Gold photocatalysis in sustainable hydrogen peroxide generation

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Abstract

Hydrogen peroxide (H₂O₂) is a mild and green oxidant widely employed in organic syntheses, medical sector, disinfection, bleaching, environmental remediation and biological processes. However, its production via the expensive, multiple steps and energy intensive anthraquinone process renders it less sustainable. Photocatalysis is a viable, sustainable and promising strategy to produce H₂O₂ from green sources: water and molecular O₂. This article presents the key developments of photocatalytic H₂O₂ production using gold (Au) nanoparticles supported on semiconductor photocatalysts. Several photocatalytic systems containing Au nanoparticles and the roles of Au nanoparticles in enhancing the photocatalytic H₂O₂ production including increasing visible light absorption, facilitating the charge carrier separation and transfer, and as a catalytic Au active site are discussed. Factors defining the photocatalytic activity such as the effects of Au particle size and loading, localised surface plasmon resonance, mixed-gold component, and design of photocatalysts are reviewed. Finally, the challenges and prospect for further developments of Au photocatalysis in sustainable H₂O₂ synthesis are highlighted.

1. Introduction

Hydrogen peroxide (H₂O₂) is a mild and green oxidant which decomposes exothermically to water and molecular oxygen. The rate of decomposition of H₂O₂ can be controlled by its concentration, temperature, pH, and the presence of stabilizers or impurities. In an acidic medium, it forms a strong oxidant, more powerful than chlorine and potassium
permanganate, such as piranha solution (in H$_2$SO$_4$) for cleaning glassware. The active oxygen content in H$_2$O$_2$ is 47 w/w% which makes it a desirable source of oxygen [1]. It is also a source of hydroxyl radical (•OH). As a result, H$_2$O$_2$ is commonly used in organic syntheses (e.g. olefin epoxidation, aromatic hydroxylation, alcohol oxidation), advanced oxidation process (e.g. Fenton process), bleaching, disinfection, and wastewater treatment [2]. More recently, in-situ production of H$_2$O$_2$ has been proposed as a convenient portable and transportable fuel cell. An increasingly important role of H$_2$O$_2$ in biological processes including wound healing and cell growth [3,4].

The most common, large-scale industrial production of H$_2$O$_2$ is the anthraquinone process. The process involves multiple steps: 1) hydrogenation of anthraquinone in the presence of a palladium (Pd) catalyst, 2) autooxidation of hydroquinone in the presence of air to produce H$_2$O$_2$ and regeneration of anthraquinone, 3) extraction of H$_2$O$_2$ from the solution through a separation column [5,6]. While the net reaction is simple (H$_2$ + O$_2$ → H$_2$O$_2$), the process is expensive, tedious, and risky. The mixture of H$_2$ and O$_2$ entails a risk of explosion. The search for economical, safer, more efficient, and sustainable processes is crucial to meet the industrial demands and reduce environmental impacts.

Photocatalytic H$_2$O$_2$ production is a promising, safer and greener approach as compared to the traditional advanced oxidation process. Importantly, recent progress has shown feasibility of photocatalytic H$_2$O$_2$ production without the need of H$_2$ as a reactant which eliminates the risk of explosion. The synthesis of H$_2$O$_2$ from cheap, widely available water and O$_2$ is an ideal, desirable and promising alternative. Two key steps in a green, efficient generation of H$_2$O$_2$ are two-electron reduction of O$_2$ (step 3 in Figure 1) and water oxidation to H$_2$O$_2$ (step 7). Several possible steps of reduction and oxidation reactions involved as well as decomposition of H$_2$O$_2$ (step 4 and 5) are outlined in Figure 1 [7,8]:
Despite its promise, there are some issues associated with the photocatalytic $\text{H}_2\text{O}_2$ production. First, the sluggish kinetics of water oxidation causes a rapid recombination of photogenerated electron-hole pair. Second, the decomposition of formed $\text{H}_2\text{O}_2$ occurs in the reaction solution by the UV light irradiation, reaction with radicals/intermediates or photogenerated electrons or/and holes (step 4 and 5 in Figure 1) [9]. The yield of $\text{H}_2\text{O}_2$ production is governed by the competing rate constants of $\text{H}_2\text{O}_2$ formation ($k_f$) and decomposition ($k_d$). The $k_f$ has been observed to follow the zero-order kinetics and the $k_d$ is the first-order; the kinetics is described by the equation: $[\text{H}_2\text{O}_2] = (k_f/k_d)[1-\exp(-k_d t)]$. In principle, to obtain high $\text{H}_2\text{O}_2$ yields usually requires manipulating the reaction rates to maximise the $k_f$ and minimise the $k_d$ of $\text{H}_2\text{O}_2$ simultaneously.

Gold (Au) nanoparticle catalysts are highly active in a plethora of chemical reactions [10,11]. Hutchings’s group has pioneered the use of gold catalysts in the synthesis of $\text{H}_2\text{O}_2$ from elemental $\text{O}_2$ and $\text{H}_2$ at low temperature [12,13]. Subsequently, Teranishi et al. demonstrated high yield of $\text{H}_2\text{O}_2$ (of millimolar order) in a photocatalytic reaction from $\text{O}_2$ and water using Au/TiO$_2$ photocatalysts under UV light [14]. The high photocatalytic activity was attributed to enhanced charge separation and spatial separation of oxidation (TiO$_2$.
surface) and reduction (Au surface) sites. Another merit of incorporating Au nanoparticles is the visible light absorption due to the localised surface plasmon resonance (LSPR) that is beneficial for wide band gap semiconductors such as TiO$_2$, SrTiO$_3$, ZnO, and g-C$_3$N$_4$. It has been demonstrated that an Au cathode in a photoelectrochemical cell was able to reduce O$_2$ to H$_2$O$_2$ under solar light irradiation without an applied bias [15].

