Development of $\text{Ag}_{0.04}\text{ZrO}_2$/rGO heterojunction, as an efficient visible light photocatalyst for degradation of methyl orange

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Methyl orange (MO) is mutagenic, poisonous, and carcinogenic in nature, hence, effective methods are required for its degradation. We have synthesized pure ZrO$_2$, Ag-doped ZrO$_2$, and Ag-doped ZrO$_2$/rGO as hybrid photocatalysts by facile hydrothermal method. These photocatalysts were characterized by powder XRD, scanning electron microscopy, EDX, FTIR, photoluminescence, UV–Vis diffuse reflectance (DRS), and Raman spectroscopy. The photodegradation of MO (10 ppm) was studied with pure ZrO$_2$, Ag-doped ZrO$_2$, and Ag-doped ZrO$_2$/rGO (10 mg/100 mL catalyst dosage) photocatalysts at 100 min irradiation time under UV–Visible light. The pH effect and catalyst dosage on photodegradation of MO was investigated. $\text{Ag}_{0.04}\text{ZrO}_2$/rGO photocatalyst exhibited the maximum photocatalytic degradation of MO (87%) as compared to $\text{Ag}_{0.04}\text{ZrO}_2$ (60%) and pure ZrO$_2$ (26%). Reusability experiments ensured the excellent stability of photocatalyst after five consecutive experiments. To the best of our knowledge, this is the first report on the facile hydrothermal synthesis of $\text{Ag}_{0.04}\text{ZrO}_2$/rGO photocatalyst for photocatalytic degradation of methyl orange.

Environmental contamination, particularly water contamination, has become one of the most pressing challenges in recent years. Diverse toxins from industrial effluents build up in the water, posing a threat to humans, animals, microbes, and aquatic life. The dyes, which are organic in origin, are among the pollutants that give water color. Furthermore, according to the World Bank, the textile industry contributes 17–20 percent of industrial water pollution through dyes. The majority of dyes, including methyl orange are comprised of azo dyes, which have a nitrogen π-bond in their structure. The azo dye methyl orange (MO) is one of the most widely used dyes in the textile, food, leather, and pharmaceutical industries. For the detection of hydrogen gas and hydrochlorides, MO is also utilized as a coloring agent. The addition of MO to water is a major source of worry since it has a significant impact on water quality and creates dangerous scenarios for aquatic life. The toxicity, mutagenesis, and carcinogenic characteristics of MO are the most concerning features of its use. Because MO is difficult to degrade; selective approaches are required. Coagulation, reverse osmosis, membrane filtering, oxidation, reduction, complexometric, ion exchange, anaerobic, and aerobic techniques are all commonly employed for MO degradation. Among these techniques, photocatalytic degradation appears to be the most promising for MO degradation. Hence, many oxides and sulfides of semiconductors such as TiO$_2$, SnO$_2$, Fe$_2$O$_3$, ZnO, WO$_3$, CdS, WS$_2$, ZnS, and MoS$_2$, as well as their binary and ternary mixed oxides or sulfides have been reported for the photodegradation of organic pollutants like antibiotics and dyes.

ZrO$_2$, a cost-effective and nontoxic transition metal oxide, has high thermal and chemical stability, low thermal conductivity, and high corrosion resistance. Controllable morphology, mesoporous structure, and crystallinity make nanosized ZrO$_2$ an active photocatalyst as it enhances the light absorption capability enabling reactants to approach surface active sites mesoporous structure. So far, ZrO$_2$ has been widely studied due to its relatively wide bandgap values (3.25–5.1 eV) and highly negative conduction band potential. However, intrinsic ZrO$_2$ with such a wide band gap is found to be only responsive to ultraviolet (UV) light, which is impracticable for the use of visible light. For the best use of solar energy ZrO$_2$ lattice incorporated with a suitable metal on a...
conducting substrate is widely used to form an impurity state, which can shift its absorption edge into the visible light region. Reduced graphene oxide (rGO) a conducting substrate, acts as an excellent electron mediator, integrating rGO with photocatalysts increases the surface area hence the absorption capacity of the catalyst which resultantly improves electron transport\cite{24}. The combination of a reduced conducting substrate and photocatalyst reduces the bandgap energy, enhances visible light absorption, stabilizes nanocomposite, and enables electron–hole separation throughout the heterojunction\cite{25–27}. To the best of our knowledge, the synthesis of Ag-doped ZrO$_2$/rGO is not reported yet.

