Au–TiO$_2$-Loaded Cubic g-C$_3$N$_4$ Nanohybrids for Photocatalytic and Volatile Organic Amine Sensing Applications

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ABSTRACT: A green and efficient approach for efficient nanohybrid photocatalysts in extending the light response to the visible spectrum is a hot research topic in sustainable energy technologies. In this work, novel Au–TiO$_2@m$-CN nanocomposite was synthesized using hard template of cubic ordered mesoporous KIT-6 via the nanocasting process. The as-prepared Au–TiO$_2@m$-CN nanohybrids exhibit enhanced photocatalytic activities with improved stability and reusability using methyl orange dye. The enhanced photocatalytic performance is a result of the conjugated effect of catalytic active Au and TiO$_2$ nanoparticles supported on highly efficient visible light sensitizer, graphitic carbon nitride (m-CN or g-C$_3$N$_4$) and ordered mesoporous morphology. Besides, the sensing performance of Au–TiO$_2@m$-CN nanohybrids was also tested for the detection of amine gases, wherein a significant response was reported for triethylamine at low operating temperatures. This study reveals a simple and scalable methodology to design and develop next generation of layered mesoporous materials for multifunctional applications.

KEYWORDS: nanocasting, mesoporous, photocatalysis, triethylamine, graphitic carbon nitride

INTRODUCTION

In the past decade, several research attempts have been dedicated to semiconducting photocatalysts that degrade environmental pollutants and split water under the solar light irradiation. A suitable redox reaction potential and strong light absorption are required for photocatalytic reaction, which most of the semiconducting photocatalysts do not possess. In this context, TiO$_2$ has gained significant attention as a semiconducting photocatalyst with great stability, low cost, high activity, and nontoxicity, yet its high energy band gap ($E_g \approx 3.6$ eV) limits its functionality to mainly absorb ultraviolet (UV) light, which represents only 4% of the solar spectrum. Hence, in order to maximize the absorption of solar light and transportation of charge, TiO$_2$ nanohybrids have been extensively explored in the recent years. Suwarnkar et al. prepared Ag-doped TiO$_2$ and observed 99% degradation of methyl orange (MO) dye within 90 min. Sakhivel et al. reported noble metallic nanoparticles as dopants to boost the properties of TiO$_2$ by increasing the charge carrier transportation. They observed that because of excellent electronic conductivity and catalytic properties, metallic (Ag, Au) nanoparticles could provide new opportunities for realizing high degradation performances. Yet the achievements made are far from the idea goal of harnessing the abundant visible light.

Recently, graphitic carbon nitride (g-CN), which is a metal-free polymeric with semiconductor properties and visible light activated band gap (2.70 eV), has been proposed as a photocatalyst in the applications involving water splitting and decomposition of organic pollutants for advantages of earth abundance, appropriate reduction potential, exceptional physical properties, unique electronic structure, and outstanding visible light absorption. However, the quick recombination of photo-generated electron and hole pairs and small surface area limit the photocatalyst performance of g-CN materials. Hitherto, a variety of techniques involving template inversion of mesoporous silica (KIT-6, SBA-15, colloidal silica) and exfoliation were employed in increasing the surface area of the g-CN for sensing, hydrogen production, and visible light photocatalysis applications. The negative potential (−1.12 eV vs NHE) of g-CN implies that it can easily form heterojunctions with TiO$_2$ to attain superior visible light degradation performance. In this context, Shi et al. have synthesized nitrogen-doped TiO$_2$/g-C$_3$N$_4$ photocatalysts through a cyanamide precursor by utilizing in situ impregnation calcination method. Under visible light ($\lambda \geq 420$ nm), the nanocomposite was able to produce hydrogen in the absence of a noble metal as co-catalyst. Wei et al. have prepared noble metal (Ag, Pt, Au)-doped TiO$_2$/g-C$_3$N$_4$ heterostructured nanofibers by a combination of electrospinning and thermal oxidation/reduction process and reported excellent photocatalytic activity. Similarly, Shen et al. have synthesized TiO$_2$ nanobelts laminated on g-C$_3$N$_4$ nanosheet and demonstrated...
excellent degradation performance of MO (95%) and hydrogen evolution. Wei et al. have prepared mesoporous TiO$_2$/g-C$_3$N$_4$ microspheres using a facile nanocoating process with cyanamide as the g-CN precursor. They have reported excellent phenol degradation using the photocatalyst. Albanna et al. have synthesized metal-free nanocomposites (g-C$_3$N$_4$ nanosheets/TiO$_2$ mesocrystals) and realized that the presence of TiO$_2$ increases the photocatalytic efficiency for H$_2$ evolution. The results endorse that the g-CN and TiO$_2$ heterojunctions exhibited higher degradation performance for azo dye than pristine TiO$_2$ or g-CN. In addition, TiO$_2$ has also remained an important counterpart material in designing high-performance gas-sensing materials. The key requisite for gas sensors remains the high intrinsic surface area of the material, which improves the sensing performance by providing enormous surface active sites for gaseous molecules to desorb upon and also enhances the rate of adsorption, transportation, and desorption of charge carriers across the sensor surface. TiO$_2$ also has been utilized to form composites with 2D materials for achieving superior gas-sensing performance.

In this work, we report a novel two-step method (hydrothermal and nanocasting) to prepare Au–TiO$_2$-loaded cubic g-CN nanohybrids using the hard template of ordered mesoporous silica, KIT-6, to obtain high photodegradation efficiency (90.4%) toward the organic pollutant MO dye under 90 min irradiation of visible light and optimized conditions of dye concentration, pH, and catalyst dosage. Comparative degradation studies of organic dyes, including cresol red (CR), acid orange (AO7), direct blue (DB), and methylene red (MR), have also been conducted. The prepared catalyst shows excellent reusability without noticeable losses, suggesting excellent applicability of Au–TiO$_2$@g-CN nanohybrids in degrading aqueous dye solutions. Meanwhile, the Au–TiO$_2$@g-CN nanohybrids respond to a variety of volatile organic amines (VOAs), such as triethylamine (TEA), butylamine, triethanolamine, and benzylamine, for potential sensing applications. Au nanoparticles, because of their exceptional catalytic nature and sensing characteristics, were employed for enhancing the performance of the TiO$_2$@g-CN nanocomposite. The novel outcomes of this study can be highly useful in designing 2D layered materials and also show promising glimpse in designing mesoporous materials with extended multi-functionality.

