

Article

Fabrication of a $\text{Cu}_2\text{O-Au-TiO}_2$ Heterostructure with Improved Photocatalytic Performance for the Abatement of Hazardous Toluene and α -Pinene Vapors

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Abstract: In the current research, a $\text{Cu}_2\text{O-Au-TiO}_2$ heterostructure was fabricated via a step-wise photodeposition route to determine its possible application in the photocatalytic oxidation of hazardous vapors. The results of electron microscopy and X-ray photoelectron spectroscopy confirm the successful fabrication of the $\text{Cu}_2\text{O-Au-TiO}_2$ heterostructure. Strong absorption in the visible region, along with a slight red-shift in the absorption edge, was observed in the UV-vis diffuse reflectance spectrum of $\text{Cu}_2\text{O-Au-TiO}_2$ composite, which implies that the composite can generate a greater number of photoexcited charges necessary for photocatalytic reaction. Toluene and α -pinene, as common gas contaminants in the indoor atmosphere, were employed to assess the photooxidation efficiency of the $\text{Cu}_2\text{O-Au-TiO}_2$ composite. Importantly, photocatalytic activity results indicate that the $\text{Cu}_2\text{O-Au-TiO}_2$ composite showed excellent photodegradation performance compared to pure TiO_2 and $\text{Cu}_2\text{O-TiO}_2$ and Au-TiO_2 , where photocatalytic efficiency was approximately 92.9% and 99.9% for toluene and α -pinene, respectively, under standard daylight illumination. The increased light-harvesting capacity and boosted separation efficiency of electron-hole pairs were mainly accountable for improved degradation performance of the $\text{Cu}_2\text{O-Au-TiO}_2$ composite. In addition, the degradation efficiencies for toluene and α -pinene by the $\text{Cu}_2\text{O-Au-TiO}_2$ composite were also examined under three different light sources: 0.32 W white, blue and violet LEDs. The findings of this work suggested a great promise of effective photooxidation of gas pollutants by the $\text{Cu}_2\text{O-Au-TiO}_2$ composite.

Keywords: TiO_2 ; Cu_2O ; plasmonic effect; heterojunction; vapor degradation; environmental remediation

1. Introduction

Owing to dramatic urbanization and significant economic development, office staff move to high-rise commercial buildings and residents migrate to newly constructed high-rise apartments [1,2]. Unfortunately, high concentrations of volatile organic compounds (VOCs) are found in the indoor air of these houses, which are released primarily from household products such as furniture, paints, decorations, glues, etc. [3]. VOCs, including these two pollutants, in indoor environments can cause the sick building syndrome such as headache, dizziness, allergy, and eyes/nose irritation, which refers to a fusion of various diseases [4,5]. Therefore, the concentration level of these indoor pollutants has to be controlled to reduce the risk of health hazards to building residents.

Titanium dioxide (TiO_2) is the most widely used material among the photocatalysts available, due to its abundance, low cost, and the high physical and chemical stability [6,7]. Despite these benefits, the photocatalytic performance of TiO_2 is restricted by its large bandgap and rapid electron-hole recombination. Among them, coupling with narrow bandgap material to create a composite based on TiO_2 has received great attention due to the merit in capturing a large portion of the solar spectrum

and enhancing the efficiency of charge separation [8]. Cuprous oxide (Cu_2O), a direct bandgap semiconductor material, becomes the potential candidate to sensitize TiO_2 because of some interesting features, such as earth abundance, ecofriendly, and its suitable band structure with TiO_2 [9,10]. Moreover, as a narrow bandgap (1.9–2.2 eV) semiconductor, Cu_2O can extend the light absorption to the visible range. Accordingly, some previous works have shown that the photocatalytic efficiency of the $\text{Cu}_2\text{O}/\text{TiO}_2$ composite can be improved because of extended light absorption and charge transfer between Cu_2O and TiO_2 , which promotes the charge separation [11,12]. Aguirre et al. [13] reported that during photocatalysts performance and the detection of photogenerated hydroxyl radicals in the heterostructure at variance with the results obtained for pure Cu_2O were taken as evidence that TiO_2 protects Cu_2O from undergoing photocorrosion. Moreover, Sun et al. [14] reported that Cu_2O -doped TiO_2 nanotube arrays ($\text{Cu}_2\text{O}/\text{TNA}$ s) could greatly reduce the recombination of photogenerated holes and electrons during ibuprofen degradation.

Nevertheless, Cu_2O can be easily oxidized into CuO by means of photoexcited holes under ambient environmental conditions, leading to the poor interface between TiO_2 and Cu_2O , which will subsequently affect the photocatalytic performance of the $\text{Cu}_2\text{O}/\text{TiO}_2$ composite. In this regard, noble metal embedded composites, i.e., semiconductor-metal-semiconductor hybrid systems, have received a great deal of attention in photocatalytic application due to their effective charge separation capacity and strong redox capabilities [15]. In addition, surface plasmon resonance (SPR) effect of metal can also enhance the light absorption and scattering of incident light on the near-surface of TiO_2 composites. For instance, Sinatra et al. [16] recorded the photocatalytic production of H_2 from water through $\text{Au}/\text{Cu}_2\text{O}-\text{TiO}_2$ system and studied the SPR effect of Au nanoparticles and pn-junction at the $\text{Cu}_2\text{O}-\text{TiO}_2$. Recently, Li et al. [17] demonstrated the fabrication of TiO_2 -Au- Cu_2O as a Z-scheme heterostructure, which displayed greater photoelectrocatalytic activity for water and CO_2 reduction than binary TiO_2 - Cu_2O catalyst. However, the photocatalytic degradation of pollutants using $\text{Cu}_2\text{O}-\text{Au}-\text{TiO}_2$ has rarely been reported.

In this work, the $\text{Cu}_2\text{O}-\text{Au}-\text{TiO}_2$ composite was fabricated with enhanced degradation efficiency for VOCs, including toluene and α -pinene. The phase structure of the prepared catalysts was identified by X-ray diffraction studies, while optical properties were probed using photoluminescence (PL) and UV-vis diffuse reflectance spectroscopy (UV-vis DRS) measurements. The morphological studies were examined through field-emission scanning electron microscopy (FE-SEM) as well as field-emission transmission electron microscopy (FE-TEM) analyses. Moreover, the detailed chemical structure of the $\text{Cu}_2\text{O}-\text{Au}-\text{TiO}_2$ composite was investigated by using an X-ray photoelectron spectroscopy (XPS). The photocatalytic evaluation of the prepared samples was determined for the removal of VOCs (toluene and α -pinene) under a standard 8 W daylight lamp. Furthermore, the effect of the light source on the degradation of pollutant gas molecules over the $\text{Cu}_2\text{O}-\text{Au}-\text{TiO}_2$ composite was studied in detail using three different light sources, including 0.32 W white, blue, and violet LEDs. For this aim, the three critical features that the study should focus on are the proper characterization, the evaluation of photocatalytic activity, and proposal of a meaningful mechanism [18,19].