Pristine semiconductor photocatalysts usually exhibit a high rate of charge carrier recombination and limited visible light absorption (for wide band gap materials) leading to low kinetics of H$_2$O$_2$ formation and low apparent quantum yield (AQY). Deposition of Au nanoparticles on the surface of photocatalysts brings about several benefits: 1) high selectivity for O$_2$ reduction to H$_2$O$_2$ compared to other metals (Pt, Pd, Ag), 2) enhancing charge carrier separation and transfer, 3) extending light absorption into the visible region, 4) behaving as a cocatalyst, and 5) modifying the surface chemistry of the photocatalyst. These factors contribute to many-fold increases in H$_2$O$_2$ production as compared to the pristine supports. For example, Au/WO$_3$ shows a 60-fold increase as compared to WO$_3$ [16] and Au/TiO$_2$ by 80-fold increase as compared to TiO$_2$ [17].

While there exists numerous reviews on Au plasmonic photocatalysts and Au photocatalysis in organic transformation and energy conversion [18–20], there is a lack of dedicated reviews on H$_2$O$_2$ production since the seminal work by Hiroaki Tada’s group in 2010 [14]. Photocatalytic H$_2$O$_2$ production using supported Au nanoparticles is still at its infancy, and thus a review is necessary to provide the current status and recent progress in the field for newcomers and existing researchers. This article presents the key developments and recent progress in the field in the last decade. Various photocatalytic materials and designs containing Au nanoparticles will be reviewed. Factors contributing to high photocatalytic efficiency in H$_2$O$_2$ production such as Au loading and particle size, gold-mixed cocatalysts, photocatalytic supports, and the presence of additives will be discussed. To close, we highlight challenges and prospect for future developments of Au photocatalysis in H$_2$O$_2$ generation and the related fields stemming from it such as Fenton reaction, photocatalytic oxidation and epoxidation, environmental remediation, portable fuel cells and biosensors.

2. Effects of Au particle size and loading

TiO$_2$ as one of the most highly studied photocatalysts has severe drawbacks in photocatalytic H$_2$O$_2$ synthesis such as fast recombination of photogenerated electrons and holes, limited visible
light absorption and decomposition of H₂O₂ [21]. Loading of Au nanoparticles on TiO₂ photocatalytic systems could reduce the decomposition of H₂O₂ on TiO₂ but unfortunately may directly decompose it by the accumulated electrons in Au nanoparticles. Teranishi et al. reported that when the Au size on TiO₂ was larger than 3.5 nm, the production yield of H₂O₂ increased as a function of the Au particle size [14]. The decreasing rate of H₂O₂ decomposition when increasing the Au size was attributed to the reduced number of catalytic active sites. Likewise, a similar trend of size-dependent photocatalytic activity was also reported for Au/ZnO in following order: 4.9 < 6.0 < 6.6 < 9.8 nm Au size (Figure 2b) [22]. The k_f of H₂O₂ increases gradually as the Au size increases but the k_d of H₂O₂ decreases significantly (Figure 2c). In contrast, Au/WO₃ photocatalysts show a decrease in the photocatalytic activity as the Au size increases due to the increased plasmonic activity in H₂O₂ decomposition under visible light and lower interfacial contact between Au and WO₃ that stalls the photogenerated electron transfer [16].

Figure 2. The concentration of H₂O₂ formation a) of different photocatalysts under different conditions, b) as a function of Au particle size in 4% ethanol aqueous solution, and c) plots of the rate constants for formation and decomposition of H₂O₂. Adapted from Ref. [22]. Copyright 2020, Elsevier.

Nevertheless, such a linear correlation is not always the case even in other similar photocatalytic systems. Often, a volcano-type (or inverse volcano-type) plot is found to describe the photocatalytic activity of Au catalysts where there is an optimum size for the highest photocatalytic activity [23]. For example, using Au/TiO₂, Xu et al. found that the optimum Au size of 5.3 nm gave the highest rate of H₂O₂ formation while smaller (2.3 nm) or larger (10.1 nm) Au nanoparticles are kinetically less active (Figure 3) [24]. The broad size distribution of the 5.3 nm-Au/TiO₂ sample containing varying Au sizes was suggested to play
a crucial role for high photocatalytic activity. More recently Kim et al. achieved a millimolar H$_2$O$_2$ production within 5 minutes using varying sizes of Au nanoislands on a porous TiO$_2$ film under UV light with an 80-fold increase compared to that of bare TiO$_2$ [17]. It has been shown that the work function of Au nanoparticles is size-dependent, and may dictate whether Au nanoparticles behave as an electron source or reservoir [25,26]. The authors reasoned that potential gradients are built at the Au-TiO$_2$-Au interfaces due to the size-dependent Au work functions leading to the efficient electron transfer to the surface. In their work, small Au nanoparticles act to reduce O$_2$ to H$_2$O$_2$. Nonetheless, this finding is in contrast to that of Teranishi et al possibly due to the different catalytic design (porous thin film vs powder) [27].