**Experimental Section**

**Material Preparation.** In this study, the hard template of mesoporous KIT-6 was utilized for the preparation of mesoporous g-C$_3$N$_4$ (m-CN), TiO$_2$@m-CN, Au–TiO$_2$@m-CN, and Au–TiO$_2$. The KIT-6 and nanocasted m-CN were prepared as per our previous report. The mesoporous TiO$_2$@m-CN was obtained by the addition of aqueous TiCl$_4$ (1 mL, titanium tetrachloride, Merck) in CH$_3$N$_2$ solution (1 g/mL, cyanamide, Sigma-Aldrich). The solution was then added drop-wise to 0.6 g KIT-6 to produce a thick solution and stirred at room temperature for 1 h to induce homogeneity in the solution. The obtained solution was then dried at 80 °C for 4 h and later transferred in a closed crucible and heated for 6 h at 550 °C. The yellow powder was then stirred for 24 h with 2 M and 50 mL NH$_4$HF$_2$ (ammonium hydrogen difluoride, Sigma-Aldrich) solution to eliminate the silica template. The resulting bright yellow products were washed with excess of distilled water followed up by drying in an oven for 4 h at 100 °C to recover TiO$_2$@m-CN nanostructures. In a similar process, the mesoporous Au–TiO$_2$@m-CN was synthesized by the addition of HAuCl$_4$·3H$_2$O (14.75 mg, tetraclorouracil acid, Fisher Scientific) to 1 mL TiCl$_4$ aqueous solution and stirred for 1 h. Later, the solution was added to the aqueous cyanamide solution and a similar synthesis protocol was practiced as utilized for TiO$_2$@m-CN above.

The effect of m-CN matrix in the Au–TiO$_2$@m-CN nanocomposite was studied by preparing pure mesoporous Au–TiO$_2$, which was also synthesized by using KIT-6 but in the absence of m-CN. For this, 1 g TiCl$_4$ was added to 20 mL ethanol and stirred for half hour followed by the addition of 14.75 mg HAuCl$_4$·3H$_2$O (1 wt % Au) in the prepared solution. The solution was then stirred drop-wise upon 1 g Au–KIT-6 and the obtained slurry solution was stirred at 50 °C to allow the complete ethanol evaporation. Afterward, the product was dried for 1 h at 80 °C and later calcined for 4 h at 550 °C. In the end, the pure mesoporous Au–TiO$_2$ was obtained by the removal of Au–KIT-6 through NaOH (2 M) solution and following the processes of washing and filtration and later drying the sample for 6 h at 80 °C.

**Characterization of Materials.** Both low-angle and wide-angle X-ray diffraction data were recorded on Bruker D8 ADVANCE diffractometer using CuKα monochromatic radiation having $\lambda = 0.154$ nm at 40 kV and 50 mA. The FEI Tecnai F30 G2 transmission electron microscope (TEM) was used to determine pore morphology of the prepared samples at an acceleration voltage of 300 kV (field emission gun). The elemental mapping and overall structure of the as-synthesized samples were examined by scanning electron microscopy (SEM), which is equipped with an energy-dispersive X-ray spectroscopy (SEM–EDX, FEI Quanta 200F). The N$_2$ sorption isotherms were measured on Autosorb iQ2 instrument (Quantachrome) at 77 K to estimate the pore dimensions and surface area of the materials. The photocatalytic properties were evaluated on UV–vis spectrophotometer (Shimadzu UV-2401). The X-ray photoelectron spectroscopy (XPS) measurements were obtained on PHI 5000 instrument using Al Kα (1486.6 eV) radiation. The photoluminescence (PL) spectra were obtained on PerkinElmer LS-55 Fluorescence spectrometer under room temperature conditions.

**Evaluation of Photocatalytic Performance.** The photocatalytic activity of the prepared samples was evaluated by monitoring the removal of MO dye by utilizing the visible light irradiation. Typically, 0.2 g/L of catalyst, H$_2$O$_2$ solution, and 100 mL of 100 ppm MO dye solution were mixed thoroughly followed by stirring for 15 min in dark to acquire an adsorption/desorption equilibrium between catalysts and MO dye. After that, the mixture was irradiated perpendicularly using a Xe lamp (300 W) from a distance of 10 cm. After every 5 min, 2 mL aliquots were collected and centrifuged in triplicates followed by filtration. The solution was moved instantly in a quartz cuvette to record the absorbance spectra in the 300–800 nm range. The effect of pH on the degradation was studied by varying the pH value using 1 M solution of NaOH and HCL. The catalytic performance was also studied by varying the catalyst dosages and dye concentration. The influence of catalyst presence was studied by performing the experiments in the absence of catalysts. The degradation performance (D %) was evaluated by using the equation

$$D = \left( \frac{C_0 - C}{C_0} \right) \times 100 $$

where $C_0$ (mg L$^{-1}$) is the dye initial concentration (ppm) and $C$ (mg L$^{-1}$) is the dye concentration at any time “t.” The mineralization of dye was studied by total organic carbon (TOC) analysis on a multi-N/C 2000 Analytic Jena analyzer.