This study aims to synthesize the silver doped ZrO$_2$/rGO photocatalysts and degrade methyl orange (MO) under visible light. In the current study, we have synthesized the photocatalysts by facile hydrothermal method. This is the first report on the facile hydrothermal synthesis of Ag$_{0.04}$ZrO$_2$/rGO photocatalyst to the best of our knowledge. These photocatalysts were characterized by powder XRD, SEM, EDX, FTIR, photoluminescence (PL), EPR, and UV–Vis diffuse reflectance (DRS). The photodegradation of MO with ZrO$_2$, Ag-doped ZrO$_2$, and Ag-doped ZrO$_2$/rGO was evaluated under visible light. Ag$_{0.04}$ZrO$_2$/rGO photocatalyst exhibits the highest catalytic activity among the prepared catalysts.

Results and discussion

X-ray diffraction (XRD). The XRD spectra of the Ag$_x$ZrO$_2$ (x = 0.01–0.05) are shown in Fig. 1a. The XRD patterns of Ag$_x$ZrO$_2$ (x = 0.01–0.05) photocatalysts are similar to that of ZrO$_2$ and no peak is observed for Ag. The XRD pattern of Ag$_x$ZrO$_2$ (x = 0.01–0.05) shows the well-defined diffraction peaks corresponds to the monoclinic phase of ZrO$_2$ at 17.5° (100), 24.3° (110), 28.3° (-111), 31.5° (111), 34.3° (020), 40.7°, (−211), 50.3° (220), 58.2° (−222), 63° (311), 65.9° (−231) attributing to crystal planes with the JCPDS file No. 65-1023. The only difference between the XRD patterns is the decrease in intensity of a characteristic peak of zirconia at 28.3°, with the increase in the amount of Ag. Figure 1b shows the comparison of XRD pattern of Ag$_{0.04}$ZrO$_2$/rGO and Ag$_{0.04}$ZrO$_2$ with pure ZrO$_2$, indicating that Ag is intrinsically doped in ZrO$_2$ which improves the catalytic activity of the photocatalyst\cite{28}.

SEM and EDX study. The SEM micrographs of pure ZrO$_2$ are shown in Fig. S1a–c and EDX are shown in Fig. S1d. Pure ZrO$_2$ shows the large-sized cavities of thick rod-like structure\cite{29,30}. The SEM micrographs of Ag$_{0.04}$ZrO$_2$ are shown in Fig. S2a–d which shows that the crystallinity has decreased with increasing concentration of Ag and EDX is in Fig. S2e. The crystallinity is regained when the heterostructure with rGO is formed. The SEM micrographs of Ag$_{0.04}$ZrO$_2$/rGO photocatalyst are shown in Fig. 2a–d having dense nanorods which are aligned vertically. The average diameter of the nanorods is 100 nm. The large network structure of Ag$_{0.04}$ZrO$_2$/rGO nanorods may not only increase the active sites for a photocatalytic reaction but also provide channels for solution diffusion during the intercalation/de-intercalation process toward photocatalyst.

Elemental analysis of Ag$_{0.04}$ZrO$_2$/rGO nanorods was done by EDX which is shown in Fig. 2e. The spectrum shows the O, Ag, Zr, and C with an atomic percentage of 49.68, 3.19, 21.27, and 25.86, respectively\cite{31}.

Fourier transform infrared spectroscopy. FTIR spectroscopy was used to identify chemical bonds as well as functional groups of synthesized material by producing an infrared absorption spectrum. ZrO$_2$, Ag$_{0.04}$ZrO$_2$, and Ag$_{0.04}$ZrO$_2$/rGO photocatalysts were characterized with FTIR spectroscopy. In Fig. S3a, a comparison of the FTIR spectra of pure ZrO$_2$ and Ag$_{0.04}$ZrO$_2$ is presented. Both the FTIR spectra show the band around 559 cm$^{-1}$ which arises due to the Zr-O vibration in zirconia. Figure S3b shows the FTIR spectrum of Ag$_{0.04}$ZrO$_2$/rGO (1:1). In this spectrum, the band at 561 cm$^{-1}$ is due to the Zr-O vibrations in the photocatalyst. This spectrum also shows the bands of rGO\cite{32}.