Interestingly, the effects of bimodal Au size distribution on TiO$_2$ were investigated and proven to exhibit a superior photocatalytic performance than the individual unimodal photocatalysts [28]. Using photoelectrochemical measurements, it was found that, upon the visible light illumination, the charge transfer proceeded from small Au to large Au nanoparticles via the CB of TiO$_2$ known as interfacial electron transfer (IET), illustrated in Figure 4. As a result, small Au nanoparticles act as an oxidation site for water oxidation and large Au nanoparticles as a reduction site for O$_2$ reduction to H$_2$O$_2$ [27]. It can be seen that the Au particle size is non-trivial in defining the photocatalytic efficiency. The role of Au nanoparticles either as the electron source or reservoir is highly dependent of the Au particle size, the LSPR effect, light wavelength and photocatalytic systems. It is therefore crucial to

Figure 3. Size effect of Au nanoparticles supported on TiO$_2$ in photocatalytic H$_2$O$_2$ formation rate. Adapted from Ref. [24]. Copyright 2021, Elsevier.
design photocatalysts with controlled Au particle size to maximize the rate and yield of \( \text{H}_2\text{O}_2 \) formation.

![Illustration of interfacial electron transfer](image)

**Figure 4.** Illustration of interfacial electron transfer from a small to a large Au nanoparticle via the conduction band of TiO\(_2\). Adapted from Ref. [27]. Copyright 2016, Wiley VCH.

For sustainable photocatalysis, it is desirable to reduce the material and process costs while maintaining high photocatalytic performance. While Au itself is a noble metal, its photocatalytic efficiency outperforms many other precious metals including Pt, Pd, and Ag nanoparticles [29]. Importantly, several works have demonstrated that a tiny amount of Au loading is required to achieve high yield and rate of \( \text{H}_2\text{O}_2 \) formation, usually much less than 1 wt% (refer to Table 1). Meng et al. suggested that the lower activity of 1% Au/ZnO as compared to 0.1% Au/ZnO is ascribed to the slow kinetics of \( \text{H}_2\text{O}_2 \) formation and blocking of light absorption in ZnO by a higher Au loading [30]. A similar observation was reported for Au/TiO\(_2\) (P25) where a larger Au loading (>2 wt%) reduces the efficiency of catalytic sites [31]. Zuo et al. found that in Au/gC\(_3\)N\(_4\) systems, the most active photocatalyst contained 0.01 wt% Au loading [29]. Surprisingly, almost no decomposition of \( \text{H}_2\text{O}_2 \) was observed in the 0.01% Au/gC\(_3\)N\(_4\) over 12 hours. It could also be possible that higher Au loading causes aggregation which reduces the interfacial contact area between Au nanoparticles and the photocatalytic support thus reducing the photocatalytic activity.

The metal-support interaction (MSI) plays a defining role in many Au-based heterogeneous catalysts [32–35]. The perimeter interface between Au nanoparticles and the
support is believed to be the catalytically active sites in many reactions [11]. In photocatalysis, a strong interfacial contact facilitates a charge transfer between Au nanoparticles and the photocatalytic support. Hirakawa et al. showed that similarly sized Au nanoparticles (~6.9 nm) but calcined at different temperatures (623 vs 673 K under air flow) exhibited a one-fold difference in the \( \text{H}_2\text{O}_2 \) formation yield [36]. The difference was attributed to the stronger degree of interfacial adhesion between Au and BiVO\(_4\) at higher temperature which consequently improved the kinetics of photogenerated electron transfer. However, at larger temperatures severe aggregation occurs which dramatically reduces the number of active sites and catalytic activity.

Other calcination conditions (atmosphere, duration) influence the metal-support interaction which in turns affects the Au particle size, aggregation, and leaching. Chang et al. found that calcination of Au/gC\(_3\)N\(_4\) under nitrogen (N\(_2\)) resulted in smaller Au sizes (5.0±2 nm), less agglomeration, reduced leaching, and gave a higher \( \text{H}_2\text{O}_2 \) yield (by +23.7%) as compared to that of calcined under air [37]. It has also been observed that the influence of metal-supported interaction is more dominant than the Au size in many Au-based catalysts [38–40]. A summary of the photocatalytic efficiency of Au photocatalysis in \( \text{H}_2\text{O}_2 \) production is provided in Table 1.
Table 1. Performance of Au-based photocatalysts in \( \text{H}_2\text{O}_2 \) production