**Fabrication of Sensing Elements and Sensing Measurements.** The sensing performance was monitored using Ag–Pd interdigitated electrodes (electrodes separation distance and electrode width of 0.2 mm), which were printed on ceramic substrate (13.4 mm × 7 mm × 0.5 mm). A dilute paste of sample/ethanol (1:20) was poured upon the ceramic substrate by using a pipette (10 µL) and
dried for 2 h at 60 °C. The sensing experiments were performed in a customized gas-sensing set-up as per our earlier report.16,17

RESULTS AND DISCUSSION

Characterization. The crystallographic structure of KIT-6, m-CN, TiO2@m-CN, Au–TiO2@m-CN, and Au–TiO2 samples is shown in Figure 1. A wide peak at 2θ = 22° was observed for KIT-6, which is a standardized peak for pristine materials.34–36 The nanocasted samples with m-CN content (m-CN, TiO2@m-CN, Au–TiO2@m-CN) display two distinct peaks at 12.5° ([100] plane) and 27.5° ([002] plane) corresponding to the reflections of CN.12,13 For TiO2-loaded samples (TiO2@m-CN, Au–TiO2@m-CN, and Au–TiO2), the peaks centered at 25.3°, 37.8°, 48.1°, 53.9°, 55.1°, 62.7°, and 68.7° denote the presence of TiO2 in an anatase crystalline phase (JCPDS no. 21-1272). For Au–TiO2@m-CN and Au–TiO2 nanohybrids, three distinct peaks for Au at 2θ = 38.1°, 44.2°, and 64.3° corresponding to (111), (200), and (220) respectively, were observed (JCPDS no. 04-07834), and the average crystallite size calculated from Scherrer’s equation for metallic Au nanoparticles was 3.18 nm. Besides, the Au peaks confirm the presence of Au nanoparticles in the TiO2@m-CN nanohybrids. The small-angle X-ray scattering pattern of the as-synthesized KIT-6, m-CN, TiO2@m-CN, Au–TiO2@m-CN, and Au–TiO2 materials is shown in Figure 1B. The peak at 2θ = 0.84° corresponding to the (211) plane represents the characteristic peak for the mesoporous materials. Besides, the presence of two shoulder peaks between 2θ = 1°–2° indicates the ordered structure of KIT-6 with the Ia3d symmetry.16 However, these shoulder peaks were absent in the nanocasted samples, which suggests that mesoporous ordering was reduced in the process of template removal step. The prominent peak corresponding to the (211) plane was found to be slightly shifted toward higher angles in the nanocasted samples (as compared to the KIT-6) because of the decrease in scattering contrast amid the mesoporous framework and pore channels.

The N2 sorption isotherms and pore measurement curves for as-prepared materials are shown in Figure 2A,B, respectively. The KIT-6 silica shows a type IV adsorption curve with an H1-type hysteresis loop, which denotes the process of capillary condensation within the mesoporous framework of the KIT-6 template.37 The N2 sorption isotherms and pore measurement curves for as-synthesized KIT-6, m-CN, TiO2@m-CN, Au–TiO2@m-CN, and Au–TiO2 nanohybrids. Figure 1. (A) Wide-angle XRD and (B) low-angle XRD spectra of (a) KIT-6, (b) m-CN, (c) TiO2@m-CN, (d) Au–TiO2@m-CN, and (e) Au–TiO2 nanohybrids.

Table 1. Physicochemical Properties of KIT-6, m-CN, TiO2@m-CN, Au–TiO2@m-CN, and Au–TiO2 Nanohybrids

<table>
<thead>
<tr>
<th>sample</th>
<th>S BET (m2/g)</th>
<th>Dp (nm)</th>
<th>Vp (cm3/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KIT-6</td>
<td>842</td>
<td>8.6</td>
<td>1.29</td>
</tr>
<tr>
<td>m-CN</td>
<td>185</td>
<td>5.8</td>
<td>0.96</td>
</tr>
<tr>
<td>TiO2@m-CN</td>
<td>143</td>
<td>5.1</td>
<td>0.75</td>
</tr>
<tr>
<td>Au–TiO2@m-CN</td>
<td>118</td>
<td>4.7</td>
<td>0.66</td>
</tr>
<tr>
<td>Au–TiO2</td>
<td>64</td>
<td>4.2</td>
<td>0.48</td>
</tr>
</tbody>
</table>