Figure 1. (a) XRD patterns of Ag$_x$ZrO$_2$ (x = 0.01–0.05), (b) comparison of XRD patterns of Ag$_{0.04}$ZrO$_2$/rGO and Ag$_{0.04}$ZrO$_2$ with pure ZrO$_2$. 
UV–Vis diffuse reflectance spectroscopy. UV–Vis DRS absorbance of ZrO$_2$, Ag$_{0.04}$/ZrO$_2$, and Ag$_{0.04}$ZrO$_2$/rGO results are displayed in Fig. 3. It can be seen that ZrO$_2$ exhibits absorption in the UV region due to its large bandgap. The absorption is red-shifted by doping of Ag into ZrO$_2$ as in the case of Ag$_{0.04}$/ZrO$_2$ while Ag$_{0.04}$ZrO$_2$/rGO shows strong adsorption in the visible region due to the formation of heterostructure which decreases the recombination rate of e$^-$/h$^+$ pairs. This improved change in absorption of Ag$_{0.04}$ZrO$_2$/rGO increases the photocatalytic activity$^{33}$.

The Tauc equation was used to calculate the bandgap energy of the synthesized photocatalysts$^{34}$:

\[(h\nu)^{1/n} = A (h\nu - E_g)\]  

Figure 2. (a–d) Scanning electron micrographs of Ag$_{0.04}$ZrO$_2$/rGO and (e) EDX of Ag$_{0.04}$ZrO$_2$/rGO.
where, \( h \) is Planck’s constant, \( \nu \) is the vibrational frequency, \( \alpha \) is the absorption coefficient, \( E_g \) is the bandgap energy (eV), \( A \) is a proportionality constant, and \( n \) refers to the type of electron transition (for directly allowed transitions, \( n = 1/2 \)). The value of \( \alpha \) is directly proportional to the Kubelka–Munk function \( F(R_{\infty})^2 \): 

\[
(h\nu F(R_{\infty}))^2 = A(h\nu - E_g)
\]  

(2)

The Tauc plot shows the bandgap energy by the projection of the tangent on the x-axis to the turning point of curvature. The result is shown in Fig. 3b.

The bandgap energies of \( \text{ZrO}_2 \), \( \text{Ag}_{0.04}\text{ZrO}_2 \), and \( \text{Ag}_{0.04}\text{ZrO}_2/r\text{GO} \) are 3.48, 3.11, and 2.99 eV, respectively. The incorporation of Ag as dopant has lowered the bandgap energy of \( \text{Ag}_{0.04}\text{ZrO}_2 \) (3.06 eV) while the addition of rGO has further lowered the bandgap of \( \text{Ag}_{0.04}\text{ZrO}_2/r\text{GO} \) thus increasing the photocatalytic activity.

**Photoluminescence analysis.** Photoluminescence (PL) spectroscopy is used to observe the separation and transfer of photogenerated electrons and holes in the photocatalyst/heterojunctions. Figure 4 shows the PL spectra of \( \text{ZrO}_2 \), \( \text{Ag}_{0.04}\text{ZrO}_2 \), and \( \text{Ag}_{0.04}\text{ZrO}_2/r\text{GO} \) photocatalysts with an excitation wavelength of 325 nm. The shorter and longer wavelength emission of \( \text{ZrO}_2 \) and \( \text{Ag}_{0.04}\text{ZrO}_2/r\text{GO} \) photocatalysts could result from near-band-edge transitions and oxygen vacancies respectively.

The redshift in the spectrum of \( \text{Ag}_{0.04}\text{ZrO}_2/r\text{GO} \) could be attributed due to interfacial charge transfer from \( \text{Ag}_{0.04}\text{ZrO}_2 \) to rGO. This charge transfer decreases the PL intensity of \( \text{Ag}_{0.04}\text{ZrO}_2/r\text{GO} \) photocatalyst. The intensity is observed in the following order: \( \text{ZrO}_2 > \text{Ag}_{0.04}\text{ZrO}_2 > \text{Ag}_{0.04}\text{ZrO}_2/r\text{GO} \). The electron/hole pairs are well separated in \( \text{Ag}_{0.04}\text{ZrO}_2/r\text{GO} \), which exhibits higher photocatalytic activity.