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Light source</th>
<th>Reaction solution</th>
<th>( \text{H}_2\text{O}_2 ) yield</th>
<th>Time</th>
<th>AQY (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25% Au/TiO(_2)</td>
<td>( \lambda&gt;300 \text{ nm} )</td>
<td>4% EtOH/water</td>
<td>( \sim7 \text{ mM} )</td>
<td>24 h</td>
<td></td>
<td>[14]</td>
</tr>
<tr>
<td>0.25% Au/TiO(_2)</td>
<td>( \lambda&gt;300 \text{ nm} )</td>
<td>4% EtOH/water, pH 2, 5 °C</td>
<td>17 mM</td>
<td>23 h</td>
<td></td>
<td>[41]</td>
</tr>
<tr>
<td>0.88% Au/TiO(_2)-CO(_3)^2-</td>
<td>( \lambda&gt;430 \text{ nm} )</td>
<td>4% HCOOH/water, pH 1.7</td>
<td>1 mM</td>
<td>1 h</td>
<td>5.4% (530 nm)</td>
<td>[27]</td>
</tr>
<tr>
<td>0.61% Au/TiO(_2)</td>
<td>( \lambda&gt;320 \text{ nm} )</td>
<td>4% MeOH/water, phosphate, pH 9, 20 °C</td>
<td>1.39 mM</td>
<td>10 h</td>
<td></td>
<td>[42]</td>
</tr>
<tr>
<td>Au/TiO(_2)</td>
<td>367 nm</td>
<td>4% EtOH/water, 0.1M NaF, pH 3</td>
<td>59 µmol/mg</td>
<td>16 h</td>
<td></td>
<td>[43]</td>
</tr>
<tr>
<td>Au/TiO(_2) porous film</td>
<td>UV 365 nm</td>
<td>5% EtOH in citrate buffer, pH 3.8</td>
<td>1 mM</td>
<td>5 min</td>
<td></td>
<td>[17]</td>
</tr>
<tr>
<td>Au/TiO(_2)/CF</td>
<td>( \lambda&gt;420 \text{ nm} )</td>
<td>4% HCOOH/water</td>
<td>( \sim3 \text{ mM} )</td>
<td>8 h</td>
<td></td>
<td>[24]</td>
</tr>
<tr>
<td>Au/TiO(_2)/F</td>
<td>Xe arc lamp</td>
<td>4% alcohol/water</td>
<td>( \sim6.5 \text{ mM} )</td>
<td>12 h</td>
<td></td>
<td>[44]</td>
</tr>
<tr>
<td>0.35% Au/WO(_3)</td>
<td>( \lambda&gt;420 \text{ nm} )</td>
<td>4% CH(_3)OH/water, H(_2)O</td>
<td>544 µM</td>
<td>5 h</td>
<td></td>
<td>[16]</td>
</tr>
<tr>
<td>0.35% Au/WO(_3)</td>
<td>( \lambda&gt;420 \text{ nm} )</td>
<td>4% CH(_3)OH/water, Ni(^{2+})</td>
<td>177 µM</td>
<td>5 h</td>
<td></td>
<td>[45]</td>
</tr>
<tr>
<td>0.43% Au/ZnO</td>
<td>UV 365</td>
<td>4% EtOH/water</td>
<td>( &gt;1 \text{ mM} )</td>
<td>1 h</td>
<td></td>
<td>[22]</td>
</tr>
<tr>
<td>0.1% Au/ZnO</td>
<td>Xe lamp</td>
<td>4% EtOH/water, 0.1M NaF</td>
<td>18.3 mM</td>
<td>12 h</td>
<td></td>
<td>[30]</td>
</tr>
<tr>
<td>0.5% Au/MoS(_2)</td>
<td>Xe lamp</td>
<td>Water, pH 9, 10 °C</td>
<td>0.850 mM</td>
<td>6 h</td>
<td></td>
<td>[46]</td>
</tr>
<tr>
<td>Au(_{0.2})/BiVO(_4)</td>
<td>( \lambda&gt;420 \text{ nm} )</td>
<td>The sunlight</td>
<td>0.792 mM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au/BiOBr</td>
<td>( \lambda&gt;420 \text{ nm} )</td>
<td>5% HCOOH/water</td>
<td>318 µM</td>
<td>2.5 h</td>
<td></td>
<td>[47]</td>
</tr>
<tr>
<td>0.01% Au/gC(_3)N(_4)</td>
<td>( \lambda&gt;420 \text{ nm} )</td>
<td>10% EtOH/water, pH 8.5</td>
<td>2.03 mM</td>
<td>30 h</td>
<td></td>
<td>[29]</td>
</tr>
<tr>
<td>2% Au/gC(_3)N(_4)</td>
<td>Xe lamp</td>
<td>5% IPA/water, pH 3</td>
<td>1.32 mM</td>
<td>4 h</td>
<td></td>
<td>[37]</td>
</tr>
<tr>
<td>Au/C(_3)N(_4)</td>
<td>( \lambda&gt;420 \text{ nm} )</td>
<td>9% IPA/water</td>
<td>990 µM</td>
<td>1 h</td>
<td></td>
<td>[48]</td>
</tr>
<tr>
<td>Au/N-QGD</td>
<td>Xe lamp</td>
<td>water</td>
<td>49.7 µmolg(^{-1})h(^{-1})</td>
<td></td>
<td></td>
<td>[49]</td>
</tr>
<tr>
<td>Au/BiVO(_3)-gC(_3)N(_4)</td>
<td>420 nm LED</td>
<td>Citrate buffer</td>
<td>1.35 mM</td>
<td>6.7%</td>
<td></td>
<td>[50]</td>
</tr>
<tr>
<td>0.1% Au/Bi(_2)O(_3)-TiO(_2)</td>
<td>Xe arc lamp</td>
<td>4% EtOH/water</td>
<td>11.2 mM</td>
<td>12 h</td>
<td></td>
<td>[51]</td>
</tr>
</tbody>
</table>
3. Effects of photocatalytic supports

Photocatalytic activity depends strongly on the type of photocatalytic supports. Apart from the position of the conduction band (CB) and valence band (VB) that are suitable for the redox potentials for H₂O₂ formation, the choice of photocatalytic supports is very important to stabilize Au nanoparticles and form a strong contact structure between Au nanoparticles and the support. Additionally, the surface properties of photocatalysts such as isoelectronic point, acidity/basicity and complexation regulate the adsorption and degradation of intermediate and H₂O₂; surface modification by ions is described in section 6. Besides TiO₂, other photocatalysts such as BiVO₄, WO₃, ZnO, gC₃N₄ and MoS₂ are widely used in photocatalytic H₂O₂ production.

