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1 Introduction

The majority of research in the field of photocatalytic water splitting places a large emphasis on the development of heterogeneous photocatalysts and the modification of their bandgap to absorb a wider solar spectrum.¹⁻⁶ In particular, TiO₂ heterogeneous photocatalysis still widely pursued for photocatalysis applications owing to its exceptional properties such as suitable band alignment to water redox potentials, biological and chemical inertness, availability, environmental friendliness, low cost, and long-term stability against photo- and chemical-corrosion.7 However, the H2 production efficiency via photocatalytic water splitting on unmodified TiO₂ is limited, mainly due to the rapid recombination rate of photogenerated carriers. Thus, research has largely been devoted to the modification of this semiconductor for an improved and optimized system towards efficient photocatalysis. One such research emphasizes metal nanoparticle loading, which functions not only to separate the generated electron-hole pair to reduce recombination, but also provides separate O2 and H2 evolution sites, which helps to reduce backward reaction.8-12

Several studies have been conducted on different metals. In particular, noble metals such as Pt and Rh are very good promoters of H_2 production. However, they can also catalyze the backward reaction.^{13,14} This can be suppressed with the addition

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Non-noble metal Cu-loaded TiO₂ for enhanced photocatalytic H₂ production

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Here we have demonstrated the preparation of high-quality, monodispersed and tunable phases of Cu nanoparticles. Structural and chemical composition studies depict the evolution of $Cu-Cu_2O-CuO$ nanoparticles at various process stages. The loading of Cu and Cu oxide nanoparticles on TiO_2 catalyst has enhanced the photocatalytic H₂ production. Comparatively, H₂ treatment produces well-dispersed Cu nanoparticles with thin oxide shells that show the highest H₂ production amongst the samples. The relatively higher photocatalytic performance is deemed to result from reduced structural defects, higher surface area and dispersivity as well as favorable charge transfer, which inhibits recombination. The Cu nanoparticles are shown to be a promising alternative to noble metal-loaded TiO_2 catalyst systems due to their low cost and high performance in photocatalytic applications.

of additives, such as NaOH¹⁴ and Na₂CO₃,¹⁵ with the latter being more effective.¹⁶ On the other hand, transition metals and metal oxides do not require any additives as they do not promote the backward reaction.¹³ Amongst the transition metals and metal oxides studied, Cu and Cu oxide nanoparticle-loaded catalysts are of great interest due to their advantages such as non-toxicity, abundance, high optical absorption coefficient and low band gap energies (1.4–2.3 eV).^{17–20} These characteristics make them prospective candidates for low-cost photocatalytic applications. Moreover, it is interesting to study the oxidation of nanostructured Cu as it possesses multiple oxidation states forming Cu₂O and CuO phases. It is of fundamental interest to be able to prepare high-quality, monodispersed, tunable phases of Cu nanoparticles. Further investigation of Cu-loaded catalysts can be realized through the preparation of different phases of Cu oxide.

In the present paper, we have derived structural and chemical composition understanding of the evolution of Cu–Cu₂O–CuO nanoparticles at different process stages. We also demonstrated a marked enhancement in photocatalytic H_2 production of TiO₂ photocatalyst with the loading of Cu and Cu oxide nanoparticles. Comparatively, H_2 treatment produces well-dispersed Cu nanoparticles with very thin oxide shells which exhibit reduced structural defects, and increased dispersivity and specific surface area which result in the highest H_2 production amongst the samples. It is believed that this study provides some insight into non-noble Cu metal nanoparticles for promising low-cost and high-performance photocatalytic applications.

2 Experimental details

A wet impregnation method was carried out with P25 TiO_2 (Degussa, Aeroxide) added to a 1 g per 6 ml $Cu(NO_3)_2 \cdot 3H_2O$ and deionised water mixture. The mixture was sonicated for 30 min,

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and stirred for 2 h. The resultant homogenous mixture was dried overnight and calcined at 350 °C for 4 h. The as-prepared TiO₂– CuO catalyst was obtained as determined from XRD results (shown later). Different stages of photocatalysts were prepared. Stage 1 involved reduction of the as-prepared photocatalyst under 15 sccm of H₂/Ar (5 : 95) at 800 mTorr, 600 °C, for 6 h. Stage 2 involved partial oxidation of reduced photocatalyst in 15 sccm of O₂/Ar (50 : 50) at 300 °C for 5 to 15 min. Stage 3 involved prolonged oxidation under the same conditions for 20–30 min.