*aS BET: total surface area. bDp: pore size. cVp: pore volume.*

The morphologies of mesoporous KIT-6 and Au–TiO2@m-CN as obtained from high-resolution TEM (HRTEM) results are shown in Figure 3. As observed, the KIT-6 material shows a long range of 3D meso-ordered pore channels with pore diameter of ~8.45 nm, well agreeing with the results obtained from pore size distribution curves. In addition, the nanocasted Au–TiO2@m-CN shows Figure 3c,d a similar mesopore morphology even after the process of heat treatment and KIT-6 removal, thus revealing the excellent restoration of the original structure of parent template. However, as evident from the physico-chemical properties, listed in Table 1, a slight reduction in pore attributes was observed for the nanocasted Au–TiO2@m-CN because of the shrinkage of mesopore architecture on account of nanocasting procedures. The HRTEM image in Figure S1 shows the presence of Au nanoparticles inside the pore channels of Au–TiO2@m-CN nanohybrid. Figure 3e shows the SEM image of the Au–TiO2@m-CN nanocomposite. As can be seen, several round-shaped particles with size between 100 and 300 nm were observed. In Figure 3f–j, the elemental mapping results reveal the uniform presence of C, N, Ti, O, and Au elements in the Au–TiO2@m-CN nanocomposite.
The XPS spectrum for C 1s in the Au−TiO$_2$@m-CN nanocomposite in the energy range of 282−291 eV is shown in Figure S2. The two peaks recorded at 284.6 and 287.8 eV can be respectively related to the C−C bond in g-CN and sp$^2$ hybridization of C-atoms to the three N-atoms (C−(N)$_3$) in the g-CN material. The N 1s spectrum demonstrates three distinct peaks at 398.6, 399.8, and 401.5 eV, which respectively correspond to the nitrogen bonding of sp$^2$ hybridized aromatic nitrogen in C=N−C, ternary nitrogen in (N−(C)$_3$), and heptazine bonding with −NH or −NH$_2$ groups. The XPS spectra of Ti 2p illustrate that the peaks at 458.4 and 463.9 eV respectively denote the binding energies for Ti 2p$_{1/2}$ and Ti 2p$_{3/2}$ electrons and justify the existence of Ti$^{4+}$ in the TiO$_2$ crystal lattice. The Au 4f core-level XPS spectrum displays doublet peaks at 83.2 and 87.4 eV, which respectively denote the binding energies for Ti 2p$_{1/2}$ and Ti 2p$_{3/2}$ electrons and justify the existence of Ti$^{4+}$ in the TiO$_2$ crystal lattice. The O 1s spectrum shows an asymmetric profile and the single peak at 531.1 eV respectively denote the binding energies for Ti 2p$_{1/2}$ and Ti 2p$_{3/2}$ electrons and justify the existence of Ti$^{4+}$ in the TiO$_2$ crystal lattice. The Au 4f core-level XPS spectrum displays doublet peaks at 83.2 and 87.4 eV, which respectively correspond to the Au 4f$_{7/2}$ and Au 4f$_{5/2}$. Moreover, the splitting energy between the two peaks is equal to 3.2 eV, which denotes the presence of metallic gold (Au$^0$) according to the standard spectrum of Au, which is in good agreement with the Handbook of X-ray Photoelectron Spectroscopy. The O 1s spectrum shows an asymmetric profile and the single peak at 531.1 eV corresponds to the existence of physically adsorbed oxygen on the Au−TiO$_2$@m-CN material. The UV–vis diffuse reflectance spectrum in Figure S3a shows the absorption edges of Au−TiO$_2$@m-CN positions in the visible region. The tauc plot (inset) demonstrates a band energy gap of $\sim$3.0 eV, which further concludes that the Au−TiO$_2$@m-CN material can absorb large amounts of visible light and can be used as a visible-light irradiation photocatalyst. The PL intensity is a useful tool for determining the recombination rate of electron and hole. A higher intensity denotes the faster recombination rate, whereas a lower intensity illustrates the trapping and transferring of electrons across the interface. Figure S3b shows the PL spectra of as-prepared samples under excitation at 330 nm. As can be seen, a broad emission peak was noted for m-CN at $\sim$458 nm, which is approximately equal to the band gap of pure g-C$_3$N$_4$. On coupling of m-CN with Au−TiO$_2$, the peak intensity of Au−TiO$_2$@m-CN decreases, which indicated that the nanohybrid had a lower recombination rate of photo-generated charge carriers.

**Evaluation of Photocatalysts.** The photodegradation performance of m-CN, TiO$_2$@m-CN, Au−TiO$_2$@m-CN, and Au−TiO$_2$ for AOPs was evaluated under visible-light irradiation by evaluating the time-dependent degradation profile of MO. The stability of the dye was also evaluated by performing degradation experiments without the use of the Au−TiO$_2$@m-CN photocatalyst, effect of absence of light irradiation (Au−TiO$_2$@m-CN photocatalyst was present), and importance of H$_2$O$_2$ (light was irradiated but catalyst was not present) in a photocatalytic reaction system (Figure 4A). The degradation profiles in Figure 4A are the results of photocatalytic experiments performed under the conditions of catalyst dosage of 0.2 g/L, with 100 ppm MO concentration at pH 4. As clearly observed in Figure 4A, MO showed excellent stability for 15 min under dark conditions. In 90 min of irradiation time, the pure m-CN displays only 32% degradation of MO dye. Nevertheless, the addition of TiO$_2$ in the m-CN matrix increases the photocatalytic degradation...
performance (to 52%). The addition of TiO$_2$ nanoparticles enables the photo-generated electron to get transferred from the surface of m-CN to TiO$_2$, thereby increasing the photocatalytic efficiency of the TiO$_2$@m-CN nanocomposite. The pure Au–TiO$_2$ catalyst (without the presence of m-CN) shows only 70% degradation of MO dye in 90 min. The photocatalytic degradation rate was further enhanced with the addition of Au nanoparticles in the TiO$_2$@m-CN material. The Au nanoparticles reduce the rate of recombination of hole ($h^+$) and electron ($e^-$), which allows more dopant nanoparticles to involve in the redox reaction, thereby forming active oxygen species. It was also observed that the Au–TiO$_2$@m-CN catalyst doesn’t show any apparent degradation activity toward MO when no light was irradiated; on the contrary, ~80% of the MO dye degraded within 90 min when irradiated with light. The degradation performance by using the Au–TiO$_2$@m-CN catalyst (without H$_2$O$_2$) demonstrates the 75.6% degradation of MO dye under the same experimental conditions. Overall, Au–TiO$_2$@m-CN exhibits the maximum degradation efficiency among all the prepared materials because of the presence of both catalytically active Au and TiO$_2$ nanoparticles in the mesoporous m-CN matrix.

The first-order kinetic results (Langmuir Hinshelwood) for determining the apparent rate constant of the degradation process of dye were calculated by using the equation\(^{22}\)

$$\ln \left( \frac{C_0}{C} \right) = kt$$  \hspace{1cm} (2)

where $C$ is the MO concentration at time $t$, $C_0$ denotes the initial concentration of MO, and $k$ represents the first-order rate constant. As can be seen, Figure 4B represents the linear transformation of Figure 4A curve. The degradation spectra of MO dye in Figure 4C exhibited the maximum absorption peak, $\lambda_{max}$ at 550 nm. A decrement in $\lambda_{max}$ was clearly observed with time, which is directly related to the reduction of MO dye. The equilibrium adsorption capacity was estimated by using the formula\(^{20}\)

$$q_e = \frac{(C_0 - C_f)V}{m}$$  \hspace{1cm} (3)

where $C_0$ (mg/L), $C_f$ (mg/L), $m$ (g), and $V$, respectively, denote the initial and final concentrations of dyes, weight of the photocatalyst, and volume of the original mixture.