2. Results and Discussion

2.1. Characteristics of the Prepared Photocatalysts

The phase structure of the fabricated samples was assessed by using their XRD patterns. As presented in Figure 1, the bare TiO_2 sample shows the main diffraction peaks at 2θ of 25.32° , 37.85° , 48.02° , 53.89° , 55.08° , and 62.76° belongs to the reflections of (101), (004), (200), (105), (211), and (204), respectively. These peaks are well-matched with the standard sample XRD pattern of anatase TiO_2 (JCPDS # 21-1272). Along with these main peaks, the TiO_2 consists of two additional low-intensity peaks associated with the rutile and brookite phases, as shown in Figure 1. It is also observed from the figure that the other fabricated Au- TiO_2 , $\text{Cu}_2\text{O}-\text{TiO}_2$, and $\text{Cu}_2\text{O}-\text{Au}-\text{TiO}_2$ samples exhibited the XRD pattern similar to that of bare TiO_2 . The coexisted anatase and rutile phases could improve the

separation efficient of photoexcited electrons and holes in terms of a mixed-phase heterojunction, which is favorable to enhance the photocatalytic activity [17]. The possible reason for the absence of Au and Cu_2O XRD peaks is their low content and small particle size in Au-TiO_2 , $\text{Cu}_2\text{O-TiO}_2$, and $\text{Cu}_2\text{O-Au-TiO}_2$ composites [20]. Nevertheless, the presence of Au and Cu_2O in the $\text{Cu}_2\text{O-Au-TiO}_2$ composite can be easily ratified by XPS, UV-vis DRS, and TEM mappings, as discussed later.

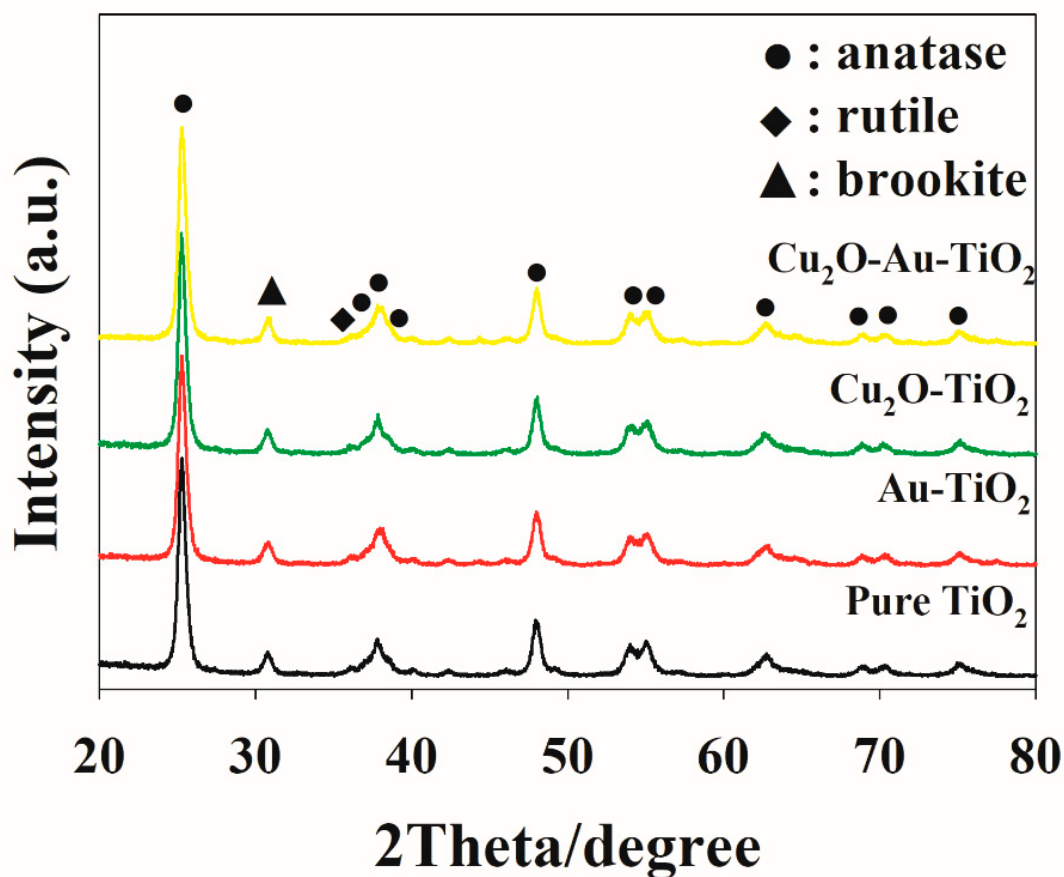


Figure 1. XRD patterns of the prepared pure TiO_2 , Au-TiO_2 , $\text{Cu}_2\text{O-TiO}_2$, and $\text{Cu}_2\text{O-Au-TiO}_2$.

The surface morphologies of the fabricated catalysts were unveiled by SEM micrographs. As shown in Figure 2, all of the prepared TiO_2 , Au-TiO_2 , $\text{Cu}_2\text{O-TiO}_2$, and $\text{Cu}_2\text{O-Au-TiO}_2$ samples possessed similar spherical-like morphology. The presence of Au and Cu_2O in the $\text{Cu}_2\text{O-Au-TiO}_2$ composite could be revealed by EDS results. Figure 3 shows that the prepared Au-TiO_2 and $\text{Cu}_2\text{O-TiO}_2$ were composed of Ti, O, and Au/Cu elements. Whereas the $\text{Cu}_2\text{O-Au-TiO}_2$ composite consists of Ti, O, Au, and Cu elements, indicating that both Au and Cu_2O could be impregnated into pure TiO_2 to create the $\text{Cu}_2\text{O-Au-TiO}_2$ composite.