The fabricated photocatalysts were analyzed using an X-ray diffractometer (Philips EMPYREAN, PANalytical) to obtain crystallographic information. Morphology and structural characteristics were studied using a field-emission scanning electron microscope (FESEM, JEOL JSM-700/F) and a transmission electron microscope (FETEM, JEOL JEM2010F), respectively. The absorption spectra of photocatalysts were obtained using a UV-visible spectrophotometer (Shimadzu UV-VIS-NIR Spectrophotometer). X-Ray photoelectron spectroscopy (XPS, VG ESCALAB MKII) was employed to study the chemical composition of the photocatalyst. Brunauer-Emmett-Teller (BET) measurements were conducted using Quantachrome Nova 1200 with N₂ as the adsorbate at liquid nitrogen temperature. Photoluminescence (PL) was carried using a He-Cd laser $(\lambda \sim 325 \text{ nm}, \text{max power} \sim 200 \text{ mw})$ at room temperature. As for the H₂ evolution measurement, 0.04 g of photocatalyst was used for 40 ml of reaction mixture contained in a quartz tube. The 40 ml reaction mixture consists of 10% methanol by volume and 90% tap water. The reaction mixture was purged with Ar gas for 15 min before carrying out the reaction. The reaction mixture was illuminated with a 300 W Xe lamp (Excelitas, PE300BFM) for 3.5 h. Then, 100 µl of gas sample was drawn at about 30 min intervals to sample the gas composition using a gas chromatographer (Shimadzu, GC-2014AT).

3 Results and discussion

Fig. 1a–c shows the as-prepared 2.5 wt% CuO loaded photocatalyst with subsequent H_2 reduction and O_2/Ar (50 : 50) oxidization for 20 min, respectively. Similarly, Fig. 1d–f shows 9.0 wt% of CuO-loaded photocatalyst with subsequent reduction and oxidization, respectively. Fig. 1d shows the presence of large nanoparticles in the 9.0 wt% loaded TiO₂ photocatalyst. The aggregation of the nanoparticles may be due to sintering of relatively high 9.0 wt% Cu loading as compared to 2.5 wt% loading at an annealing temperature of 350 °C. It is observed that both 2.5 and 9.0 wt% loaded photocatalyst that have been reduced in ambient H_2 show better dispersion than the asprepared photocatalyst.

TEM images of Fig. 2a and b show the as-prepared 2.5 wt% loaded photocatalyst with CuO nanocrystals of diameter 3-5 nm which are well-dispersed on the TiO₂ nanoparticles. In contrast, the as-prepared 9.0 wt% loaded photocatalyst consists of larger CuO nanocrystals, diameter of ~10–30 nm (Fig. 2d and e). Furthermore, TEM images are taken at different reduction and



Fig. 2 Low and high resolution TEM images of (a–b) 2.5 and (c–d) 9.0 wt% loaded catalyst of the as-prepared photocatalysts.



Fig. 1 SEM images of (a-c) 2.5 and (d-f) 9.0 wt% loaded catalyst of as-prepared, H₂-reduced and oxidized photocatalyst, respectively.