ZnO has a band gap (3.37 eV) and band position similar to that of TiO₂. Contrary to TiO₂, ZnO does not adsorb H₂O₂ thus leading to a high photoactivity in H₂O₂ generation. It was reported that Au/ZnO generated over 1 mM of H₂O₂ in 1 hour, an order of magnitude higher than Au/TiO₂ (Figure 2A) [22]. The apparent difference of photocatalytic activity was attributed to the reduced decomposition of H₂O₂ on Au/ZnO based on the H₂O₂ adsorption study. Similarly, Meng et al. showed an exceptionally high yield (18.3 mM) of H₂O₂ using Au/ZnO as compared to 1.9 mM over Au/TiO₂ [30]. However, the use UV light irradiation and dissolution of ZnO in aqueous solution limits the practical use of Au/ZnO photocatalysts.
Bismuth-based semiconductors have been investigated as visible light responsive photocatalysts. BiVO₄ is a promising photocatalyst with the CB of 0.03 V which is lower than the one-electron O₂ reduction to •OOH (-0.13 V) but higher than two-electron O₂ reduction (0.68 V) making it selectively forms H₂O₂ via two-electron reduction. However, bare BiVO₄ hardly forms H₂O₂ due to the lack of active sites, and therefore requires the use of cocatalysts e.g. Au, Pd, Pt nanoparticles. Loading 0.2% Au nanoparticles on BiVO₄ increases the formation of H₂O₂ in water to 40.2 μM under the visible light irradiation [36]. Upon excitation by the visible light, the photogenerated electrons from the CB of BiVO₄ migrate to Au nanoparticles which reduce O₂ to H₂O₂. A similar role of Au nanoparticles was reported in an oxygen vacancy rich Au/BiOBr photocatalyst under the visible light irradiation [47].

Many works on photocatalytic H₂O₂ production are usually performed in an acidic medium due to the favourable proton-coupled electron transfer and instability of H₂O₂ in basic media; only few studies under basic conditions have been reported using appropriate photocatalytic supports. A high photocatalytic activity (0.85 mM in 6 hours) was observed over Au/MoS₂ in a basic medium (pH 9) due to the hole oxidation of OH⁻ to •OH which eventually dimerized to generate H₂O₂ i.e., •OH + •OH → H₂O₂ [46]. Interestingly, two Au species which are single atoms and nanoparticles were observed on MoS₂ (Figure 5). Moreover, Au/MoS₂ generate a high yield of 0.792 mM H₂O₂ in 6 hours under the real sunlight in pure water which holds a great promise for a real-world application.
Figure 5. (a) HAADF-STEM image of Au single atom in Au(0.50)@MoS₂, (b) TEM image of Au nanoparticles in Au(0.50)@MoS₂, (c) HRTEM images of MoS₂ and (d) Au(0.50)@MoS₂. Adapted from Ref. [46]. Copyright 2019, Elsevier.

Carbonaceous materials like graphitic carbon nitride (gC₃N₄) and graphene quantum dot (GQD) are a promising class of photocatalytic materials owing to their low cost, tunable band gap and surface functionality. It was found recently that Au/gC₃N₄ produced a high H₂O₂ yield of ca. 2 mM in an alkaline (pH 8.5) medium [29]. In another work, small Au nanoparticles (~5 nm) were found to anchor strongly on gC₃N₄ resulting in less aggregation and leaching, and an excellent H₂O₂ yield of 1.32 mM in 4 hours in an acidic (pH 3) medium [37]. These findings suggest that gC₃N₄ might be a versatile photocatalytic support for H₂O₂ generation across all pH with adjustable surface properties. Recently, Jiang et al. reported that an efficient electron transfer from the N atom in C₃N₄ to Au nanoparticles was observed in graphene-like Au/C₃N₄, which gave a high production rate of H₂O₂ close to 1 mMh⁻¹ [48].

Recently there is a growing interest in simultaneous generation of H₂ and H₂O₂ in photocatalytic water splitting due to the ease of membraneless separation and immediate use of H₂O₂ as an oxidant in organic reactions. Using an Au/N-GQD photocatalyst, a
simultaneous formation of H₂ and H₂O₂ is driven by the hot electrons in Au nanoparticles and photogenerated holes of the VB in N-GQD, respectively (Figure 6) [49].

![Figure 6. Proposed scheme of simultaneous H₂ and H₂O₂ generation over Au-N-GQD. Adapted from Ref [49]. Copyright 2021, Elsevier.](image)

In general, it is difficult to have a narrow band gap semiconductor and energetic redox potentials for H₂O₂ generation using a single component photocatalyst because such requirements are mutually exclusive. Thus, construction of heterojunction structures by coupling different semiconductor photocatalysts has been explored as a viable approach to design high-performance photocatalysts that exhibit superior photocatalytic efficiency than the corresponding individual photocatalysts.

Over Au/BiVO₄-gC₃N₄, the decomposition of H₂O₂ by photogenerated holes of BiVO₄ is suppressed by the efficient hole transfer to gC₃N₄ whereas the O₂ reduction proceeds on Au nanoparticles [50]. Besides the catalytic active site, Au nanoparticles can serve other roles thanks to the LSPR effect. In Au/CdS-gC₃N₄, the role of Au nanoparticles is to extend the visible light absorption range, CdS to provide the active site for O₂ reduction and gC₃N₄ to improve to photostability of CdS and enhance the charge transfer [57]. Likewise, Au nanoparticles generate hot-electrons via the LSPR and accelerate the electron transfer to the CB of ZnCr–LDH and eventually to RGO where the O₂ reduction to H₂O₂ occurs [61].
Feng et al. developed a highly active three-component Au/Bi$_2$O$_3$-TiO$_2$ photocatalyst that afforded 11.2 mM H$_2$O$_2$ in 12 hours which was promoted by Au and Bi$_2$O$_3$ nanoparticles [51]. The author proposed that the photogenerated electrons from the CB of Bi$_2$O$_3$ migrated to Au nanoparticles, and holes to the VB of TiO$_2$, giving an effective charge carrier separation. A similar observation was reported in Au/TiO$_2$-RuO$_2$ where the excited electrons in the CB of TiO$_2$ migrated to Au nanoparticles for O$_2$ reduction and holes transferred to the VB of RuO$_2$ [53]. Awa et al. recently designed a three-component Au/SnO$_2$(NR)-TiO$_2$ photocatalyst which showed a vectorial IET across Au(on TiO$_2$)$\rightarrow$TiO$_2$$\rightarrow$SnO$_2$$\rightarrow$Au(on SnO$_2$) [52]. Interestingly, the reduction and oxidation sites in such system were identified to be both Au nanoparticles on SnO$_2$ (A/SnO$_2$) and TiO$_2$ (Au/TiO$_2$), respectively.