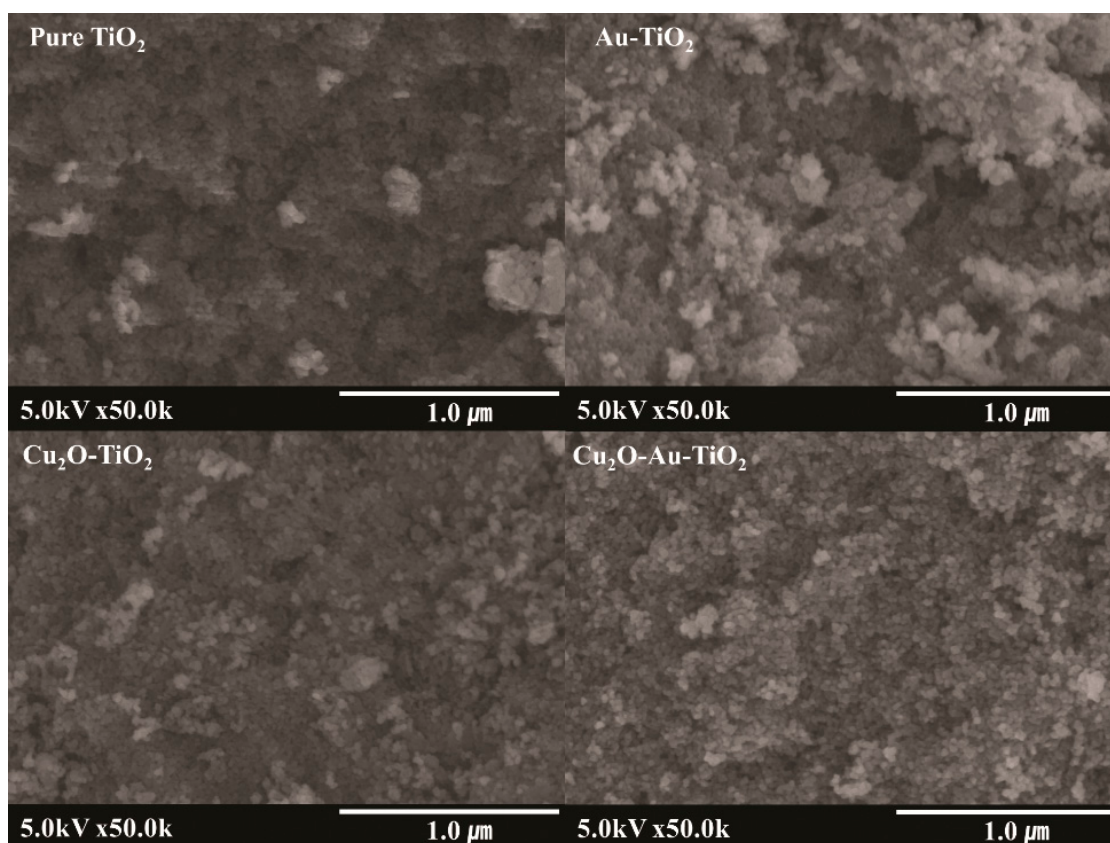


Figure 2. FE-SEM images of the prepared TiO_2 , Au-TiO_2 , $\text{Cu}_2\text{O-TiO}_2$, and $\text{Cu}_2\text{O-Au-TiO}_2$.

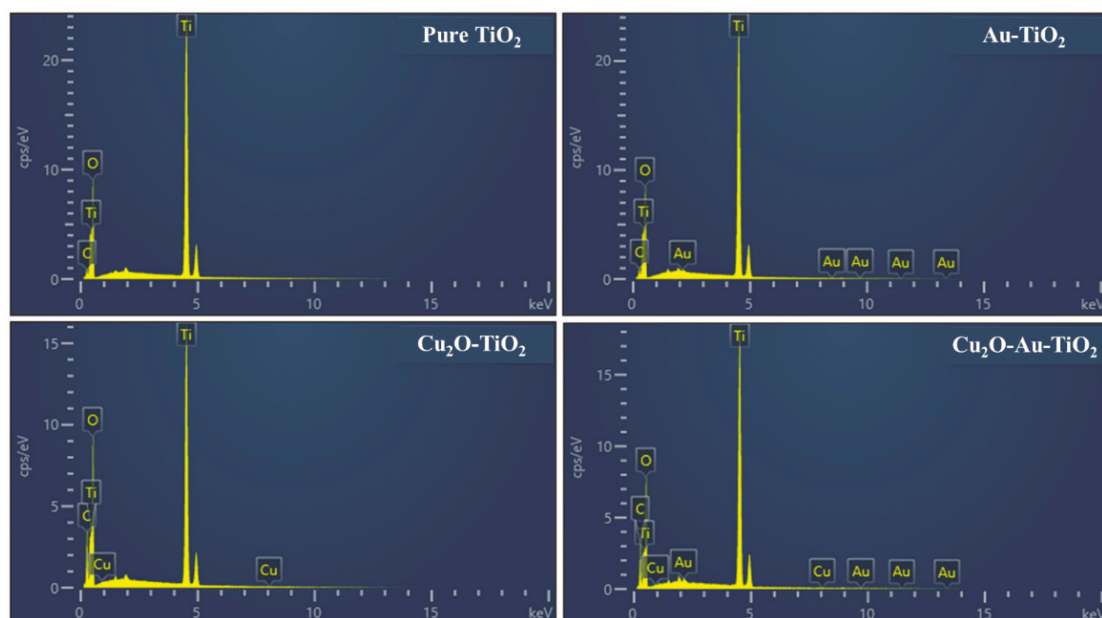


Figure 3. EDX spectra of the prepared TiO_2 , Au-TiO_2 , $\text{Cu}_2\text{O-TiO}_2$, and $\text{Cu}_2\text{O-Au-TiO}_2$.

The detailed microstructure of the prepared $\text{Cu}_2\text{O-Au-TiO}_2$ composite can be identified by TEM analysis. The presence of Au nanoparticles in the composite can be clearly seen in the TEM micrograph, as shown in Figure 4. According to the FE-TEM results, the $\text{Cu}_2\text{O-Au-TiO}_2$ sample exhibited lattice fringes of TiO_2 , Au, and Cu_2O with d spacings of 0.35, 0.227, and 0.214 nm, respectively [6,21,22]. The close integration among the three components could also be seen in the FETEM image of the

$\text{Cu}_2\text{O-Au-TiO}_2$ composite. Furthermore, the elemental mapping images of $\text{Cu}_2\text{O-Au-TiO}_2$ (Figure 5) showed that $\text{Cu}_2\text{O-Au-TiO}_2$ consists of Ti, O, Au, and Cu elements; the uniform distribution of these elements certainly verified the successful integration of Cu, Cu_2O , and TiO_2 components during the synthesis of the $\text{Cu}_2\text{O-Au-TiO}_2$ composite. These mapping studies were also unveiled the uniform distribution of Ti and O in pure TiO_2 , and coexistence of Ti, O, and Cu or Cu elements in the Au-TiO_2 and $\text{Cu}_2\text{O-TiO}_2$ samples.

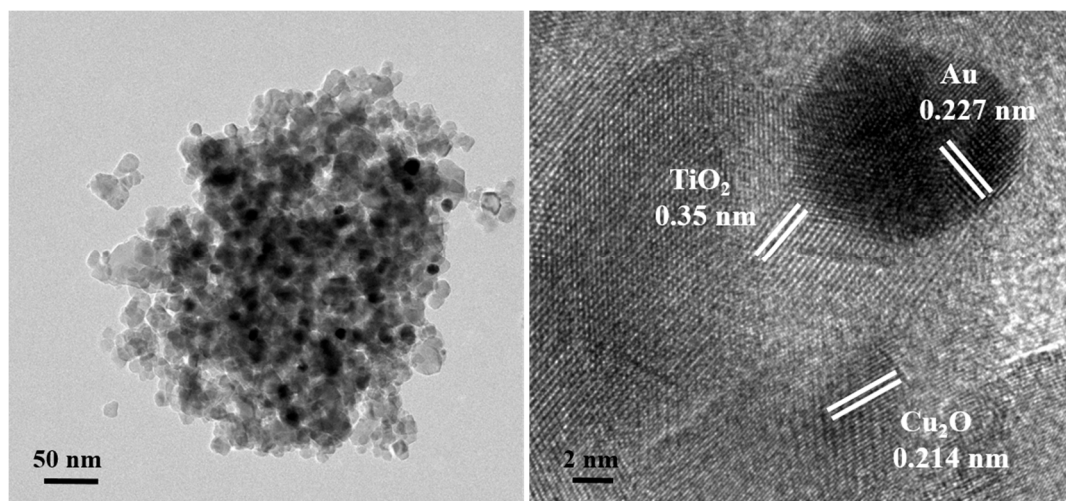


Figure 4. FE-TEM images of the prepared $\text{Cu}_2\text{O-Au-TiO}_2$.