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**Figure 3.** (a) UV–Vis DRS spectra of \( \text{ZrO}_2 \), \( \text{Ag}_{0.04}\text{ZrO}_2 \), and \( \text{Ag}_{0.04}\text{ZrO}_2/r\text{GO} \) photocatalysts. (b) \( E_g \) of \( \text{ZrO}_2 \), \( \text{Ag}_{0.04}\text{ZrO}_2 \), and \( \text{Ag}_{0.04}\text{ZrO}_2/r\text{GO} \) photocatalysts.

**Figure 4.** Photoluminescence (PL) spectra of \( \text{ZrO}_2 \), \( \text{Ag}_{0.04}\text{ZrO}_2 \), and \( \text{Ag}_{0.04}\text{ZrO}_2/r\text{GO} \).
Specific surface area analysis (BET). Figure 5a shows the nitrogen adsorption–desorption studies of ZrO₂ and Ag₀.₀₄ZrO₂/rGO photocatalysts. These studies are conducted to measure the specific BET surface area and pore structure of the photocatalysts. The BET surface area of Ag₀.₀₄ZrO₂/rGO photocatalyst was calculated as 142.441 m²/g which is higher than ZrO₂ which is 37.3996 m²/g. An increase in the pore diameter presented in Fig. 5b from 0.08026 cm³/g for ZrO₂ to 0.98852 cm³/g for Ag₀.₀₄ZrO₂/rGO is also observed. This suggests that the higher surface area and pore volume of Ag₀.₀₄ZrO₂/rGO can be achieved by the modification of ZrO₂ with Ag and rGO. The higher specific BET surface area partly justifies the better adsorption and faster removal of pollutants interacting with the surface of the photocatalyst. Because of higher specific BET surface area, Ag₀.₀₄ZrO₂/rGO shows best photocatalytic activity. The specific surface area, mean pore diameter, pore volume, and BHJ pore diameter are summarized in Table 1.

Degradation study of methyl orange (MO). The degradation of MO was evaluated under visible irradiation with ZrO₂, AgₓZrO₂ (x = 0.01–0.05), and Ag₀.₀₄ZrO₂/rGO (1:1, 1:2 and 1:3) photocatalysts. Figure 6a,b shows the A/A° of MO using ZrO₂, AgₓZrO₂ (x = 0.01–0.05), and Ag₀.₀₄ZrO₂/rGO (1:1, 1:2 and 1:3) photocatalysts under visible radiations. Figure S5 shows the comparison of A/A° of degradation of MO ZrO₂, Ag₀.₀₄ZrO₂/rGO. The Ag₀.₀₄ZrO₂/rGO exhibits 87% degradation while Ag₀.₀₄ZrO₂ and ZrO₂ show 60% and 26% degradation of MO in 100 min. The degradation of MO is highest with Ag₀.₀₄ZrO₂/rGO photocatalyst as compared to Ag₀.₀₄ZrO₂ and ZrO₂ due to lower bandgap energy and a lower rate of recombination of e⁻/h⁺ in Ag₀.₀₄ZrO₂/rGO. Figure S6 shows the comparison of % degradation of MO (a) ZrO₂ and AgₓZrO₂ (x = 0.01 to 0.05) (b) ZrO₂ and Ag₀.₀₄ZrO₂/rGO (1:1, 1:2 and 1:3) photocatalysts.

Kinetic studies. The photocatalytic degradation follows a pseudo-first-order kinetic reaction; its kinetics can be expressed as follows:

\[ \ln \left( \frac{A_0}{A_t} \right) = kt \]

where \( k \) is the reaction rate constant and \( t \) is the reaction time. Figure 7 shows the reaction kinetics of degradation of MO by ZrO₂, Ag₀.₀₄ZrO₂/rGO, and Ag₀.₀₄ZrO₂/rGO (1:1) photocatalysts.