Fabrication of thin film photocatalysts is appealing for controlling interface/surface properties using deposition methods such chemical vapour deposition (CVD), atomic layer deposition (ALD), epitaxial growth or sputtering. Kaynan et al. developed an Au/Si(NW)-TiO$_2$ film where Au clusters were embedded within the permeable TiO$_2$ shell giving a strong Au-TiO$_2$ interface that facilitated the charge transfer [59]. Such a film could also bring benefits in biological applications that require H$_2$O$_2$. Phillips et al. demonstrated that Au-sputtered Si NW films produced 6.2 $\mu$M/cm$^2$ H$_2$O$_2$ in 30 minutes in water under visible light and without any sacrificial agents suitable for intracellular H$_2$O$_2$ production [63]. However, the exact mechanism requires further studies, but it is believed the gold-silicon interface is responsible for the production of H$_2$O$_2$. Such finding could replace Au/CdSe/CdS nanorod systems due to the concern of Cd toxicity [64].

One plausible approach to enhance light absorption and hot-electron lifetime of plasmonic Au nanoparticles is to confine the electromagnetic field by coupling with another metal. Willis et al. incorporated an Al film in an Au/ZnO/TiO$_2$/Al stack to enhance the visible light absorption, hot-electron lifetime and the charge injection into the CB of ZnO thereby increasing the H$_2$O$_2$ formation by 3-fold [60]. Figure 7 shows that the formation of H$_2$O$_2$ occurs on ZnO and ethanol is oxidised on Au nanoparticles.
Figure 7. (a) Schematic diagram of the microreactor for in-situ \( \text{H}_2\text{O}_2 \) generation. The inset shows the active sites for \( \text{O}_2 \) reduction and ethanol oxidation. (b) Photocatalytic \( \text{H}_2\text{O}_2 \) yield with Al backing film (red) and without Al (blue). Adapted from Ref. [60]. Copyright 2020, American Chemical Society.

4. **Mixed-gold metal systems**

The use of Au nanoparticles is more favourable than other noble metals (Pt, Pd, Ag) due to the higher activity and selectivity towards \( \text{H}_2\text{O}_2 \) formation. It has been found that the photocatalytic activity of metal supported on \( \text{WO}_3 \) followed the decreasing order: \( \text{Au} \rangle \text{Pd} \rangle \text{Ag} \rangle \text{Pt} \rangle \text{Ni} \rangle \text{Cu} \rangle \text{Co} \) [16]. Understanding the molecular interaction provides insights for such high catalytic activity and selectivity. DFT calculations showed that the formation of \( \text{H}_2\text{O}_2 \) is more favourable over Au/TiO\(_2\) (as compared to Pt/TiO\(_2\)) due to more favourable adsorption energy (-5.79 eV vs -4.76 eV for Pt/TiO\(_2\)) [65]. Importantly, it was found that the O-OH was not broken on Au/TiO\(_2\) which led to a stable and selective formation of \( \text{H}_2\text{O}_2 \).
whereas on Pt/TiO$_2$ the O-H bond breaking occurred leading to the formation of water. This finding is consistent with other experimentally observed low yields of H$_2$O$_2$ formation on Pt/TiO$_2$ photocatalysts. Nevertheless, multimetallic cocatalysts might give unique catalytic activity due to the altered structure (alloy, core-shell), electronic and surface properties.

A strong H$_2$O$_2$ adsorption on Au nanoparticles often lead to its decomposition. This issue can be resolved by designing multimetallic cocatalysts containing Au and another metal to regulate the electronic structure and adsorption properties. Multimetallic cocatalysts are often employed to take advantage of the individual merits of every component, often called synergistic effect [66]. For example, Shi et al. exploited the high selectivity of two-electron O$_2$ reduction by Au and adsorption of O$_2$ by Pd to design an active and selective well-dispersed AuPd alloy nanoparticles on the electron-rich (010) facet of single crystal BiVO$_4$ [58]. The AuPd/BiVO$_4$ exhibits superior stability against H$_2$O$_2$ decomposition and higher activity (2.29 mM) than the corresponding Au/BiVO$_4$ (1.15 mM) and Pd/BiVO$_4$ (1.37 mM) as well as high reusability, as shown in Figure 8. Surprisingly, the high photocatalytic activity of AuPd/BiVO$_4$ was attributed to the well-dispersed Au and Ag atom distribution (compared to isolated Au and Ag atoms) in the AuPd alloy nanoparticles instead of the charge separation and transfer.
Figure 8. (A) Photocatalytic H$_2$O$_2$ production using various samples; (B) recycling test using AuPd/BiVO$_4$(010) (19:1); (C) photocatalytic H$_2$O$_2$ decomposition over time; (D) the $k_f$ and $k_d$ plots of various samples: (a) BiVO$_4$, (b) Au-BiVO$_4$(010), (c) AuPd/BiVO$_4$(010) (49:1), (d) AuPd/BiVO$_4$(010) (19:1), (e) AuPd/BiVO$_4$(010) (9:1), (f) AuPd/BiVO$_4$(010) (2:1) and (g) Pd/BiVO$_4$(010). Adapted from Ref. [58]. Copyright 2022, Elsevier.