oxidation stages of 9.0 wt% photocatalyst to depict the phase and structural evolution of Cu nanoparticle-loaded TiO2. Fig. 3a shows photocatalyst after H₂ reduction (stage 1) without undergoing any oxidation. It can be seen that the as-prepared CuO is reduced to Cu nanocrystal with the presence of a thin oxide shell. The possibility of spontaneous oxidation of nanometre-sized metal particles is not ruled out as Cu is prone to surface oxidation upon exposure to ambient atmosphere even at room temperature.²¹ It has been reported that the dominant phase of the shell grown at room temperature oxidation is Cu₂O.²² In addition, it has been shown that the spontaneous growth of oxide (Cu₂O) on the surface of Cu at room temperature can attain a thickness of ~10-13 nm.22,23 Thus, it is postulated that the spontaneous Cu-Cu₂O_{thin} core-shell nanostructure is formed at this stage. Fig. 3b shows the photocatalyst after undergoing H₂ reduction and 5 min oxidization (stage 2). The core of the nanocrystal is composed of a single crystal with an interplanar spacing of d = 2.08 Å which is attributed to Cu(111). The Cu nanocrystal is observed with the presence of a comparatively better-defined oxide shell (Cu-Cu₂O_{thick}). After prolonged oxidation of 30 min (stage 3), the core-shell structure is no longer observed, as the oxide grows thicker which then transforms the entire Cu nanocrystal into a Cu₂O nanocrystal (Fig. 3c).

XRD studies as shown in Fig. 4a were conducted on the evolution of Cu nanoparticle-loaded catalysts of 9.0 wt% loading at different process stages. The as-prepared TiO_2 loaded nanoparticles exhibit characteristic peaks of CuO at calcination

temperature of 350 °C. After reduction in ambient H_2 , the CuO peaks are not discernible while a new diffraction peak of Cu is observed. Subsequent, prolonged oxidization of 20–30 min resulted in Cu peak disappearance, and Cu₂O is the only Cu-containing compound detected. Hence, the spectrum of controlled oxidation for more than 30 min suggests complete Cu transformation into Cu₂O nanocrystals. The XRD results are in agreement with the TEM on the observations of phase transformation at different stages.

XPS analysis on Cu 2p was carried out to obtain chemical state information at various stages to correlate the XRD studies. Fig. 4b shows the as-prepared photocatalysts display a Cu 2p_{3/2} peak at 934.8 eV with a well-developed shake-up satellite peaks while the fully H₂ reduced and prolong oxidized (20 min) photocatalyst shows no apparent or weak shake-up satellite peaks.²⁴ It has been well known that CuO possesses shake-up satellite peaks between Cu 2p3/2 and Cu 2p1/2 at a binding energy of ~944.1 eV. The satellite feature observed for CuO is related to the open 3d⁹ shell configuration in the Cu ground state. The fully reduced and oxidized photocatalyst shows Cu 2P3/2 peaks at 932.7 and 932.8 eV, respectively, which can be attributed to Cu₂O.²⁴ It is noted that the XRD spectrum of the fully H₂ reduced photocatalyst shows a Cu phase without any apparent evidence of a Cu₂O phase while XPS evidently shows the presence of Cu₂O. Given that XPS is a surface technique while XRD is a bulk characterization technique, it is believed that the Cu₂O is present only at the surface of the Cu nanocrystals and is likely to form a thin outer shell.



Fig. 3 TEM images of the catalyst at different process stages for (a) H_2 reduction and (b) O_2/Ar oxidized for 5 min and (c) 30 min.

The chemical and structural characterizations lead to a plausible transformation mechanism as shown schematically in



Fig. 4 $\,$ (a) XRD and (b) XPS spectra of (i) as-prepared, (ii) $H_2\mbox{-reduced}$ and (iii) 20 min oxidized photocatalysts.

Fig. 5. At stage 1, the as-prepared CuO nanoparticles are reduced to Cu metal with the spontaneous formation of a thin Cu₂O shell (Cu-Cu₂O_{thin}). Room temperature-induced oxidation occurs through oxygen atoms adsorbing and tunnelling into the Cu metal to establish equilibrium between the metal and the adsorbed oxygen. The spontaneous oxidations for many metals occur rapidly until the formation of an oxide passivation layer prevents them from further exposure to the ambient. At stage 2, after undergoing a short oxidation process of 5-15 min, O2 reacts with the outer surfaces of Cu nanocrystals to produce a thicker Cu₂O shell (Cu-Cu₂O_{thick}). In this case, the core-shell nanostructure is believed to form via solid-gas reactions involving thermal diffusion of O2 and Cu reactants. The oxidation can be qualitatively interpreted as O2 diffusing from the surface of the nanocrystal inwards while Cu moves in the opposite direction.^{22,23} Subsequently at stage 3, complete transformation of the Cu core into Cu2O nanocrystal has occurred. Due to the high surface-to-volume ratio of the Cu nanocrystals, high oxidation kinetics with increased solubility of oxygen into nanocrystallite can be expected to transform the entire Cu-nanocrystal into Cu2O in a relatively short duration.25 In this case, Cu₂O is formed instead of CuO since the oxidation temperature of 300 °C is relatively lower than the as-prepared photocatalyst at 350 °C.