These results illustrate that MO is degraded by Ag₀.₀₄ZrO₂/rGO more efficiently than pure ZrO₂ or Ag₀.₀₄ZrO₂. The degradation rate constant (k) is calculated from the slope of the straight line. The degradation rate constant of Ag₀.₀₄ZrO₂/rGO with 1:1 (0.0204) is higher than that of doped Ag₀.₀₄ZrO₂ (0.00871) and pure ZrO₂ (0.00289).
Figure 6. Comparison of degradation of MO (a) pure ZrO$_2$ and Ag$_x$ZrO$_2$ ($x = 0.01$–$0.05$), (b) pure ZrO$_2$ and Ag$_{0.04}$ZrO$_2$/rGO (1:1 to 1:3) and (c) % degradation of MO with pure ZrO$_2$, Ag$_{0.04}$ZrO$_2$, and Ag$_{0.04}$ZrO$_2$/rGO.

Figure 7. Reaction kinetics of degradation of MO with ZrO$_2$, Ag$_{0.04}$ZrO$_2$, and Ag$_{0.04}$ZrO$_2$/rGO.
Effect of pH on the photocatalytic performance. The pH is a major factor that affects the surface charge of the photocatalyst, the nature of the dye, and the ability of the dye to absorb into the photocatalyst surface. The degradation of MO was performed at pH 1, 3, 5, 7, 9 and 11 at a fixed dose of Ag0.04ZrO2/rGO (Fig. 8a,b). The degradation of MO is higher in acidic pH and is less in basic pH. However, under acidic conditions, MO change to a quinone structure. A visible color change, along with an absorbance peak shift was observed at lower pH values, further supporting the existence of a quinone structure of MO. The quinone structure is more prone to oxidation over the azo structure due to the sulfonic groups (−SO3−) aiding in capturing hydrogen and further enhancing the hydrophobicity of the catalyst surface. The enhanced degradation of MO at lower pH 03 is due to the formation of hydroxyl radicals during the reaction (OH− + h+ → OH·), the hydroxyl radicals are scavenged more slowly at a lower pH allowing them to react more readily with the dye.

Effects of dosage of the catalyst. To examine the effect of dosage of photocatalyst, different experiments were performed at 10 ppm MO concentration and pH 3, by varying the dose of Ag0.04ZrO2/rGO photocatalyst between 5 and 15 mg/100 mL. It can be seen in Fig. 8c,d that the degradation rate of MO increases with the increasing dosage of Ag0.04ZrO2/rGO. However, it is interesting to find that the degradation rate first increased with the increased dosage of catalyst (5–10 mg), then decreased with the further increase of catalyst (15 mg). The reason is that by increasing the catalyst dosage the surface area of the catalyst for the adsorption of MO increases which increases the MO degradation. But when the catalyst dosage is increased to 15 mg, a blockage of the light penetration occurs, which decreases the degradation of MO43.

Reusability. To check the reusability of the catalyst, Ag0.04ZrO2/rGO photocatalyst was washed with deionized water several times and dried in the oven after every experiment. Ag0.04ZrO2/rGO photocatalyst was used for the degradation of MO in five repeated experiments. In every experiment, the irradiation time was 100 min. The Ag0.04ZrO2/rGO photocatalyst exhibited a high visible light photostability after five repeated experiments, although a slight decrease of photocatalytic activity is observed compared to the first-run result from 87 to 78% degradation, respectively as shown in Fig. 8e,f.

Phocelelectrochemical measurements. Figure 9a shows the electrochemical impedance spectroscopic measurements of the pure ZrO2, Ag0.04ZrO2 and Ag0.04ZrO2/rGO photocatalysts under visible light irradiation. The smallest semicircle is observed for the photocatalyst Ag0.04ZrO2/rGO, showing the lowest charge transfer resistance in the as prepared photocatalyst.

Chronoamperometric response is shown in Fig. 9b at a potential of 0.8 V under the chopped light illumination. The photocurrent increases immediately from OFF to ON state proving that the present system is sensitive to light illumination and efficient in the generation and separation of electron–hole pairs through p–n junction.

Figure 9c,d show the Mott-Schottky plots of Ag-doped ZrO2 and rGO. Flat band potential (Efb) is measured from these plots. The slope of Mott-Schottky plots of Ag0.04ZrO2 (−0.32 V vs Ag/AgCl) is positive as compared to rGO (−0.82 V vs Ag/AgCl) showing the n-type nature of Ag0.04ZrO2 and p-type nature of rGO, indicating the formation of an effective p–n junction between Ag0.04ZrO2 and rGO for the degradation of MO.