The degradation and adsorption performance of mesoporous the Au–TiO$_2$@m-CN nanohybrid over the MO dye were determined by varying the pH of the dye solution, as shown in Figure 5A. The results reveal a little absorption of the MO dye, and so a less degradation performance was observed under the alkaline condition (pH 8). In the aqueous suspension, g-CN is amphoteric with its isoelectric point (IEP) at pH 2.0034.\(^{12}\) This reveals that the surface of g-CN is mainly negatively charged when the pH is lesser than IEP.\(^{12}\) In the reaction system, the dissolved O$_2$ reacts with the first photoinduced electron ($e^-$) to produce moderate oxidant $\cdot$O$_2^-$(eq 4), which on reacting with the H$^+$ and second $e^-$ forms H$_2$O$_2$(eq 5)\(^{14,20,22,42}\). Because of the appropriate band positions of g-CN, the produced H$_2$O$_2$ reacts with the third photoinduced $e^-$ to produce most reactive $\cdot$OH radical (eq 6), which later assists in achieving a higher degradation efficiency of 85.8% for the Au–TiO$_2$@m-CN nanohybrid at pH 2. Also, the positively charged surface of the Au–TiO$_2$@m-CN nanohybrid readily absorbs the negatively charged dye molecules of MO because of electrostatic interaction.

$$O_2 + e^- \rightarrow \cdot O_2^-$$  \hspace{1cm} (4)

$$\cdot O_2^- + 2H^+ + e^- \rightarrow H_2O_2$$  \hspace{1cm} (5)

$$H_2O_2 + e^- \rightarrow \cdot OH + \cdot OH^-$$  \hspace{1cm} (6)

Figure 5B shows the effect of concentration of MO dye on its photocatalytic degradation activity. As can be seen, a reduction in degradation efficiency from 85.8 to 72% was observed when the initial concentration of MO dye was increased from 100 to 500 ppm. This could be because the absorption of organic species on the surface of mesoporous Au–TiO$_2$@m-CN nanohybrid increases when the concentration of the dye is increased in the system. This results in a reduction in the photon path length that enters the solution and slows down the formation rate of OH$^*$ radicals. In this case, the redox reaction and the degradation efficiency of the photocatalyst get reduces. The effect of catalyst dosage on the degradation performance of MO dye was also studied by varying the catalyst amount (0.1–0.5 g/L). As can be seen in Figure 5C, the dye degradation efficiency first increases with catalyst dosage (0.1–0.3 g/L) because of an increase in the HO$^*$ radical concentrations. However, the degradation efficiency decreases with further increase in catalyst amount (0.3–0.5 g/L) because of the accumulation of photocatalyst nanoparticles, which increases the light scattering and opacity and causes a reduction in the availability of active surface sites. Therefore, the ideal concentration of the catalyst was 0.3 g/L, which degrades 90.4% MO dye within 90 min of irradiation time. The performance of mesoporous Au–TiO$_2$@m-CN nanohybrid was also monitored by the degradation profile of

Figure 5. (a) Effect of pH, (b) dye concentration, (c) catalyst concentration, and (d) comparison with other azo dyes for Au–TiO$_2$@m-CN nanohybrid.
various azo dyes, such as CR, AO7, DB, and MR under the same experimental condition. As can be seen in Figure 5D, a degradation efficiency of 77, 79, 82, and 86% has been observed for CR, AO7, DB, and MR, respectively, for Au–TiO2@m-CN (0.3 g/L) at pH 2. A comparison of MO degradation performance using different materials in Table S1 shows that the Au–TiO2@m-CN has the best efficiency than earlier reported works.

Mechanism for the Degradation of MO. A probable schematic diagram showing the process of charge transfer for mesoporous Au–TiO2@m-CN nanohybrids has been illustrated in Figure 6. The high surface area of Au–TiO2@m-CN coupled with a uniform pore structure results in its high absorptivity toward MO. In the dark condition, a small amount of MO dye was absorbed by Au–TiO2@m-CN nanohybrids to create an adsorption–desorption equilibrium. The normal hydrogen electrode (NHE) versus band positions for Au–TiO2@m-CN nanohybrid is illustrated in Figure 6. Owing to the lesser work function (W0) of m-CN (∼4.3 eV)12 than that of TiO2 (4.5 eV),44 the m-CN (h+) and m-CN (e−) were formed under visible light irradiation. These excited electrons were transported from the conduction band of m-CN to that of TiO2, which later on get transferred to the Au surface. The absorbed oxygen gets reduced by these excited Au nanoparticles, and superoxygen anionic free radicals (•OOH) are generated, which further react with H2O to create •OOH active species by eqs 7–13 as follows

\[
\begin{align*}
\text{m-CN} + \text{visible light} & \rightarrow \text{m-CN(e}^\cdot \text{h}^\cdot) \quad (7) \\
\text{TiO}_2(\text{m-CN(e}^\cdot)) + \text{Au} & \rightarrow \text{TiO}_2@\text{m-CN} + \text{Au(e}^\cdot) \quad (8) \\
\text{Au(e}^\cdot) + \text{O}_2(\text{ads}) & \rightarrow \text{Au} + \text{•O}_2^- \quad (9) \\
\text{•O}_2^- + \text{H}^+ & \rightarrow \text{•OOH} \quad (10) \\
\text{•OOH} + \text{H}^+ + \text{e}^- & \rightarrow \text{H}_2\text{O}_2 \quad (11) \\
\text{H}_2\text{O}_2 + \text{e}^- & \rightarrow \text{•OH} + \text{OH}^- \quad (12) \\
\text{Au}^+(\text{h}^+) , \text{TiO}_2(\text{h}^+) , \text{m-CN(h}^+) , \text{•OH} , \text{•O}_2^- , \text{e}^- + \text{MO} & \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (13)
\end{align*}
\]

As the removal of dye color alone does not determine the mineralization of the dye and the dye solution after decolorization can be more harmful than the dye itself, therefore, TOC analysis was carried out to determine the mineralization level of the MO dye during the photocatalytic process. For the analysis of TOC, the mesoporous Au–TiO2@m-CN nanohybrids were irradiated by visible light. The results in Figure 7A demonstrate that the dye decolorization was faster than the degree of mineralization. The rate of TOC removal reaches around 69% after 2 h. The reason for fast decolorization and high TOC value could be the cleavage of the azo bond, which causes a reduction in the conversion of the N atom of the MO dye into oxidized nitrogen compounds because of the short life of the hydroxyl radicals and their negligible interaction with the aliphatic chain.45,46 The results reveal that the degradation activity after 90 min leads to a complete mineralization of the MO dye.