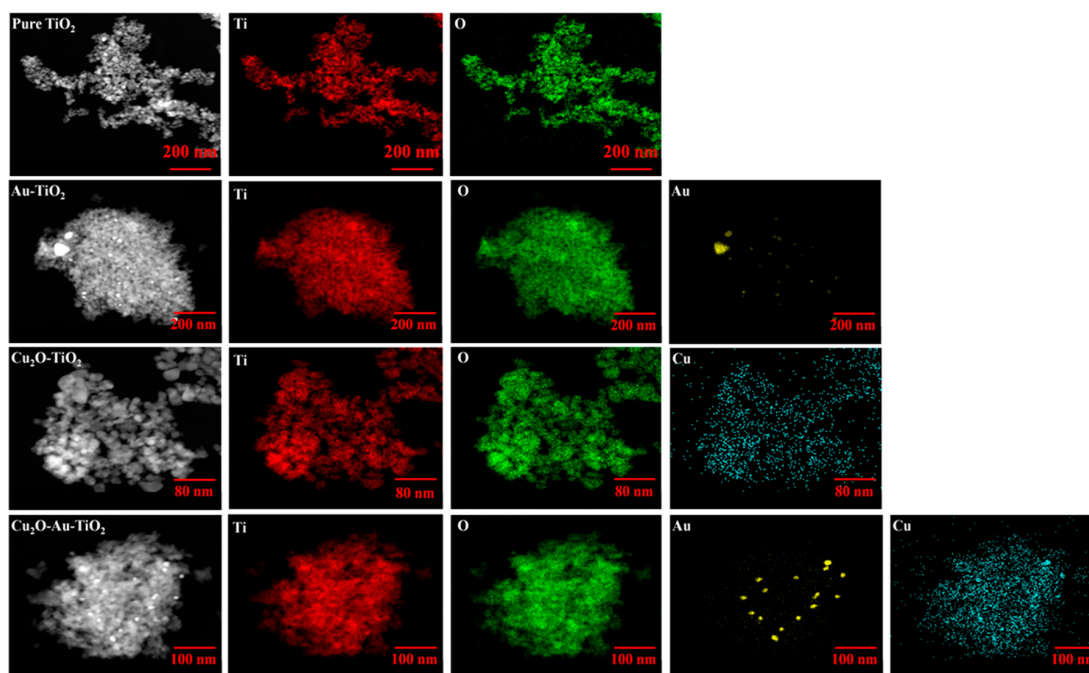


Figure 5. Elemental mapping images of the prepared pure TiO_2 , Au-TiO_2 , $\text{Cu}_2\text{O-TiO}_2$, and $\text{Cu}_2\text{O-Au-TiO}_2$.

To scrutinize the surface chemical composition and oxidation states of elements in the $\text{Cu}_2\text{O-Au-TiO}_2$ composite, XPS analysis was performed. The full survey spectrum shown in Figure 6a revealed that the composite comprised of Ti, O, Cu, and Au elements. The adventitious peak that belonged to C 1s (Figure 6f) was possibly attributed to the XPS instrument atmosphere. The high-resolution Ti 2p spectrum in Figure 6d displays two peaks at 464.5 and 458.6 eV indexed to $\text{Ti } 2p_{1/2}$ and $\text{Ti } 2p_{3/2}$, respectively, verifying that Ti presents in its +4-oxidation state in the composite

sample [23]. The O 1s profile (Figure 6e) shows the high intense peak at ca. 530.5 eV, which belongs to the lattice oxygen moieties from Ti–O/Cu–O bonds [24]. The small shoulder peak next to the main peak related to O–H units maybe originated from the water molecules adsorbed on the surface of the sample. As can be seen in Figure 6b, the Cu 2p spectrum shows two peaks of a spin-orbit couple (Cu 2p_{3/2} and Cu 2p_{1/2}) located at the binding energies of 932.1 and 952.5 eV, which are consistent with the values reported for Cu₂O [16]. This result verifies that Cu in the composite sample exists in the form of Cu₂O rather than CuO or Cu. In addition, the XPS spectrum of Au 4f exhibited the typical peaks at 84.0 eV and 87.6 eV (Figure 6c), validating the presence of Au⁰ in the Cu₂O–Au–TiO₂ catalyst [25]. The peak intensities of Au in XPS pattern, as shown in Figure 6c, were relatively weak, which was attributed to the low quantity of Au in the Cu₂O–Au–TiO₂ composite. Therefore, all of these outcomes confirm the successful formation of Cu₂O–Au–TiO₂ composite catalyst.

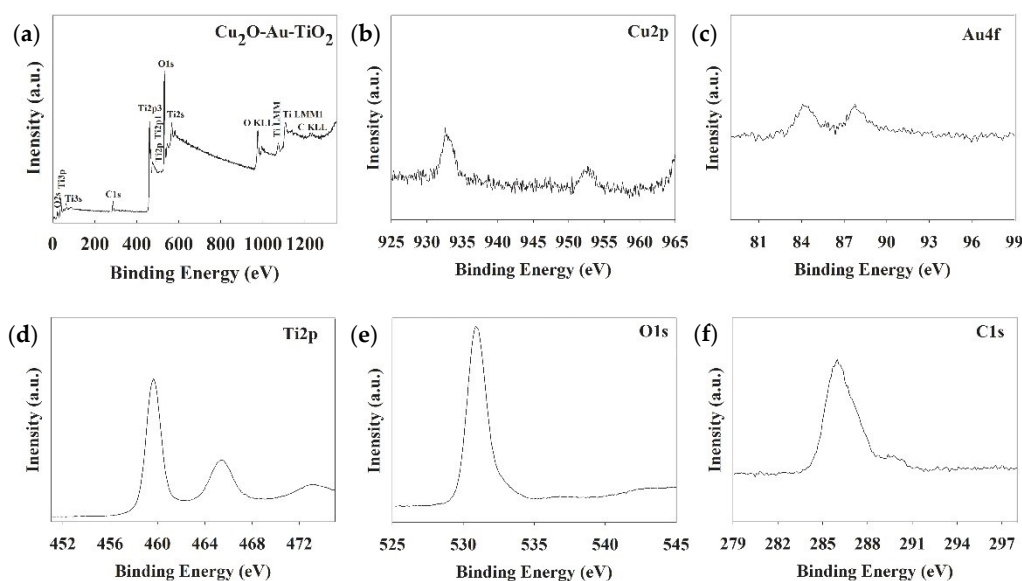


Figure 6. XPS profiles of the prepared Cu₂O–Au–TiO₂. (a) survey spectra of Cu₂O–Au–TiO₂; (b) Cu 2p spectra; (c) Au 4f spectra; (d) Ti 2p spectra; (e) O 1s spectra; (f) C 1s spectra.

The photocatalytic efficiency of a catalyst depends fairly on its ability to absorb light because the strong light response helps to produce more photogenerated charges [26]. As such, UV–vis DRS studies were conducted over the fabricated photocatalysts, as shown in Figure 7. By applying the following Equation (1), the bandgap energy (E_g) of the prepared catalysts can be easily estimated from the UV–vis DRS curves.

$$E_g = 1240/\lambda, \quad (1)$$

where λ is the wavelength (nm). The spectrum of the prepared bare TiO₂ possessed an absorbance edge at ca. 400 nm (3.1 eV), which agrees well with the inherent bandgap of TiO₂ (3.2 eV) [27]. Even though the absorbance pattern of the fabricated Cu₂O–TiO₂ was similar to that of bare TiO₂, Cu₂O–TiO₂ illustrated a relatively higher absorbance than bare TiO₂ in the visible light region and a slight red-shift in the UV light region. In the case of Cu₂O–Au–TiO₂, the light absorbance increased dramatically in the visible range, and a slight red-shift was also noticed in the UV region. These red-shifts in the absorption edges perhaps imply that heterogeneous conjunction created between the components of the Cu₂O–TiO₂ and Cu₂O–Au–TiO₂ composites [15]. Interestingly, depositing Au nanoparticles onto TiO₂ and Cu₂O–TiO₂ enhances their optical absorption over the wavelength range of 400–700 nm, which can be ascribed to the typical surface plasmon resonance (SPR) absorption of Au nanoparticles [28]. A broad plasmon band at around 530 nm observed in both Au–TiO₂ and Cu₂O–Au–TiO₂ composites further confirm the SPR effect of Au nanoparticles. It is worth mentioning that both Au–TiO₂ and Cu₂O–Au–TiO₂ composites exhibited greater light absorption than TiO₂ and Cu₂O–TiO₂ in the range of 400–700 nm, which helps as

direct evidence for the presence of Au in the composites. Therefore, the significantly improved optical absorption of the fabricated $\text{Cu}_2\text{O-Au-TiO}_2$ composite will thus generate a greater number of photoexcited charges necessary for photocatalytic oxidation of gaseous pollutants.

