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H₂ generation with (mixed) plasmonic Cu₄,Au-TiO₂ photocatalysts: Structure-reactivity relationships assessed by in situ spectroscopy


Dedicated to Prof. Dr. Bernhard Lücke on the occasion of his 80th birthday

Abstract: Monometallic Cu- and bimetallic Cu/Au-TiO₂-catalysts were prepared by impregnation (IM) and reductive precipitation (RP) methods in sequential (SP) and simultaneous mode (CP) and tested for photocatalytic H₂ generation from H₂O/methanol mixtures with visible (400 – 700 nm) and UV-vis light (320 – 500 nm). Comprehensive studies by HR-STEM, XPS and different in situ methods (XANES, UV-vis and EPR spectroscopy) revealed that IM leads to dispersed surface Cu species with no clear particle formation being poorly active under visible light, while plasmonic Cu³ nanoparticles formed by RP are about three times more active under the same conditions. In CuAu-TiO₂ catalysts prepared by RP-SP, highly dispersed Cu surface species boost especially H₂ production under UV-vis light, due to the effective separation within TiO₂ and electron trapping by Cu, while small Cu²⁺ and Au²⁺ particles remain widely separated. When CuAu-TiO₂ catalysts are prepared by RP-CP, mixed Cu-Au particles of uniform size (4-8 nm) provide the highest H₂ evolution rates under visible light, due to effective surface plasmon resonance absorption.

Introduction

Due to global warming and increasing concerns about the depletion of fossil resources, there is a growing need for the development of sustainable energy carriers such as H₂ from water. Photocatalytic water reduction using sunlight, which contains mainly visible radiation, would be an attractive and environmentally benign alternative to the still dominating H₂ production from fossil resources. However, up to now sufficiently effective photocatalysts making the “up-hill” water-splitting reaction economically feasible are still not available.[1] TiO₂ is one of the most investigated and promising semiconductor photocatalysts due to its high chemical and photochemical stability, abundance and non-toxicity.[2] However, UV light, comprising only about 4 % of the solar radiation, is needed to excite transitions of electrons from the valence band into the conduction band, from which they can reduce protons at the TiO₂ surface. With pristine TiO₂, fast recombination of separated electrons and holes usually leads to low quantum efficiencies. Therefore, the introduction of coinage metal nanoparticles (Au, Ag, Cu) is a promising route to overcome the limitations of TiO₂ based photocatalysts since these offer two important advantages for efficient photocatalytic performance: i) they form a Schottky barrier at the metal-semiconductor interface, which hinders fast recombination of separated charge carriers and, thus, raises their lifetime and ii) they can harvest visible light due to surface plasmon resonance (SPR) absorption.[3] So far, almost exclusively the SPR properties of Au nanoparticles (absorbing at ca. 550 nm) were investigated for photocatalytic water reduction by visible light.[4, 5] Though the other coinage metals Ag and Cu also show SPR in the visible region, their application for photocatalytic water reduction is limited to a few examples only.[5] Moreover, Cu-based photocatalysts were mostly investigated in water reduction using UV-light containing excitation sources,[5] while the impact of SPR-active Cu particles on H₂ production under pure visible light has hardly been explored explicitly. This is also true for detailed analysis by in situ methods of the structure of the active Cu species and their formation from precursor stages under photocatalytic water reduction conditions. This, however, should provide more authentic information than ex situ studies of the catalysts before and after use and may be very helpful for rational catalyst design. Thus, we have shown by in situ EPR spectroscopy for Au/TiO₂ catalysts that SPR-promoted direct electron transfer from Au particles to TiO₂ is the initial step in visible-light driven H₂ generation[7] and that this property is sensitive to the nature of the TiO₂ support, i. e., to the content of Ti³⁺ defects and surface OH groups.[8]

In this work, we extend our studies to plasmonic monometallic Cu and mixed CuAu particles supported on TiO₂, since replacement of Au by less expensive Cu would be an economically attractive, low-cost alternative. In situ methods such as X-ray absorption near edge structure (XANES), UV-vis and Electron Paramagnetic Resonance (EPR) spectroscopy were applied in addition to Scanning Transmission Electron Microscopy (STEM) and X-ray Photoelectron Spectroscopy (XPS) to study the influence of different synthesis protocols on catalyst structure and relations between the latter and H₂ production rates under UV-vis and pure visible light, respectively. In order to achieve an efficient photocatalytic H₂ production rate, and thereby to allow mechanistic studies in relation to specific reactivities, we used the sacrificial reductant methanol as hole scavenger, which is more easily oxidized than OH⁻ ions in water molecules.[9] By scavenging the positive holes in the valence band, the recombination of the photoinduced charge carriers is suppressed which leads to higher H₂ production rates.
Results and Discussion