A work by Tsukamoto et al. unrevealed that while the rate constant of H$_2$O$_2$ formation ($k_f$) is quite similar for Au$_{0.1}$Ag$_{0.4}$/TiO$_2$ (0.57 mM h$^{-1}$) and Au$_{0.5}$/TiO$_2$ (0.53 mM h$^{-1}$), the former (0.14 h$^{-1}$) exhibits a lower rate constant of H$_2$O$_2$ decomposition ($k_d$) than the latter (0.35 h$^{-1}$) [54]. The finding was attributed to reduced H$_2$O$_2$ adsorption by Ag in AuAg alloy thereby reducing its degradation rate. In other work, DFT calculations on a series of AuAg clusters supported on TiO$_2$ revealed the presence of mid-gap states in AuAg$_3$/TiO$_2$ and Au$_2$Ag$_2$/TiO$_2$ that are suitable for visible light absorption and H$_2$O$_2$ formation [67]. Recently, a core-shell Cu@Au/BiVO$_4$ nanostructure has shown an improvement in charge transfer mediated by the Cu core which reduces an accumulation of negative charge on Au nanoparticles that is otherwise responsible for weaker adsorption of O$_2$ and HOO$^*$ as illustrated in Figure 9D [56].

Figure 9. A) The energy band diagram of BiVO$_4$, (B) Band bending and the charge density of Au/BiVO$_4$. (C) The volcano plot of Au positions of various samples in an oxygen reduction for the two-electron (blue) and four-electron (red) reductions, (D) Band bending in the
Cu@Au/BiVO₄ photocatalyst design. Adapted from Ref [56]. Copyright 2021, American Chemical Society.

5. Effects of additives

In principle, the production of H₂O₂ from water oxidation and molecular O₂ reduction is an ideal, green process. Nonetheless, water and O₂ alone are not sufficient to give high apparent quantum yield of H₂O₂ formation due to the sluggish kinetics of water oxidation half-reaction which leads to a recombination of photogenerated holes and electrons. Two plausible approaches to circumvent this issue have been employed. First, addition of additives to alter the reaction conditions. Second, surface modification of photocatalysts to adjust the surface properties and acidity/basicity.

A little amount (within 5%) of alcohols - usually methanol, ethanol or isopropanol - are added as an electron donor or hole scavenger. Tert-butyl alcohol was found to perform less efficiently than ethanol by three orders of magnitude [41]. Addition of benzylic alcohols boosts the formation of H₂O₂ up to 40 mM due to the formation of side-on peroxo species on TiO₂ from benzyl alcohols and O₂ in water that ultimately forms H₂O₂ [68]. Recently, furfuryl alcohol has been suggested as a promising hole scavenger in photocatalytic H₂O₂ formation [69]. Formic acid is also used as it serves a dual role to provide an acidic environment and electron donor. Milimolar orders of H₂O₂ yield have been achieved using formic acid on Au/TiO₂ photocatalysts[24,27].

An effective approach to reduce the rate of H₂O₂ decomposition via the reductive Ti-OOH pathway is to modify the surface of TiO₂ with other reagents. Complexation of the TiO₂ surface with fluoride ions (F⁻) is known to inhibit the formation of peroxo/superoxo species [70]. However, too much fluoride ions will create defects and cause destruction of the crystallinity of TiO₂. Au modified F-TiO₂ was found to exhibit a four-fold increase in the H₂O₂ production as compared to Au/TiO₂ [44]. Additionally, NaF can be added to the reaction mixture as a source of F⁻ ions. Teranishi et al. observed that surface modified Au/TiO₂ with carbonate ions (CO₃²⁻) enhanced the yield by more than one order of magnitude [27]. The chemisorbed CO₃²⁻ ions on TiO₂ hinder the decomposition of H₂O₂ that usually proceeds through the formation of Ti-OOH species.
The effects of addition of metal ions and inorganics anions to the reaction solution have also been reported. Ni$^{2+}$ and F$^{-}$ ions play both positive and negative roles in the presence and absence of methanol over the Au/WO$_3$ photocatalyst, respectively [45]. In the presence of methanol, Ni$^{2+}$ and F$^{-}$ facilitate methanol oxidation while in its absence, they prevent O$_2$ adsorption and reduction. Cu$^{2+}$, Fe$^{3+}$ and Co$^{2+}$ were found to catalyse decomposition of H$_2$O$_2$ and thereby decreasing the overall yield of H$_2$O$_2$ generation (Figure 10).

**Figure 10.** The H$_2$O$_2$ yield using Au/WO$_3$ as a function of (A) irradiated time for different cations: (a) no ions, (b) Ni$^{2+}$, (c) Co$^{2+}$, (d) Cu$^{2+}$, and (e) Fe$^{3+}$; and (B) ionic strength for (a) 0-5.0 mM Ni(ClO$_4$)$_2$ and (b) 0-20 mM NaClO$_4$. Adapted from Ref. [45]. Copyright 2021, Elsevier.

Synthesis of H$_2$O$_2$ in alkaline/basic media is challenging because of two reasons: H$_2$O$_2$ decomposes faster in alkaline media, and the formation of H$_2$O$_2$ in acidic media is facilitated by the proton-coupled oxygen reduction. As a result, many works reported high H$_2$O$_2$ production rate in acidic conditions (Table 1). However, Xiong et al. showed that high H$_2$O$_2$ up to 1.39 mM yield could be achieved at pH 9 using Au/TiO$_2$ with the addition of phosphate or borate ions [42]. Using photoelectrochemical measurements, their role was identified as to mediate the hole transfer that improves the charge separation.
6. Challenges and perspectives

Gold photocatalysis holds a promise for safe, green, economical and sustainable in-situ production of H$_2$O$_2$ with reduced environmental impacts and energy consumption as compared to the traditional, industrial anthraquinone process. Numerous works reviewed here highlight impressive performance that can afford up to millimolar H$_2$O$_2$ yields within several hours. Despite the potential, the current status and progress of Au photocatalysis in H$_2$O$_2$ production is still at its infancy, and immense effort and further research are needed to achieve the current performance of commercial H$_2$O$_2$ production.