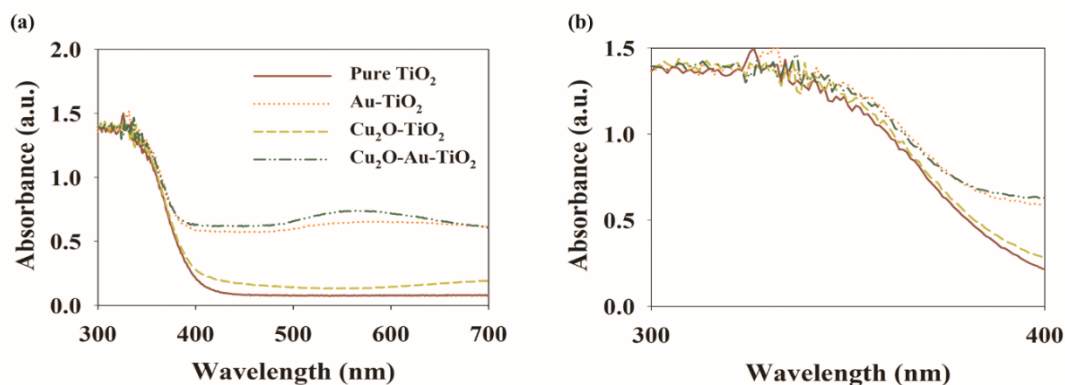


Figure 7. (a) Full wavelength of UV-vis DRS patterns of the prepared pure TiO_2 , Au-TiO_2 , $\text{Cu}_2\text{O-TiO}_2$, and $\text{Cu}_2\text{O-Au-TiO}_2$ and (b) the specific wavelength of UV-vis DRS patterns of the prepared pure TiO_2 , Au-TiO_2 , $\text{Cu}_2\text{O-TiO}_2$, and $\text{Cu}_2\text{O-Au-TiO}_2$.

The catalyst surface properties also have a significant influence on photocatalytic efficiency; thus Brunauer–Emmett–Teller (BET)-specific surface area (S_{BET}), mean pore size, and total pore volume of the prepared samples were evaluated, and the results are summed up in Table 1. All of the prepared samples displayed similar S_{BET} values of 58.9–62.3 $\text{m}^2 \text{g}^{-1}$. Moreover, no major changes in the other surface properties were also observed for all of the samples tested, suggesting that the addition of Au and/or Cu_2O did not substantially affect the surface properties of TiO_2 . Assuming all the catalyst particles have similar spherical shapes and sizes, the mean particle size was estimated, applying the following Equation (2) [29]:

$$D = 6000 / (S_{\text{BET}} \times \rho), \quad (2)$$

where D is the mean particle size and ρ is the true density (ρ for TiO_2 is 4.2 g mL^{-1}). As presented in Table 1, the mean particle sizes of TiO_2 , Au-TiO_2 , $\text{Cu}_2\text{O-TiO}_2$, and $\text{Cu}_2\text{O-Au-TiO}_2$ were estimated to be 24.3 nm, 22.9 nm, 23.3 nm, and 23.2 nm, respectively. From the results, it could be concluded that the surface properties of $\text{Cu}_2\text{O-Au-TiO}_2$ composite had no significant impact on its photocatalytic efficiency.

Table 1. Textural properties of the prepared pure TiO_2 , Au-TiO_2 , $\text{Cu}_2\text{O-TiO}_2$, and $\text{Cu}_2\text{O-Au-TiO}_2$.

Photocatalyst	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Total Pore Volume ($\text{cm}^3 \text{g}^{-1}$)	Particle Size (nm)	Pore Size (nm)
Pure TiO_2	58.9	0.21	24.3	13.7
Au-TiO_2	62.3	0.19	22.9	13.1
$\text{Cu}_2\text{O-TiO}_2$	61.2	0.22	23.3	13.9
$\text{Cu}_2\text{O-Au-TiO}_2$	61.5	0.21	23.2	13.1

2.2. Photocatalytic Performance

The photocatalytic activities of the fabricated samples were explored by probing the photocatalytic degradation activities for toluene and α -pinene under standard daylight illumination. The adsorption equilibrium between the model pollutants and the photocatalyst surface was achieved within 2 h of the start of each adsorption process. Figure 8 represents the photocatalytic efficiencies of pure TiO_2 , Au-TiO_2 , $\text{Cu}_2\text{O-TiO}_2$, and $\text{Cu}_2\text{O-Au-TiO}_2$ catalysts toward the degradation of toluene and α -pinene. The decomposition of the model pollutants was almost completed within an initial 1 h over a 3-h photodecomposition process, and then there was no significant change in the decomposition activities. The photocatalytic activities of Au and/or Cu_2O -coupled TiO_2 catalysts toward the degradation of

toluene and α -pinene were higher than those of pure TiO_2 , which were determined in the order of $\text{Cu}_2\text{O-Au-TiO}_2 > \text{Cu}_2\text{O-TiO}_2 > \text{Au-TiO}_2 > \text{pure TiO}_2$. In particular, the prepared $\text{Cu}_2\text{O-Au-TiO}_2$ composite exhibited the best performance with the decomposition efficiencies of 92.9% and 99.9% for toluene and α -pinene, respectively. It was found that the oxidation efficiencies over $\text{Cu}_2\text{O-Au-TiO}_2$ enhanced substantially in the case of toluene compared to α -pinene. Meanwhile, the average degradation activities for toluene and α -pinene by pure TiO_2 were 16.6% and 48.6%, respectively. Besides, the corresponding degradation efficiencies of Au-TiO_2 , $\text{Cu}_2\text{O-TiO}_2$, and $\text{Cu}_2\text{O-Au-TiO}_2$ were 45.3%, 70.9%, and 92.9% for toluene and 91.9%, 98.8%, and 100% for α -pinene, respectively.