The recycling experiments were also performed in order to study the stability of the mesoporous Au–TiO2@m-CN nanohybrid for the degradation of the MO dye under similar test conditions. After each degradation experiment, the dispersed catalyst was recovered by following the process of centrifugation, washing (distilled water + ethanol), and drying (6 h at 50 °C) and utilized for the degradation of fresh MO dye solution under similar experimental conditions. This process was performed 5 times and the results are revealed in Figure 7B. As can be seen, the degradation efficiency was minutely affected because of the addition of organic species on the surface of Au–TiO2@m-CN, which directly affects the process of adsorption and reduction. Thus, it can be concluded that the Au–TiO2@m-CN nanohybrid catalyst is reusable and stable over longer duration without much loss in the photocatalytic performance. The XPS spectrum of individual elements of the Au–TiO2@m-CN photocatalyst taken after 20 experiments of stability test (dotted line) is shown in Figure S2. As can be seen, all of the elements show their peak intensity at respective binding energy and no apparent shifting in the binding energy was observed. The doublet peaks positions and peak distance for Ti and Au remain consistent after the stability test, which denotes the fact that the oxidation state of both the elements (Ti(4+) and Au(0)) remained intact after the photocatalytic test measurements. The long-term stability test of the Au–TiO2@m-CN photocatalyst toward the MO dye was recorded after a gap of 5 months. As can be seen

![Figure 6](image-url)  
**Figure 6.** The proposed mechanism for the degradation of MO dye over the Au–TiO2@m-CN nanohybrid.
The optimized working temperature was determined by investigating the prepared materials for the detection of VOAs. Levels of organic amines with the help of ultrasensitive and indoor climate, it becomes highly necessary to detect trace from these commonly and obviously present pollutants in the climate. VOAs represent such a class of household gases, which originate from dustbins, stored meat, and sewers, and owing to their toxic and stinking attributes, they are responsible for acute health problems.47−50 Considering the severe effects of these commonly and obviously present pollutants in the indoor climate, it becomes highly necessary to detect trace levels of organic amines with the help of ultrasensitive and selective chemical sensors. In this context, we have also investigated the prepared materials for the detection of VOAs. The optimized working temperature was determined by measuring the response of the prepared samples (g-CN, m-CN, TiO2@m-CN, Au−TiO2@m-CN, and Au−TiO2) in the temperature range 100−300 °C toward 50 ppm TEA. Figure 8a shows that the response of sensing materials follows a “rise → maximum → decline” pattern with a rise in the temperature. The pure g-CN shows a very poor response (R = 6.6) across the temperature range; however, being of the same composition, the ordered mesoporous m-CN, synthesized using the hard template of KIT-6 shows the highest response of 78.9 at 175 °C. The stability of the Au−TiO2@m-CN sensor was monitored over a span of 5 weeks, as shown in Figure 8c. As can be seen, the Au−TiO2@m-CN sensing responses increase with respect to an increment in the VOA concentration. The high response toward different gases can be explained on the basis of the C−H bond dissociation energies (BDE) of the respective gas molecules. As the BDE of TEA (91.2 kcal/mol)52 is less than that of butylamine (91.8 kcal/mol), triethanolamine (92.4 kcal/mol), and benzylamine (108 kcal/mol),53 the molecules of TEA dissociate easily at a lower operating temperature of 175 °C. The stability of the Au−TiO2@m-CN sensor. A variety of other VOAs including butylamine, triethanolamine, and benzylamine were also detected using the Au−TiO2@m-CN sensor. The response of the Au−TiO2@m-CN sensor for the detection of VOAs in the 1−500 ppm concentration range measured at 175 °C is shown in Figure 8b.

