Not applicable.

Open Access  This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

References

1. J. Dou, D. Gan, Q. Huang, M. Liu, J. Chen, F. Deng, X. Zhu, Y. Wen, X. Zhang, Y. Wei, Functionalization of carbon nanotubes with chitosan based on MALI multicomponent reaction for Cu2+ removal. Int. J. Biol. Macromol. 36, 476–485 (2019)
2. Q. Huang, M. Liu, J. Zhao, J. Chen, G. Zeng, H. Huang, J. Tian, Y. Wen, X. Zhang, Y. Wei, Facile preparation of polyethylenimine-tannins doped SiO2 hybrid materials for Cu2+ removal. Appl. Surf. Sci. 427, 535–544 (2018)
3. Y. Liu, H. Huang, D. Gan, L. Guo, M. Liu, J. Chen, F. Deng, N. Zhou, X. Zhang, Y. Wei, A facile strategy for preparation of magnetic graphene oxide composites and their potential for environmental adsorption. Ceram. Int. 44, 18571–18577 (2018)
4. T. Welderfael, M. Pattabi, R.M. Pattabi, Photocatalytic activity of Ag-N co-doped ZnO nanorods under visible and solar light irradiations for MB degradation. J. Water Process. Eng. 14, 117–123 (2016)
5. R. El-Shabasy, N. Yosri, H. El-Seedi, K. Shoueir, M. El-Kemary, A green synthetic approach using chili plant supported Ag/Ag2O@P25 heterostructure with enhanced photocatalytic properties under solar irradiation. Optik 192, 162943 (2019)
6. A. Mezni, N.B. Saber, M.M. Ibrahim, M. El-Kemary, A. Aldalbahi, P. Feng, L.S. Smiri, T. Altalhi, Facile synthesis of highly thermally stable TiO2 photocatalysts. New J. Chem. 41, 5021–5027 (2017)
7. C.W. Lee, D.W. Kim, I.S. Cho, S. Park, S.S. Shin, S.W. Seo, K.S. Hong, Simple synthesis and characterization of SrSnO3 nanoparticles with enhanced photocatalytic activity. Int. J. Hydrog. Energy 37, 10557–10563 (2012)
8. Z. Ghubish, R. Kamal, H.R. Mahmoud, M. Saif, H. Hafez, M. El-Kemary, Novel fluorescent nano-sensor based on amino-functionalization of Eu3+: SrSnO3 for copper ion detection in food and real drink water samples. RSC Adv. 11(30), 18552–18564 (2021)
9. I.A. de Sousa Filho, I.T. Weber, SrSnO3/g-C3N4 dry phase sunlight photocatalysis. J. Photochem. Photobiol. A 412, 113255 (2021)
10. H. Mizoguchi, H.W. Eng, P.M. Woodward, Probing the electronic structures of ternary perovskite and pyrochlore oxides containing Sn4+ or Sn5+. Inorg. Chem. 43, 1667–1680 (2004)
11. M.F. Abdelbar, M. El-Kemary, N. Fukata, Downshifting of highly energetic photons and energy transfer by Mn-doped perovskite CsPbCl3 nanocrystals in hybrid organic/silicon nanostructured solar cells. Nano Energy 77, 105163 (2020)
12. L.G. Devi, R. Kavitha, A review on plasmonic metal- TiO2 composite for generation, trapping, storing and dynamic vectorial transfer of photogenerated electrons across the Schottky junction in a photocatalytic system. Appl. Surf. Sci. 360, 601–622 (2016)
13. H. Gerischer, A. Heller, The role of oxygen in photooxidation of organic molecules on semiconductor particles. J. Phys. Chem. 95, 5261–5267 (1991)
14. M.A. Subhan, T.P. Rifat, P.C. Saha, M.M. Alam, A.M. Asiri, T. Raihan, A.K. Azad, W. Ghann, J. Uddin, M.M. Rahman, Photocatalytic, anti-bacterial performance and development of 2, 4-diaminophenylhydrazine chemical sensor probe based...