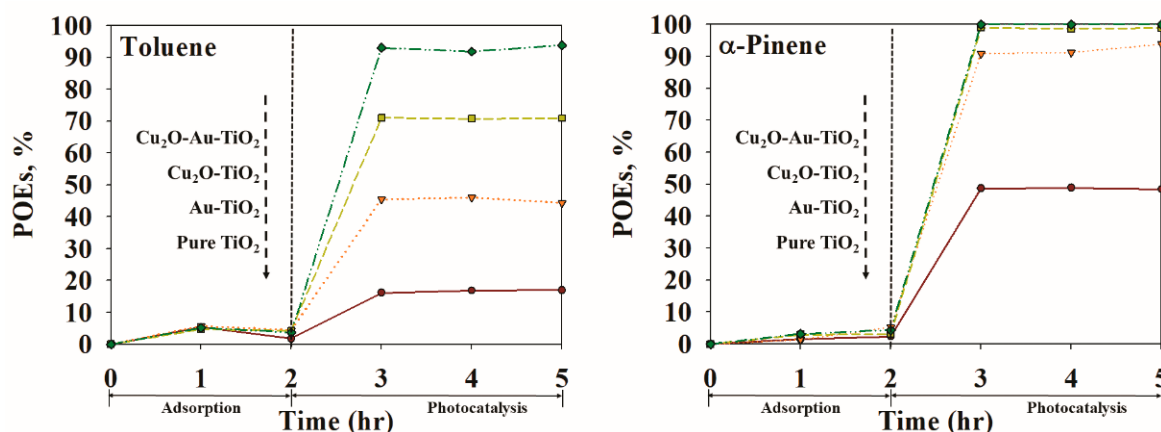


Figure 8. Photocatalytic oxidation efficiencies for toluene and α -pinene determined with pure TiO_2 , Au-TiO_2 , $\text{Cu}_2\text{O-TiO}_2$, and $\text{Cu}_2\text{O-Au-TiO}_2$.

In addition, the degradation efficiencies for toluene and α -pinene by the $\text{Cu}_2\text{O-Au-TiO}_2$ composite under standard daylight lamp were compared with three other light sources: 0.32 W white, blue, and violet LEDs, as shown in Figure 9. Light irradiation for the photodegradation process started after achieving an adsorption equilibrium between $\text{Cu}_2\text{O-Au-TiO}_2$ and model pollutants in the dark for 2 h. Similar to the photodegradation activities discussed above, the photodecomposition efficiencies increased during the first 1 h of the 3-h reaction, and there was no indication of any marked improvement in the decomposition activities thereafter. Moreover, the decomposition activities for α -pinene were assessed as relatively high in contrast to those for toluene. The average photodegradation activities for toluene and α -pinene with the $\text{Cu}_2\text{O-Au-TiO}_2$ composite corresponding to the light sources were shown to be 92.8% and 100% for standard 8 W daylight lamp, violet LED, 56.2% and 98.6% for violet LED, 8.6% and 32.7% for white LED, and 6.8% and 8.5% for blue LED, respectively, which are determined by an order of standard 8 W daylight lamp > violet LED > white LED > blue LED. Nonetheless, the photodegradation activities normalized to the given electric power were therefore calculated to be 0.11% and 0.13%/W for standard daylight lamp, 1.76% and 3.08%/W for violet LED, 0.26% and 1.02%/W for white LED, and 0.21% and 0.26%/W for blue LED, respectively, in the order of violet LED > white LED > blue LED > standard daylight lamp. The 0.32 W LEDs were therefore far more energy-efficient light sources than the standard 8 W daylight lamp for toluene and α -pinene photodegradation with the $\text{Cu}_2\text{O-Au-TiO}_2$ composite, even though under daylight illumination the photocatalytic efficiency was shown to be higher.

In general, the enhanced photocatalytic efficiency of a catalyst is most likely due to three key aspects: (1) light absorption capacity, (2) charge-carrier separation, and (3) photo-redox reactions [30,31]. In this study, it was found that the fabricated $\text{Cu}_2\text{O-TiO}_2$, Au-TiO_2 , and $\text{Cu}_2\text{O-Au-TiO}_2$ catalysts afford a relatively higher absorbance than the bare TiO_2 in the visible range and a slight red shift in the UV region (Figure 7). Particularly, the absorbance of Au-TiO_2 and $\text{Cu}_2\text{O-Au-TiO}_2$ composites increased dramatically in the range of 400–700 nm owing to the SPR absorption of Au nanoparticles. This notably increased light absorption in the 400–700 nm range could help to generate more photoexcited

electron-hole pairs upon visible light. Further, the loaded metal nanoparticles could trap the electrons, accelerate the charge transfer process, and impede the recombination of photoexcited charge carriers.

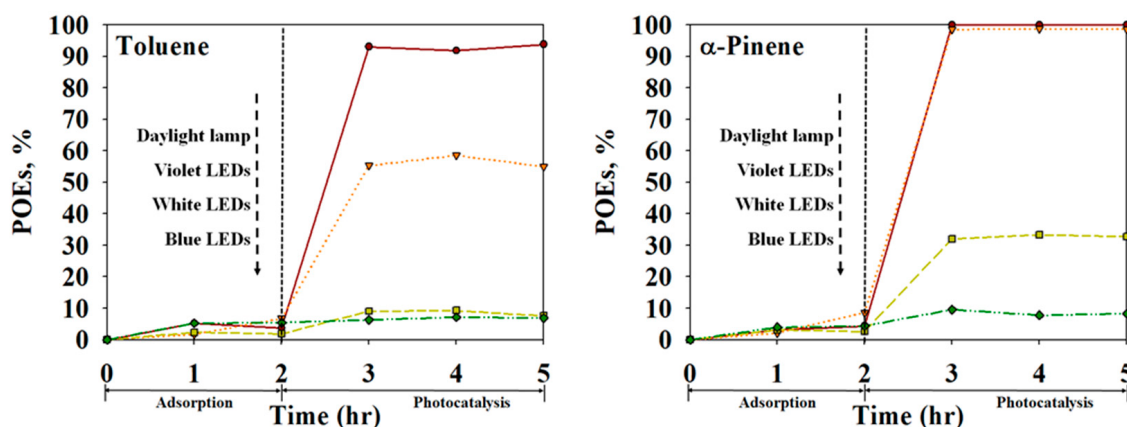


Figure 9. Photocatalytic oxidation efficiencies for toluene and α -pinene determined with $\text{Cu}_2\text{O-Au-TiO}_2$ under four kinds of light sources (standard daylight lamp, white, blue, and violet LEDs).

PL emission spectral studies were used to assess the separation efficiency of photoexcited charges in the fabricated samples as the PL emission intensity is proportional to the recombination of electrons and holes [32,33]. As presented in Figure 10, all of the tested catalysts, including TiO_2 , Au-TiO_2 , $\text{Cu}_2\text{O-TiO}_2$, and $\text{Cu}_2\text{O-Au-TiO}_2$ exhibit similar emission patterns but different PL intensities. Compared to bare TiO_2 , $\text{Cu}_2\text{O-TiO}_2$ composite displays reduced PL emission intensity, suggesting the charge transfer between Cu_2O and TiO_2 , which results in decreased recombination of photoinduced charges. Adding Au nanoparticles onto the TiO_2 structure decreases the emission intensity, signifying that the loaded metal nanoparticles would also facilitate the separation of photogenerated charges in the Au-TiO_2 . The PL emission intensities of the fabricated catalysts were measured in the order of pure $\text{TiO}_2 > \text{Au-TiO}_2 > \text{Cu}_2\text{O-TiO}_2 > \text{Cu}_2\text{O-Au-TiO}_2$, indicating that the $\text{Cu}_2\text{O-Au-TiO}_2$ showed the notably quenched PL emission intensity among the tested catalysts. Therefore, the $\text{Cu}_2\text{O-Au-TiO}_2$ sample exhibited the best photocatalytic performances in the decomposition of toluene and α -pinene, and the activities for both model contaminants were determined in the order of $\text{Cu}_2\text{O-Au-TiO}_2 > \text{Cu}_2\text{O-TiO}_2 > \text{Au-TiO}_2 > \text{pure TiO}_2$ as shown in Figure 9. These PL results certainly verified that the greater separation of charge carriers in $\text{Cu}_2\text{O-Au-TiO}_2$ is the primary reason for the extraordinary activity in the elimination of pollutants.