Gas-Sensing Properties. The multiple functionality of the Au−TiO2@m-CN nanohybrid in the chemical-sensing regime is an important aspect of advanced functional nanomaterials for selectively detecting gases commonly present in the indoor climate. VOAs represent such a class of household gases, which originate from dustbins, stored meat, and sewers, and owing to their toxic and stinking attributes, they are responsible for acute health problems.49−49 A typical fishy or sour/pungent/nasty odor is released by VOAs in the climate, and when inhaled in higher quantity by human, they can cause reactions and can severely affect hematopoietic/nervous/urinary/respiratory systems, cause strokes, and become carcinogenic when converted into nitrosamines.50−52 Considering the severe effect from these commonly and obviously present pollutants in the indoor climate, it becomes highly necessary to detect trace levels of organic amines with the help of ultrasensitive and selective chemical sensors. In this context, we have also investigated the prepared materials for the detection of VOAs. The optimized working temperature was determined by measuring the response of the prepared samples (g-CN, m-CN, TiO2@m-CN, Au−TiO2@m-CN, and Au−TiO2) in the temperature range 100−300 °C toward 50 ppm TEA. Figure 8a shows that the response of sensing materials follows a “rise → maximum → decline” pattern with a rise in the temperature. The pure g-CN shows a very poor response (R = 6.6) across the temperature range; however, being of the same composition, the ordered mesoporous m-CN, synthesized using the hard template of KIT-6 shows the highest response of 19.1 at 240 °C. When n-type TiO2 nanoparticles were loaded in mesoporous m-CN, a reduction of 40 °C in the optimized working temperature was observed and a response of 62.5 was observed for TiO2@m-CN at 200 °C. A further decrease of 25 °C in the optimized operating temperature was observed with the loading of Au nanoparticles, and the Au−TiO2@m-CN shows a highest response of 78.9 at 175 °C for 50 ppm TEA gas. On the contrary, the pure mesoporous Au−TiO2 (without m-CN) exhibits a response of 32.6 at 225 °C, which elaborates the role (discussed later) of the presence of the m-CN matrix in enhancing the response and decreasing the optimized operating temperature for detecting the TEA gas by the Au−TiO2@m-CN nanohybrid sensor. A variety of other VOAs including butylamine, triethanolamine, and benzylamine were also detected using the Au−TiO2@m-CN sensor. The response of the Au−TiO2@m-CN sensor for the detection of VOAs in the 1−500 ppm concentration range measured at 175 °C is shown in Figure 8b. As can be seen, the Au−TiO2@m-CN sensing responses increase with respect to an increment in the VOA concentration. The high response toward different gases can be explained on the basis of the C−H bond dissociation energies (BDE) of the respective gas molecules. As the BDE of TEA (91.2 kcal/mol)52 is less than that of butylamine (91.8 kcal/mol), triethanolamine (92.4 kcal/mol), and benzylamine (108 kcal/mol), the molecules of TEA dissociate easily at a lower operating temperature of 175 °C. The stability of the Au−TiO2@m-CN sensor to different concentrations (1−100 ppm) of TEA gas measured under different relative humidity conditions (10−95% RH).
commercial applications.\textsuperscript{35,36} The response and recovery time of Au–TiO$_2@m$-CN for all the tested VOAs (50 ppm) measured at 175 °C is shown in Figure 8d. As can be seen, average response/recovery times of 9.5/7 s (TEA), 15/8.6 s (butylamine), 16/11 s (triethanolamine), and 10/10.3 s (benzylamine) were recorded for the Au–TiO$_2@m$-CN sensor. The dynamic response/recovery curves of the Au–TiO$_2@m$-CN sensor for detecting TEA gas (1–50 ppm concentration range) at an operating temperature of 175 °C is shown Figure 8e. As can be seen, the sensor response increases with the increment in the TEA gas concentration and a respective response of 3.45, 19.2, 43.2, 79.8, and 147.8 was obtained for 1, 10, 25, 50, and 100 ppm TEA gas. The response/recovery curves also show the outstanding reversible nature of the sensor when quickly exchanged among TEA and fresh air. The possible reason could be the 2D layered mesoporous morphology of the Au–TiO$_2@m$-CN sensor, which allows the fast release of the TEA molecules from the surface of the sensor, and the response reaches its baseline very quickly. The average time for response and recovery of the Au–TiO$_2@m$-CN sensor toward TEA gas, respectively, varies from 9–16 and 6–12 s in the 1–50 ppm range. The time response results suggest that the sensor takes less time to recover to its initial position. When compared with the sensing results of earlier reported TEA sensor in Table S2, it was observed that the Au–TiO$_2@m$-CN sensor owns a significant higher response and quicker response/recovery time at comparatively lower working temperatures. The response of the Au–TiO$_2@m$-CN sensor toward 50 ppm of tested gases measured at varied humidity conditions [10–95% relative humidity (RH)] is shown in Figure 8f. As can be seen, a very little change in the response of the sensor was detected when the humidity conditions are low. The response decreases gradually by increasing the % RH contents in the test atmosphere, and a response of 68.5, 21.5, 12.3, and 6.6 was observed for TEA, butylamine, triethanolamine, and benzylamine, respectively, at 95% RH conditions. The results concluded that the Au–TiO$_2@m$-CN sensor responds to all tested VOAs even at highest % RH conditions. Figure 9 shows the selectivity of the Au–TiO$_2$m-CN sensor to the TEA gas among other VOAs (50 ppm) by randomly exposing the sensor at 175 °C. As observed, the response of the sensor quickly returns to its baseline state with the blow of the fresh air into the gas chamber. Inset of Figure 9 shows the results for relative sensitivity (RS = $S_{\text{TEA}}/S_{\text{test}}$) for the Au–TiO$_2@m$-CN sensor. As observed, the RS value of all test gases is higher as compared to the TEA gas, which endorses that the Au–TiO$_2@m$-CN sensor is exceedingly selective to the TEA gas.\textsuperscript{37}

**TEA-Sensing Mechanism.** On the interaction of Au–TiO$_2@m$-CN sensor with hot air at higher operating temperature (175 °C), the oxygen (O$_2$) molecules present in air in the closed chamber trap the easily accessible electrons (e$^-$) present in the conduction band of TiO$_2$ and m-CN, which results in the creation of negatively charged oxygen species (O$^{2-}$, O$^-$, and O$_2$$^-$. The trapped electrons then lead to the formation of a charge depletion region, thus causing an increase in the resistance of the sensor. However, when TEA gas was exposed on to the surface of the sensor inside the closed chamber at 175 °C, the O$^-$ discharges back the captured electrons (e$^-$) to the sensor surface, which decreases the depletion layer surrounding the sensor and ultimately leads to an increase in the carrier concentration of Au–TiO$_2@m$-CN. The interaction of gas molecules on the surface of the sensor causes the TEA gas to get oxidized and leads to the formation of the iminium cations, free radical ions (TEA$^{*+}$), and neutral amine radical, as shown in eqs 14–19 as follows:\textsuperscript{38,39,59}

\begin{align}
\text{TEA} + 1/2\text{O}_2 & \rightarrow \text{O}^{*-} + \text{TEA}^{+} \\
\text{O}^{*-} + \text{TEA}^{+} & \rightarrow \text{OH}^{*} + \text{Et}_2 - N - C^*(H) - CH_3 \\
\text{OH}^{*} + \text{Et}_2 - N & - C^*(H) - CH_3 \\
& \rightarrow \text{OH}^{-} + \text{Et}_2 N^{+} - \text{CHCH}_3 \\
\text{Et}_2 N^{+} - (\text{CH}_x)_\text{CH} & \\
& \rightarrow \text{Et}_2 - N - (\text{CH}_2)\text{CH}_\text{ads} + \text{H}_\text{ads} \tag{17} \\
\text{H}_\text{ads} + \text{O}_\text{ads} & \rightarrow \text{e}^- + \text{OH}_\text{ads} \tag{18} \\
\text{H}^+ + \text{OH}^- & \rightarrow \text{H}_2\text{O} \tag{19}
\end{align}