Mechanisms of photocatalytic degradation of MO. The potential of the valence band and conduction band, as well as the band gap energy, are important factors to determine the mechanism. The potential of the conduction band was calculated from Mott-Schottky plots which is be −0.12 eV vs RHE for Ag0.04ZrO2 and −0.62 eV vs SHE for rGO. The bandgap energies calculated by using the Tauc plot are 3.11 eV for Ag0.04ZrO2 and 1.69 eV for rGO. The potential of the valence band of Ag0.04ZrO2 (2.99 eV) and rGO (1.07 eV) was calculated by using this formula: VB = CB + Eg.

The detailed mechanisms of photocatalytic degradation of MO by Ag0.04ZrO2/rGO are shown in Fig. 10. This mechanism shows that when light falls on the photocatalyst, the electrons from the valence band of Ag0.04ZrO2 and rGO get excited and move to the conduction bands. The holes from the valence band of Ag0.04ZrO2 move the valence band of MO. The electrons from the conduction band of rGO move to the conduction band of Ag0.04ZrO2, hence reducing the electron–hole recombination as shown by the PL spectra. These photoexcited electrons react with the adsorbed oxygen and convert it to superoxide radicals which react with methyl orange and immediately decompose the dye to water and CO2. A possible mechanistic rout is given below:

\[
\text{Ag0.04ZrO2/rGO + light} \rightarrow e^- + h^+ \\
e^- + O_2 \rightarrow O_2^* \\
O_2^* + h^+ + MO \rightarrow CO_2 + H_2O
\]

Holes on the other hand react with the water molecules and produce OH radicals and react with methyl orange and immediately decompose it to H2O and CO2. Therefore, this photocatalyst system provides active sites which shows the ability to harvest large amount of light hence better degradation efficiency. Many researchers have reported the degradation of methyl orange till now and a comparison table with the present study is shown in Table 2.
Figure 8. Photocatalytic degradation of MO (a) kinetic simulation, (b) bar graph % degradation at various pH, (c) Kinetic simulation, (d) Bar graph of % degradation at different catalyst dosage, (e) Reusability of Ag$_{0.04}$ZrO$_2$/rGO up to 5 cycles, (f) Bar graph of recycling.
Conclusions
We have synthesized pure ZrO₂, Ag-doped ZrO₂, and novel Ag-doped ZrO₂/rGO photocatalysts by facile hydrothermal method. These photocatalysts were characterized by powder XRD, SEM, EDX, FTIR, photoluminescence (PL), UV–Vis diffuse reflectance (DRS), and Raman spectroscopy. The photodegradation of MO was studied with pure ZrO₂, Ag-doped ZrO₂, and Ag-doped ZrO₂/rGO photocatalysts at 100 min irradiation time under

![Figure 9](image_url)

Figure 9. (a) Shows the EIS spectra of the prepared pure and heterostructure photocatalysts (b) shows chronoamperometric on/off study of the best Ag₀.₀₄ZrO₂/rGO photocatalyst. (c) Mott-Schottky plots of Ag₀.₀₄ZrO₂ and (d) Mott-Schottky plots of rGO.

![Figure 10](image_url)

Figure 10. Mechanisms of photocatalytic degradation of MO by Ag₀.₀₄ZrO₂/rGO.
visible light. Reaction conditions were optimized for the best photocatalyst (Ag₀.⁰₄ZrO₂/rGO) by varying catalyst loading and pH of the solution. Ag₀.⁰₄ZrO₂/rGO exhibited the maximum photocatalytic degradation of MO (87%) as compared to Ag₀.⁰₄ZrO₂ (60%) and pure ZrO₂ (26%) due to lower bandgap energy and a lower rate of recombination of e⁻/h⁺ pair. Reusability experiments showed the excellent stability of photocatalyst after five consecutive experiments. Hence, this is the first report on the facile hydrothermal synthesis of novel Ag₀.⁰₄ZrO₂/rGO photocatalyst for the degradation of methyl orange (MO).

Methods

Materials. All analytical grade chemicals were used as received without further purification. AgNO₃ and Zr(NO₃)₄·5H₂O were purchased from Sigma Aldrich. Deionized H₂O was employed in all experiments.