According to the experimental results discussed in this study and earlier studies [17,34], a possible mechanism for the photodegradation of toluene and α -pinene pollutants using $\text{Cu}_2\text{O-Au-TiO}_2$ composite was schematically illustrated in Figure 11 and described as follows. Upon light illumination onto the $\text{Cu}_2\text{O-Au-TiO}_2$ composite system, both TiO_2 and Cu_2O were excited to produce electrons and holes at the conduction band and the valance band, respectively. The excited electrons at the conduction band of TiO_2 would transfer to the valance band of Cu_2O through Z-scheme mechanism using Au nanoparticles as a mediator. This electron transfer process occurred at the $\text{Cu}_2\text{O-Au-TiO}_2$ interface resulting in an obstructed recombination of photoexcited charges. It is also worth noting that Au nanoparticles deposited on the surface of TiO_2 improve the light absorption because of its intrinsic SPR property to produce a large number of photoexcited charges, as confirmed by UV-vis DRS studies. Besides, the gathered electrons at the conduction band of Cu_2O further participate in the photoreduction process. Whereas the holes accumulated at the valance band of TiO_2 participate in the photooxidation process to eliminate the VOCs (toluene and α -pinene pollutants). This is because the holes at the valance band of TiO_2 are potential enough to produce highly reactive oxidative species, hydroxyl radicals to covert the toxic pollutant molecules to CO_2 and water molecules [15]. In addition, the holes in the Cu_2O valance band are paired with the TiO_2 electrons by means of the Au mediator,

leading in the absence of holes in the Cu_2O valance band, which eventually resulting in high Cu_2O stability in the $\text{Cu}_2\text{O-Au-TiO}_2$ composite system.

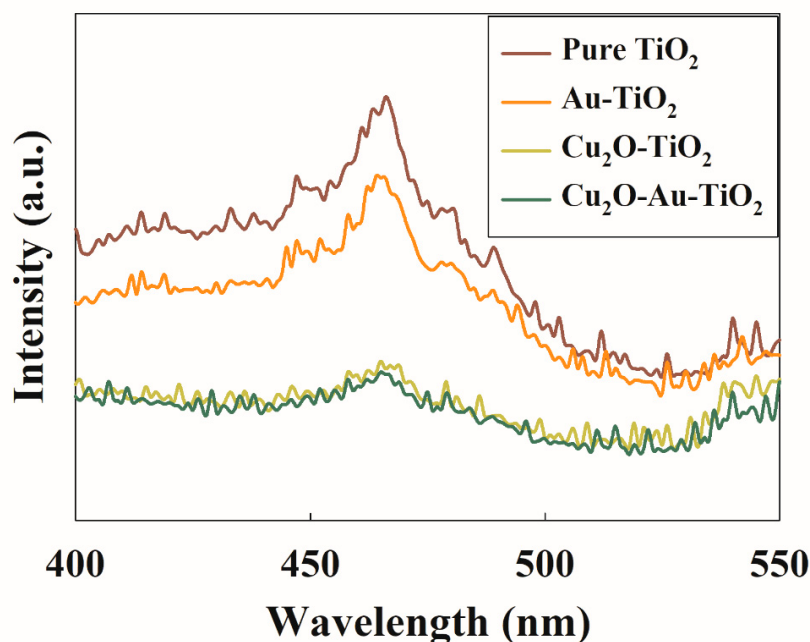


Figure 10. Comparison of the PL spectra of the prepared pure TiO_2 , Au-TiO_2 , $\text{Cu}_2\text{O-TiO}_2$, and $\text{Cu}_2\text{O-Au-TiO}_2$.

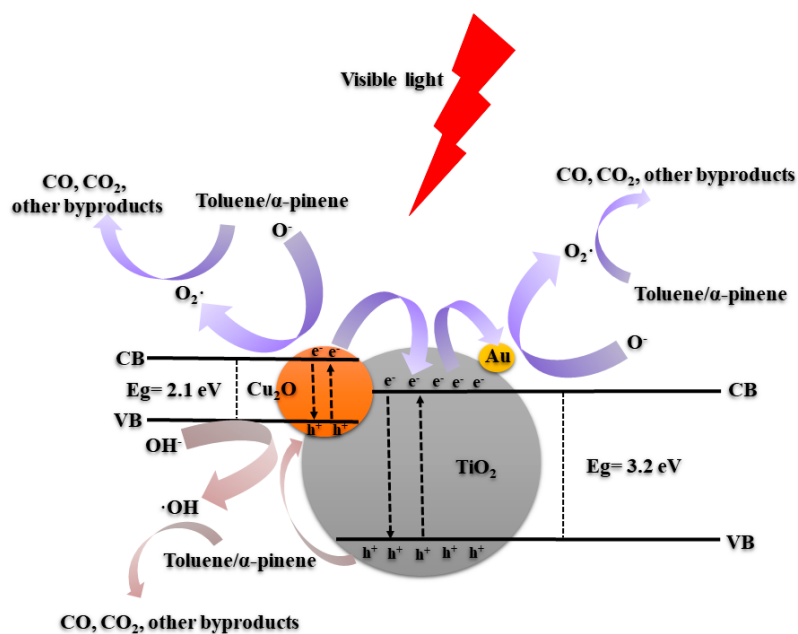


Figure 11. The schematic diagram for the charge transfer in the $\text{Cu}_2\text{O-Au-TiO}_2$.

3. Materials and Methods

3.1. Preparation of Photocatalysts

Bare TiO_2 was prepared by an ultrasonication followed by an annealing procedure used in our previous study [35]. The $\text{Cu}_2\text{O-Au-TiO}_2$ photocatalyst was fabricated by a step-wise photodeposition process described as follows: The prepared pure TiO_2 powder (1.0 g) was suspended in 100 mL of

deionized (DI) water with constant stirring at 400 rpm for 30 min. Of the Au precursor solution 10 mL prepared by dissolving 0.13 mmol of gold(III) chloride trihydrate (99.9%, $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, Sigma-Aldrich, St. Louis, MO, USA) to 25 mL of DI water was added to the above TiO_2 suspension. Then, the mixture was illuminated under a 300 W Hg lamp for 1 h. The resultant compound was collected by centrifugation (5000 rpm for 15 min), followed by washing three times with DI water, and drying overnight (12 h) in an electric oven at 80 °C. The product obtained was named as Au- TiO_2 . The as-obtained Au- TiO_2 (1.0 g) was dispersed in 100 mL of DI water by vigorous agitation at 400 rpm for 30 min, and then 10 mL of Cu precursor solution prepared by dissolving 0.38 mmol of copper(II) chloride (99%, CuCl_2 , Sigma-Aldrich, St. Louis, MO, USA) to 25 mL of DI water was added to the Au- TiO_2 suspension. The mixture was exposed to illumination with the 300 W Hg lamp for 1 h to deposit Cu_2O onto the Au- TiO_2 . Afterwards, the substance obtained in the mixture was isolated through centrifugation (5000 rpm for 15 min), washed three times repeatedly with DI water and then dried in an electric oven for 12 h. The final product was denoted as Cu_2O -Au- TiO_2 . A Cu_2O - TiO_2 was also prepared via the same method by using the bare TiO_2 as a substitute for the Au- TiO_2 . The irradiation time for the preparation of the Cu_2O - TiO_2 was 5 h.