on ternary doped Ag–SrSnO₃ nanorods. New J. Chem. 45, 1634–1650 (2021)
15. P. Junploy, T. Thongtem, S. Thongtem, A. Phuruangrat, Decolorization of methylene blue by Ag/SrSnO₃ composites under ultraviolet radiation. J. Nanomater. 67, 2014 (2014)
16. G. Venkatesh, M. Geerthana, S. Prabhu, R. Ramesh, K.M. Prabhu, Enhanced photocatalytic activity of reduced graphene oxide/SrSnO₃ nanocomposite for aqueous organic pollutant degradation. Optik 206, 164055 (2020)
17. I.A.S. Filho, I.T. Weber, SrSnO₃/g-C₃N₄ dry phase sunlight photocatalysis. J. Photochem. Photobiol. A 1, 113255 (2021)
18. L. Mulfinger, S.D. Solomon, M. Bahadory, A.V. Jeyarajasingam, S.A. Rutkowsky, C. Boritz, Synthesis and study of silver nanoparticles. J. Chem. Educ. 84, 322 (2007)
19. A. Mezni, M.M. Ibrahim, M. El-Kemary, A.A. Shaltout, N.Y. Mostafa, J. Ryl, T. Kumeria, T. Altahi, M.A. Amin, Cathodically activated Au/TiO₂ nanocomposite synthesized by a new facile solvothermal method: an efficient electrocatalyst with Pt-like activity for hydrogen generation. Electrochim. Acta 290(10), 404–418 (2018)
20. D. Yang, C. Zhang, L. Dong, X. Hou, W. Zheng, J. Xu, H. Ma, Synthesis and properties of SrSn(OH)₆ nanorods and their flame retardancy and smoke suppression effects on epoxy resin. J. Coat. Technol. Res. 16, 1715–1725 (2019)
21. C. Li, Y. Zhu, S. Fang, H. Wang, Y. Gui, L. Bi, R. Chen, Preparation and characterization of SrSnO₃ nanorods. J. Phys. Chem. Solids 72(7), 869–874 (2011)
22. D.N. Srivastava, S. Chappel, O. Palchik, A. Zaban, A. Gedanken, Sonocalytic synthesis of mesoporous tin oxide. Langmuir 18, 4160 (2002)
23. C.V. Squez, M. Luisa, O.A. Campero, J.M. Esparza, F. Rojas, Surfactantless synthesis and textual properties of self-assembled mesoporous SnO₂. Nanotechnology 17, 3347 (2006)
24. C.V. Squez, F. Rojas, M.L. Ojeda, A.A. Ortiz, Campero, structure and texture of self-assembled nanoporous SnO₂. Nanotechnology 16, 127 (2005)
25. D. Chen, J. Ye, SrSnO₃ nanostructures: synthesis, characterization, and photocatalytic properties. Chem. Mater. 19, 4585–4591 (2007)
26. P. Junploy, S. Thongtem, T. Thongtem, Photoabsorption and photocatalysis of SrSnO₃ produced by a cyclic microwave radiation. Superlattices Microstruct. 57, 1–10 (2013)
27. L.S. Daniel, H. Nagai, M. Sato, Absorption spectra and photocurrent densities of Ag nanoparticle/TiO₂ composite thin films with various amounts of Ag. J. Mater. Sci. 48, 7162–7170 (2013)
28. X. Yin, W. Que, D. Fei, F. Shen, Q. Guo, Ag nanoparticle/ZnO nanorods nanocomposites derived by a seed-mediated method and their photocatalytic properties. J. Alloys Compd. 524, 13–21 (2012)
29. D.L. Wood, J. Tauc, Weak absorption tails in amorphous semiconductors. J. Phys. Rev. 5, 3144–3151 (1972)
30. W.F. Zhang, J. Tang, J. Ye, Photoluminescence and photocatalytic properties of SrSnO₃ perovskite. Chem. Phys. Lett. 418, 174–178 (2006)
31. Z. Ghubish, M. Saif, H. Hafez, H. Mahmoud, R. Kamal, M. El-Kemary, Novel red photoluminescence sensor based on Europium ion doped calcium hydroxy stannate CaSn(OH)₆: Eu³⁺ for latent fingerprint detection. J. Mol. Struct. 1207, 127840 (2020)
32. Y. Hong, Y. Jiang, C. Li, W. Fan, X. Yan, M. Yan, W. Shi, In-situ synthesis of direct solid-state Z-scheme V₂O₅/g-C₃N₄ heterojunctions with enhanced visible light efficiency in photocatalytic degradation of pollutants. Appl. Catal. B 180, 663 (2016)
33. C. Yang, W. Dong, G. Cui, Y. Zhao, X. Shi, X. Xia, W. Wang, Highly-efficient photocatalytic degradation of methylene blue by Po-PD-modified TiO₂ nanocomposites due to photosensitization-synergetic effect of TiO₂ with PoPD. Sci. Rep. 7, 1–12 (2017)
34. N.T. Baliah, P. Muthulakshmi, S.L. Priyatharsini, Synthesis and characterization of onion mediated silver doped zinc oxide nanoparticles. J. Sci. Res. Sci. Eng. Technol. 4, 111–120 (2018)
35. H.P. Jing, C.C. Wang, Y.W. Zhang, P. Wang, R. Li, Photocatalytic degradation of methylene blue in ZIF-8. RSC Adv. 4, 54454 (2014)