Progress of Au photocatalysis in H$_2$O$_2$ production is still fundamental in nature and at the lab-scale demonstration. The apparent quantum yields are low for many photocatalytic systems particularly in the visible light region. Some long-standing challenges that delay the practical application include:

1) low yield (usually micromolar) and formation rate of H$_2$O$_2$
2) rapid H$_2$O$_2$ decomposition
3) the use of UV light instead of visible light
4) long-hour photocatalytic reaction
5) reaction in pure water without any sacrificial agent

There are complex, competing factors that govern the photocatalytic activity of H$_2$O$_2$ production. The yield of H$_2$O$_2$ formation is primarily governed by the competing rates of formation and decomposition of H$_2$O$_2$. Both rates depend on many factors including the Au particle size, loading/coverage, and contact structure with the photocatalytic support. While the photocatalytic activity varies among photocatalytic systems, the findings discussed in this review article could serve as starting point for further research and developments. There exists general understanding for strategic designs of efficient supported Au photocatalysts. We summarize key points as the guidelines for developing high-performance Au photocatalysts in H$_2$O$_2$ generation.

1) **Contact structure at the perimeter interface.** A contact structure between Au nanoparticles and the support plays a few roles. First, a strong contact structure is favourable for enhanced charge transfer between Au nanoparticle and the photocatalytic support. Second, it controls the aggregation and active sites of Au nanoparticles. Reducible metal oxides like TiO$_2$, ZnO and CeO$_2$ tends form a strong
contact with Au nanoparticles owing to the metal-support interaction (MSI). Importantly, the contact structure is also influenced by the deposition methods and calcination conditions.

2) Control of Au size and loading. Size-dependent work functions and catalytic activity, and the LSPR effects of Au nanoparticles necessitate the importance to control the Au particle size. The Au size determines the extent of visible light absorption, catalytic sites and the nature of electron’s behaviour (supply or reservoir). A control over Au size after the deposition is highly dependent on the deposition methods and calcination conditions. The Au loading must be optimised to maximise the rate of H₂O₂ formation and reduce the blocking of light absorption by photocatalyst and rate of H₂O₂ decomposition.

3) Choice of photocatalytic supports. Besides the band positions that are suitable for H₂O₂ formation, the type of photocatalytic supports determines the contact structure as mentioned above. The surface properties e.g. acidity/basicity, functionality, of photocatalysts dictate the loading, coverage and dispersion of Au nanoparticles, and eventually the aggregation and Au particle size. Moreover, the type of photocatalysts also affects the adsorption and rate of decomposition of H₂O₂ [71].

There is a plenty of room for further research and exploration to advance the progress of Au photocatalysis in H₂O₂ production. Herein we offer some perspective for future direction in this field. Firstly, the precise active site for O₂ adsorption and reduction is ambiguous; it could potentially be on an Au nanoparticle, at the interface between Au nanoparticle and the support, or on the surface of the photocatalyst. Using DFT calculations and the Au₁₀ cluster on TiO₂(110) as a model, Thetford et al. showed that O₂ is adsorbed on Au₁₀, and the formation of H₂O₂ proceeds at the interface of Au/TiO₂ and its decomposition occurs on Au nanoparticles [72]. The role of perimeter interface has also been found in other reactions [73]. Similarly, the exact site for the decomposition of H₂O₂ is still unclear. Different decomposition pathways demand different strategic designs of Au photocatalysts.

Secondly, a wide Au particle size distribution i.e., size polydispersity, impedes a precise identification of the catalytic active sites and the role of size-specific Au nanoparticles. Additionally, the aggregation of Au nanoparticles on supports might conceal the true nature of the catalytic active sites. Several approaches to prepare highly stable and resistant Au catalysts against sintering have been reported such as the use of porous supports, transformation of supports, epitaxial overgrowth, overlayer coating, and encapsulation of
Au nanoparticles in the porous support cavity [74–78]. An alternative is to explore atomically-precise Au clusters with definite size and structure and/or single Au atom catalysts [79–83].

Thirdly, the photocatalyst stability and poisoning needs further investigations. In the case of surface modification of photocatalysts with ions to boost the photocatalytic activity, it is unclear how these ions affect the stability or poisoning of Au nanoparticles. Understanding the poisoning mechanism might offer strategies of recycling method for Au photocatalysts for the long-term use.

Although this review presents discussion exclusively about photocatalytic H₂O₂ production, it is also insightful and beneficial for other photocatalytic reactions that utilize H₂O₂ as an oxidant or intermediate, for example Fenton reaction [84,85], oxidation of alcohols, or amines [71,86], epoxidation [87], water oxidation [88], fuel cells [89], environmental remediation [90] and biological processes [3,4]. For example, photocatalytic water splitting that generate H₂ and O₂ gases requires a membrane separation to collect pure H₂. A simultaneous production of H₂ and H₂O₂ would ease the separation owing to their different phases (gas and liquid), simplify the process and reduce the cost [91]. More recently, inclusion of an Au/TiO₂ thin film in an immunosensing device that forms H₂O₂ demonstrates comparable sensitivity to commercial enzyme-based biosensors [92]. This could potentially advance the alternative, cheap biosensors. In summary, there lies opportunities for a multifaceted exploration of Au photocatalysis in sustainable H₂O₂ production and other related applications.

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References