3.2. Characterization

A D/max-2500 diffractometer, Rigaku Corp., Tokyo, Japan with $\text{Cu K}\alpha_1$ radiation in the range of $2\theta = 20\text{--}80^\circ$ was used to obtain the XRD patterns of the prepared photocatalysts. PL (SpectraPro 2150i, Acton Research, Lakewood Ranch, FL, USA) was obtained at a wavelength range of 400–550 nm and UV-vis DRS were obtained for the dry pressed disk samples using a CARY 5G (Varian Inc., Palo Alto, CA, USA) in the wavelength range between 200 and 800 nm at a scanning rate of 120 nm/min for understanding the optical properties of the catalysts. XPS analysis was performed on a Quantera SXM, ULVAC-PHI, Inc. scanning XPS microscope with $\text{Al-K}\alpha$ as an X-ray source, Chigasaki, Japan. FE-TEM (Titan G2 ChemiSTEM (Cs probe), FEI Company, Hillsboro, OR, USA) at an operating voltage of 200 kV was utilized to analyze the microstructures, and FE-SEM (S-4300, Hitachi, Japan) equipped with energy-dispersive X-ray spectroscopy (EDS; EDX-350, Hitachi, Japan) was employed to study morphological properties. Surface areas were determined by using an Autosorb-iQ and Quadrasorb SI, Quantachrome Instruments, Boynton Beach, FL, USA at 77 K after degassing the materials at 150 °C for 3 h under vacuum.

3.3. Evaluation of Photocatalytic Activity

The photocatalytic experiments toward the elimination of gaseous pollutants (α -pinene and toluene) were carried out using a homemade reactor, which is shown in Figure 12. This reactor is similar to the one employed in our previous study [36], and the main units of the reactor system and their functions have been explained in detail. A Pyrex tube with a volume of 133 cm^3 and an inner diameter of 3.8 cm was served as a photoreactor, and an 8 W typical daylight lamp ($\lambda = 400\text{--}700$ nm) was used as a light source. Other lamps, including 0.32 W blue, 0.32 W violet, and 0.32 W white LEDs with wavelengths of 455, 400, and 450 nm, respectively, were also served as light sources to compare the photocatalytic activities of the catalysts. The inner wall of the Pyrex reactor was coated with a catalyst through a spinning process. To provide moisture at a specified relative humidity, high-purity air was transmitted through the water bath. Moisture air was supplied perpendicularly into the reactor to improve the mass transport of the incoming gas to the surface of the catalyst. The photocatalytic reactor device could be defined as representative operating conditions of relative humidity ($45\% \pm 5\%$), gas flow rate (1.0 L min^{-1}), and gaseous model pollutant inlet concentrations (0.1 ppm).

Before each experiment, the reactor was purged with high-purity air to eliminate any adsorbed chemical impurities. Besides, the reactor was subjected to light illumination in the absence of a catalyst to investigate the effect of light on the elimination of model contaminants. The adsorption equilibrium between the volatile organic compounds and the sample was investigated by calculating the concentrations of the compounds in input and output airflow. The light sources were activated

after achieving the adsorption equilibrium to begin the actual photocatalytic experiments. During the analysis, air samples were obtained using air drawn from the sampling ports into the stainless-steel thermal desorption (TD) tube found in Tenax GC to concentrate the model pollutants. A GC–MS, QP2020Ultra, Shimadzu, Kyoto, Japan, was applied to the quantitative study of the model pollutants. A sampled compound was transmitted to GC–MS using an automatic thermal desorption unit (TD-20, Shimadzu, Japan). The adsorbent tube was heated, and the chemical products were concentrated on an inner trap. Finally, an inner trap for the transport of the chemical species to the analysis device was thermally processed.

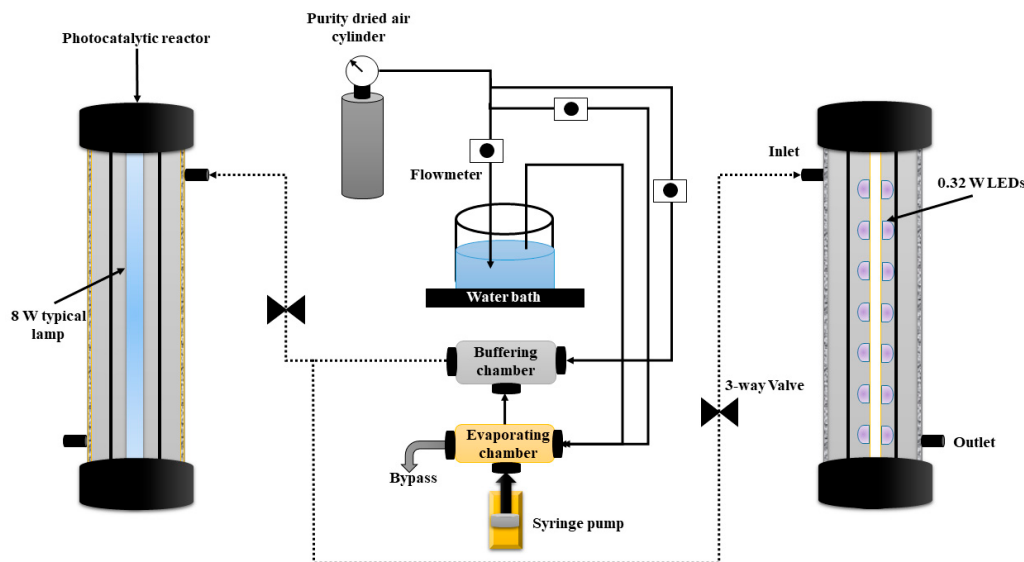


Figure 12. Schematic illustration for the photocatalytic reactor system.

4. Conclusions

In summary, $\text{Cu}_2\text{O-Au-TiO}_2$ was successfully fabricated by a facile route that includes photodeposition. The results of XRD, XRS, and electron microscopy revealed the phase, structural, and morphological aspects of the $\text{Cu}_2\text{O-Au-TiO}_2$ heterostructure. The UV–vis DRS studies displayed the strong optical absorption characteristics of the $\text{Cu}_2\text{O-Au-TiO}_2$ composite. This effective optical absorption of the composite has led to producing a higher number of photoexcited charges required for photo-oxidation of pollutants. Compared to pure TiO_2 , $\text{Cu}_2\text{O-TiO}_2$, and Au-TiO_2 catalysts, the $\text{Cu}_2\text{O-Au-TiO}_2$ composite displayed improved efficiency in the photodegradation of toluene and α -pinene. Moreover, the efficiencies of the $\text{Cu}_2\text{O-Au-TiO}_2$ composite for toluene and α -pinene degradation were also tested under three different light sources: 0.32 W white, blue, and violet LEDs. The results indicate that 0.32 W LEDs were much more energy-efficient light sources than the standard 8 W daylight lamp for toluene and α -pinene photodegradation with the $\text{Cu}_2\text{O-Au-TiO}_2$ composite, even though under daylight illumination the photocatalytic efficiency was shown to be higher. The enhancement in light-harvesting capacity and boosted separation efficiency in electron-hole pairs accounted mainly for an improvement in $\text{Cu}_2\text{O-Au-TiO}_2$ degradation performance and stability.

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