36. H.S. El-Sheshtawy, Z. Ghubish, K.R. Shouir, M. El-Kemary, Activated H₂O₂ on Ag/SiO₂–SrWO₄ surface for enhanced dark and visible-light removal of methylene blue and p-nitrophenol. J. Alloys Compd. 842, 155848 (2020)
37. S. Khezrianjoo, H.D. Revanasi-dappa, Langmuir-Hinshelwood kinetic expression for the photocatalytic degradation of Metanil Yellow aqueous solutions by ZnO catalyst. Chem. Sci. J. 85, 1–7 (2012)
38. F.H. Lin, R. Doong, Highly efficient reduction of 4-nitrophenol by heterostructured gold-magnetite nano catalysts. Appl. Catal. A 486, 32–41 (2014)
39. Y. Fu, T. Huang, B. Jia, J. Zhu, X. Wang, Reduction of nitrophenols to aminophenols under concerted catalysis by Au/g-C₃N₄ contact system. Appl. Catal. B 202, 430–437 (2017)
40. Y. Yang, Y. Guo, F. Liu, X. Yuan, Y. Guo, S. Zhang, W. Guo, M. Huo, Preparation and enhanced visible-light photocatalytic activity of silver deposited graphitic carbon nitride plasmonic photocatalyst. Appl. Catal. B 142-143, 828–837 (2013)
41. Z. Yang, X. Xu, X. Liang, C. Lei, Y. Cui, W. Wu, Y. Yang, Z. Zhang, Z. Lei, Construction of heterostructured MIL-125/Ag/g-C_{3}N_{4} nanocomposite as an efficient bifunctional visible light photocatalyst for the organic oxidation and reduction reactions. Appl. Catal. B 205, 42–54 (2017)
42. H.S. El-Sheshtawy, H.M. El-Hosainy, K.R. Shoueir, I.M. El-Mehasseb, M. El-Kemary, Facile immobilization of Ag nanoparticles on g-C_{3}N_{4}/V_{2}O_{5} surface for enhancement of post-illumination, catalytic, and photocatalytic activity removal of organic and inorganic pollutants. Appl. Surf. Sci. 467, 268–276 (2019)
43. S.M. Sadeghzadeh, R. Zhiani, S. Emrani, The reduction of 4-nitrophenol and 2-nitroaniline by the incorporation of Ni@Pd MNPs into modified UiO-66-NH_{2} metal–organic frameworks (MOFs) with tetraethia-azacyclopentadecane. New J. Chem. 42, 988–994 (2018)
44. J.H. Lee, S.K. Hong, W.B. Ko, Reduction of 4-nitrophenol catalyzed by platinum nanoparticles embedded into carbon nanocolloids. Asian J. Chem. 23, 2347–2350 (2011)
45. L. Zhang, C. Liang, H. Guo, C.-G. Niu, X.-F. Zhao, X.-J. Wen, G.-M. Zeng, Construction of a high-performance photocatalytic fuel cell (PFC) based on plasmonic silver modified Cr-BiOCl nanosheets for simultaneous electricity production and pollutant removal. Nanoscale 11, 6662–6676 (2019)
46. Z. Lihong, X. Wang, Q. Nong, H. Lin, B. Teng, Y. Zhang, L. Zhao, T. Wu, Y. He, Enhanced visible-light photoactivity of g-C_{3}N_{4} via Zn_{2}SnO_{4} modification. Appl. Surf. Sci. 329, 143–149 (2015)
47. Q. Yuan, L. Chen, M. Xiong, J. He, S.L. Luo, C.T. Au, S.F. Yin, Cu_{2}O/BiVO_{4} heterostructures: synthesis and application in simultaneous photocatalytic oxidation of organic dyes and reduction of Cr (VI) under visible light. Chem. Eng. J. Chem. E 255, 394–402 (2014)
48. P. Sanitnon, S. Chiarakorn, C. Chaungkijwanich, S. Chuangchote, T. Pongprayoon, Synergistic effects of zirconium and silver co-dopants in TiO_{2} nanoparticles for photocatalytic degradation of an organic dye and antibacterial activity. J. Aust. Ceram. Soc. 56, 579–590 (2020)
49. D. Chen, T. Li, Q. Chen, J. Gao, B. Fan, S.J. Li, L. Gao, hierarchically plasmonic photocatalysts of Ag/AgCl nanocrystals coupled with single-crystalline WO_{3} nanoplates. Nanoscale 4, 5431–5439 (2012)
50. H. Ye, S. Lu, Effect of hydrogen peroxide on the structure and photocatalytic activity of titania. Res. Chem. Interned. 41, 139–149 (2015)
51. A.S. Hashimi, M.A.N.M. Nohan, S.X. Chin, S. Zakaria, C.H. Chia, Rapid catalytic reduction of 4-nitrophenol and clock reaction of methylene blue using copper nanowires. Nanomaterials 9, 1–13 (2019)
52. G. Wu, X. Liu, P. Zhou, L. Wang, M. Hegazy, X. Huang, Y. Huang, A facile approach for the reduction of 4-nitrophenol and degradation of congo red using gold nanoparticles or laccase decorated hybrid inorganic nanoparticles/polymer-biomacromolecules vesicles. Mater. Sci. Eng. C 94, 524–533 (2019)

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.