Synthesis of graphene oxide (GO). GO was prepared by modified Hummers’ method⁴⁸. Initially, H₂SO₄ (27 ml) was mixed with H₃PO₄ (3 ml) and stirred for several min. Then graphite powder (0.225 g) was added to the mixture and then added the KMnO₄ (1.32 g) slowly. The mixture was stirred for 6 h until the color turns into dark green. Then H₂O₂ was added to the mixture and stirred for 10 min. After cooling HCl (10 ml) and H₂O (30 ml) were added and centrifuge for 10 min. at 5000 rpm. The supernatant was removed and the residue was washed the HCl and H₂O three times.

Synthesis of zirconia (ZrO₂). ZrO₂ was prepared by a simple hydrothermal method. Initially, a 0.01 M aqueous solution of zirconium nitrate was prepared and 25% ammonium hydroxide was added dropwise with constant stirring⁴⁹. After 1 h, white precipitates were collected and transferred to Teflon lined autoclave. The precipitates were hydrothermally treated at 180 °C for 24 h. The product was obtained by centrifuge, washed several times with deionized water and ethanol, and dried at 80 °C in a vacuum oven.

Synthesis of AgₓZrO₂. Ag-doped ZrO₂ photocatalysts were prepared by hydrothermal method. Zirconium nitrate aqueous solution (0.01 M) was mixed with the 0.1 mM aqueous solution of silver nitrate. To the homogenized solution, 25% ammonium hydroxide was added dropwise with constant stirring. After 1 h, the white precipitates were collected and transferred to a Teflon-lined autoclave which was then hydrothermally treated at 180 °C for 24 h. The precipitates were separated by centrifuge, washed several times with deionized water and ethanol, and dried at 80 °C in a vacuum oven.

Synthesis of Ag₀.⁰₄ZrO₂/rGO photocatalyst. The photocatalyst, Ag₀.⁰₄ZrO₂/rGO (Ag₀.⁰₄ZrO₂ : rGO in 1:1, 1:2, and 1:3 ratio) were prepared in situ by the procedure as discussed above. The aqueous solutions zirconium nitrate, silver nitrate was mixed with graphene oxide an autoclave and heated at 180 °C for 24 h. GO is thermally reduced to rGO under the reaction conditions⁵⁰. The black precipitates of the nanocomposites were separated by centrifuge, washed several times with water and ethanol, and dried at 80 °C under vacuum.

Characterization. X-ray diffractometer (DRONE-8, Russia), using Cu Ka radiation as the X-ray source, operated at 45 kV and 100 mA was utilized to study the crystalline structure and phase composition of photocatalysts. Scanning electron microscopy (MAIA3 TESCAN) was employed to determine the morphology of the photocatalysts. The absorbance of the photocatalysts was determined by utilizing the ultraviolet–visible (UV–Vis) diffuse reflectance spectroscopy (Lambda 365S, Perkin Elmer, Massachusetts, USA) in the wavelength range of 200–800 nm. Fourier transform infrared spectrometer (Alpha, Bruker) with range 550 to 4000 cm⁻¹ was used to obtain IR spectra of the compound. Perkin Elmer spectrophotometer (Massachusetts, USA FL 6500/8500) with 150 W Xe lamp (200–900 nm) was used to measure the PL of photocatalysts.

Degradation studies of methyl orange. The degradation studies of MO were performed with all prepared photocatalysts. The prepared photocatalysts (10 mg) were added in 100 mL of the aqueous solution of MO (10 ppm) and stirred initially for 30 min in the dark to attain adsorption–desorption equilibrium. Then the mixture was then exposed to UV–Visible light using a 500 W UV–Vis lamp. The 5 mL aliquot was taken every 20 min. and analyzed with UV–Vis spectrophotometer. The photocatalytic degradation treatment was studied at
pH 3 and 100 min. irradiation time. The photocatalytic degradation efficiencies of photocatalysts were calculated using the following formula\(^{(2)}\):

\[
\text{Degradation efficiency (\%) = \left(\frac{A_0 - A}{A_0}\right) 100}
\]

where \(A_0\) is the initial absorbance of MO solution and \(A\) is the absorbance after irradiation.

### Data availability

All data generated or analyzed during this study are included in this article and its supplementary information file.

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