In the end, TEA oxidizes into vinylamine and water as follows: TEA + O$_\text{ads}$ $\rightarrow$ Et$_2$N–CH–CH$_2$ + H$_2$O + e$^-$, and the e$^-$ were freed from the adsorbed oxygen, which return to the conduction band of the Au–TiO$_2$m-CN nanocomposite, which leads to an increase in the conductivity of the sensor. For the Au–TiO$_2@m$-CN sensor, the enhanced response is governed by various factors, including high surface area of the sensor, heterojunction formation between n-type TiO$_2$ and m-CN materials, and the availability of m-CN and highly catalytic metallic Au nanoparticles. The high surface area of the sensing material is directly related to the availability of the surface active sites.\textsuperscript{50,61} Besides, the ordered porous architecture of the sensor accelerates the processes of adsorption, transmission, and desorption of the gas molecules across the sensor surface, thereby leading to an increase in the response of the sensor.\textsuperscript{62,63} In this work, the ordered mesoporous channels of Au–TiO$_2@m$-CN sensor assist in the rapid adsorption, faster transmission, and quick desorption of the TEA molecules from their surface, which, on the other hand, helps in improving the response to TEA gas and also dictates the faster response/recovery time of the Au–TiO$_2@m$-CN sensor. The heterojunction formation in semiconductor-based sensors plays a crucial role in determining the sensor response. In the case of Au–TiO$_2@m$-CN, two components (TiO$_2$ and m-CN) are involved and so the electronic movement occurs...

![Figure 9. Dynamic sensing performance of the Au–TiO$_2@m$-CN sensor toward 50 ppm of various gases. (Inset) ratio between the response of TEA and other test gases.](image-url)
between two homojunction (TiO₂ ↔ TiO₂ and m-CN ↔ m-CN) and one heterojunction (TiO₂ ↔ m-CN). Across the heterojunction, the electronic movement is directed from material possessing lower work function (Wₚ) to material having higher Wₚ, and this process forms a potential barrier between the two components by achieving an equilibrium and causing the formation of another Fermi energy level.²⁵,²⁶,²⁸ In the case of the Au−TiO₂@m-CN sensor, the electrons from the conduction band of m-CN (Wₚ = 4.3 eV)¹² are transferred to that of TiO₂ (Wₚ = 4.5 eV)⁴³,⁴⁴ by band bending, which forms a potential barrier among them. This newly formed potential barrier obstructs the electronic motions which further causes the electrons present on surface of sensor to be an obvious site for desorption of oxygen species thereby increasing the response towards TEA gas. The presence of high surface area and cubic ordered mesoporous m-CN material in Au−TiO₂@m-CN provides long-range regular ordering of pore channels, which contrarily helps in the smoother propagation of the charge carriers. Besides, the presence of ordered mesoporous m-CN matrix avoids agglomeration and assists in homogeneous dispersion of the dopant nanoparticles across the mesopores. Although detecting TEA gas, the sensor Au−TiO₂@m-CN (R/a/R = 79.8) shows 2.5 time better response than the sensor Au−TiO₂ (R/a/R = 32.6) and also marks an impressive reduction of 50 °C in the optimized operating temperature. These important results highlight the usefulness of the 2D mesoporous cubic m-CN matrix in sensing applications. It is known that Au nanoparticles have good catalytic and excellent conducting properties, and because of spillover effect, the process of chemical sensitization and catalytic oxidation increases. This increases the rate of adsorption of active oxygen species on the surface of the Au−TiO₂@m-CN sensor. Specifically, the process of chemical sensitization increases the sorption rate of oxygen, which captures electrons present in the conduction band of TiO₂ and m-CN, and gets converted into oxygen ions (O⁻) as 2Au + O₂(gas) → Au/O and O + e⁻ → O_ads. When the reducing TEA gas comes in contact with the sensor surface, the e⁻ are transferred back to the surface of the sensor. As a result, the resistance decreases and the response of the Au−TiO₂@m-CN sensor increases. Thus, it can be concluded that the unique ordered mesoporous morphology of Au−TiO₂@m-CN plays a significant role in enhancing the photocatalyst performance and sensing response. Such type of multifunctional hybrid materials can become a smarter solution in terms of expense viability and performance for applications related to energy and environment domain.

**CONCLUSIONS**

In summary, we have prepared a novel nanohybrid consisting of g-C₃N₄ sheets well coupled with TiO₂ and metallic Au nanoparticles, using hard template of mesoporous silica, KIT-6. Owing to its 3D cubic ordered mesoporous 2D layered architecture with high specific surface area and meso-ordered homogeneous pore channels, the cubic mesoporous Au−TiO₂@m-CN nanohybrid exhibited enhanced visible light photocatalytic degradation performance toward a variety of azo dyes. The excellent surface area and pore properties of g-C₃N₄ sheets enhance the accessibility and dispersibility of TiO₂ and Au nanoparticles, thereby promoting the transportation and diffusion of dye molecules. In addition, the Au−TiO₂@m-CN nanohybrid unveiled excellent sensing performance toward the detection of VOAs, commonly present in the indoor climate. The synergistic approach highlighted in this study could extend the utility of functional 2D layered materials in designing high-performance visible light photocatalysts, gas sensors, and battery materials that are not only economically viable but also excellent performers.

**ASSOCIATED CONTENT**

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**Notes**

The authors declare no competing financial interest.

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