Fig. 6a shows the UV-vis diffuse reflection spectra of the samples of various samples which include pristine TiO_2 and Cu-loaded TiO_2 . The absorption at wavelengths shorter than 400 nm can be attributed to the intrinsic band gap absorption of pristine TiO_2 . From the absorption spectra, all 9.0 wt% Cu-loaded photocatalysts show enhanced absorption over the visible light region as compared to bare TiO_2 photocatalyst. PL emission measurement was used to investigate the defects present in the 9.0 wt% photocatalyst. Under the same intensity of excitation irradiation, the lower emission intensity implies that less defects are present and possibly more charge carriers are trapped and recombined *via* a radiationless path, or transferred at the particle surface.²⁶ The PL spectra show a broad



Fig. 5 Schematic of structural-phase evolution of Cu loaded on TiO₂ photocatalyst at different stages.



Fig. 6 (a) UV-vis spectra of Cu loaded on TiO_2 photocatalysts at different process stages. (b) PL emission spectra of pristine TiO_2 and as-prepared, H₂-reduced, short and prolongedly oxidized Cu loaded on TiO_2 .

emission band, which is similar to another reported work on TiO_2 -based photocatalysts.²⁷ From Fig. 6b, it is clear that the relative PL intensity of the TiO_2 is the highest, which may imply that electrons and holes of TiO_2 have a higher tendency to recombine.²⁸ On the other hand, all Cu-based loaded photocatalysts show lower defects than TiO_2 .²⁸ It is noted that the Cu-Cu₂O_{thin}-loaded TiO_2 photocatalyst has the lowest intensity of PL emission.

Fig. 7a-d displays the Brunauer-Emmett-Teller (BET) nitrogen adsorption-desorption isotherms and pore size distributions of various samples. The specific surface area of the TiO₂ nanoparticles and 9.0 wt% loaded photocatalyst at various stages, namely the as-prepared (CuO), reduced (Cu-Cu₂O_{thin}) and oxidized (Cu-Cu₂O_{thick}) were determined to be 48.7, 43.3, 51.8 and 43.4 cm^2 g⁻¹. It has been known that the higher specific surface area facilitates better access and diffusion of liquid and gaseous reactants which is beneficial for photocatalytic reactivity. It is noted that the surface area of the Cu loaded photocatalysts after H₂ reduction (Cu-Cu₂O_{thin}) is higher than the other photocatalysts. The pore size distributions of the samples determined by the Barrett-Joyner-Halenda (BJH) method show diameters of 125.2, 147.4, 148.3 and 147.5 Å. The pore diameters of the as-prepared, reduced and oxidized Cu loaded photocatalysts show insignificant changes.





Fig. 7 Nitrogen adsorption–desorption of (a) pristine TiO₂; (b) Cu loaded on TiO₂ catalysts as-prepared; (c) H₂ reduction and (d) prolonged oxidation. The insets show pore size distributions of respective photocatalysts.

Different wt% loadings at 0, 2.5, 4.5, 9.0 and 10.5 *versus* photocatalytic activity for H_2 evolution were investigated (Fig. 8a). The H_2 evolutions of the Cu–Cu₂O_{thin}-loaded photocatalyst increase with a wt% loading upto 9.0 wt%. However, as the loading increases to 10.5 wt%, there is a decrease in H_2 evolution since excessive loadings cause agglomeration of Cu–Cu₂O_{thin} nanoparticles which shields the photosensitive



Fig. 8 H_2 production data of Cu loaded on TiO₂ at different (a) wt% loading and (b) processing stages.

TiO₂ photocatalyst and thus, reduces the photocatalytic activity. As compared to pristine TiO₂ (0 wt% loading), there is a great enhancement in H₂ production in all Cu-Cu₂O_{thin}-loaded TiO₂ catalysts. The loaded Cu-Cu₂O_{thin} nanoparticles rapidly reduce to Cu nanoparticles by accepting photogenerated electrons generated by UV light irradiation in TiO₂. The resulting Cu nanoparticles introduce active sites for H₂ evolution such that electrons generated in TiO2 can be easily transferred into Cu (work function, $\Phi = 4.65$ eV), thus they function as effective trapping centers.²⁹ Hence, reduced Cu nanoparticles loaded onto the TiO₂ photocatalyst are well-suited for charge separation, and as such, after the electron-hole pair generation, the electron is transferred into the conduction band of the semiconductor Cu, which is below that of the photocatalyst, effectively inhibiting recombination. A similar phenomenon of UV irradiation, which results in Cu²⁺ to Cu⁰ reduction to form Cu clusters, has been reported.30 These Cu clusters promote the separation and transfer of photogenerated electrons from the TiO₂ conduction band to the Cu clusters, where H⁺ is reduced to H₂.30

Fig. 8b shows the amount H_2 evolved with two photocatalytic cycle measurements based on 9.0 wt% loaded photocatalysts synthesized at various stages. In the first photocatalytic cycle, it is noted that the Cu–Cu₂O_{thin}-loaded TiO₂ catalyst exhibits a pronounced enhancement in photocatalytic activity that is ~6.6 times higher than that of unmodified TiO₂. The measured H_2 evolutions of TiO₂ and the H_2 reduced photocatalyst are ~1930 and 12 779 µmol h⁻¹ g⁻¹, respectively. However, the photocatalytic activities of Cu–Cu₂O_{thick} and Cu₂O nanostructures exhibit slower H_2 evolutions. Here, it can be observed that different phases of Cu-loaded TiO₂ have effects on the first cycle of photocatalytic performance. The Cu–Cu₂O_{thin}-loaded TiO₂ catalyst has the highest performance possibly due to the fact that the thin oxide shell can be rapidly reduced to Cu nanoparticles as compared to other samples. These postulations are verified by running a subsequent photocatalytic cycle. It is noted that Cu-Cu₂O_{thin} retains its H₂ production performance while the Cu-Cu₂O_{thick} and Cu₂O loaded TiO₂ catalyst show an increase in photocatalytic H₂ production, fairly comparable to the Cu-Cu₂O_{thin} catalyst. In general, a nanosized and welldispersed Cu loaded TiO₂ photocatalyst associated with an increase in surface area and with better dispersion has been shown to yield high H₂ production as compared to pristine TiO₂. Phase-structural transformation of the Cu and Cu oxide nanoparticles affects the photocatalytic activities only in the initial stage since the photoreduction of Cu oxide into Cu will eventually exhibit comparable photocatalytic performance. However, it is observed that Cu nanoparticles derived from Cu-Cu₂O_{thin} show slightly improved H₂ production, possibly due to lower defects (PL results) as well as higher surface area (BET result).

4 Conclusions

Structural (TEM and XRD) and chemical composition (XPS) studies depict the evolution of Cu–Cu₂O–CuO nanoparticles at different stages. It has been demonstrated that H₂-reduced Cu nanoparticles show a spontaneous Cu–Cu₂O core–shell structural formation at room temperature. The photocatalytic activity for the H₂ evolution of TiO₂ photocatalyst is markedly enhanced with the loading of Cu–Cu₂O_{thin} nanoparticles. The overall enhanced photocatalytic activity of Cu–Cu₂O_{thin}-loaded TiO₂ is due to reduced charge carrier recombination and the decrease in defects after H₂ treatment. Furthermore, the Cu–Cu₂O_{thin}-loaded TiO₂ catalyst shows the highest dispersivity and specific surface area amongst the samples.

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