Photocatalytic performance

Table 1 summarizes the metal contents and H₂ production rates for all catalysts. The bare support showed only very small H₂ evolution with UV-vis light and no activity at all under visible light. Both monometallic Cu catalysts Cu-IM and Cu-RP showed similar H₂ production of 5.2 and 6.3 mmol·g⁻¹·h⁻¹, respectively, under UV-vis light (for H₂ evolution curves see Fig. S1). However, given that Cu-RP contains only 60 % of the desired Cu content, this catalyst is much more active than Cu-IM with 1.1 wt.-% Cu. This difference is even more pronounced under visible light (400–700 nm), when H₂ production is by a factor of 2.8 higher than on Cu-IM (Table 1).

<table>
<thead>
<tr>
<th>Catalyst [a]</th>
<th>H₂ formation [mmol·g⁻¹·h⁻¹]</th>
<th>Metal content [wt. %]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UV-vis</td>
<td>vis</td>
</tr>
<tr>
<td>Cu-IM</td>
<td>5.2</td>
<td>0.19</td>
</tr>
<tr>
<td>Cu-RP</td>
<td>6.3</td>
<td>0.53</td>
</tr>
<tr>
<td>Cu/Au-SP</td>
<td>11</td>
<td>0.48</td>
</tr>
<tr>
<td>Cu/Au-CP</td>
<td>7.5</td>
<td>1.6</td>
</tr>
<tr>
<td>bare P25</td>
<td>0.4</td>
<td>none</td>
</tr>
<tr>
<td>Au/P25 [b]</td>
<td>33</td>
<td>2.4</td>
</tr>
</tbody>
</table>

[a] Conditions: 25 mg catalyst in 10 mL H₂O/MeOH (vol. ratio 1:1), 2.5 W output Hg lamp (UV-vis: 320–500 nm, vis: 400–700 nm); [b] Values taken from ref. [8]. Test conditions: 50 mg catalyst in 10 mL H₂O/MeOH (vol. ratio 1:1), 2.5 W output Hg lamp (UV-vis: 320–500 nm, vis: 400–700 nm).

In general, both bimetallic Cu/Au catalysts are more active than the monometallic Cu samples, though significant differences are observed depending whether the synthesis was performed by stepwise precipitation (Cu/Au-SP) or by coprecipitation (Cu/Au-CP). A marked improvement under UV-vis irradiation is only observed for Cu/Au-SP, while for Cu/Au-CP this is true only under visible light. In this case, the latter sample evolved more than three times the volume of H₂ as observed for Cu-RP (1.6 mmol·g⁻¹·h⁻¹, Table 1). This is remarkable, considering that our best monometallic 1% Au/P25 catalyst with twice the total metal content than Cu/Au-CP (shown for comparison in Table 1) gave only a slightly higher H₂ evolution rate of 2.4 mmol·g⁻¹·h⁻¹, yet at a lamp output of 7.5 W. [8] This illustrates that it is possible to replace noble Au partly by non-noble Cu without loss of activity. Certainly, the different activities listed in Table 1 originate from structural differences of the catalysts which are presented in the next sections.

Characterization of monometallic Cu-TiO₂ catalysts

The XRD powder patterns of all catalysts are essentially identical, showing only the anatase and rutile reflections expected for P25 (Fig. S2).

![Figure 1. In situ UV-vis spectra of the monometallic Cu-based catalysts prepared by a) impregnation (Cu-IM) and b) reductive precipitation using NaBH₄ (Cu-RP) in the as-synthesized state (black), exposed to H₂O/MeOH in the dark (red) and under subsequent UV-vis irradiation for 5 min (blue).](image)

While this difference has a crucial impact on H₂ evolution under visible light (Cu-RP is 2.8 times more active), it plays a minor role under irradiation with UV light (Table 1). This suggests that visible light driven H₂ formation inevitably requires the presence of plasmonic Cu species while, with UV light, H₂ can also be liberated from CuO species as observed previously. [10] This conclusion is also supported by HR-STEM/EDX results of the as-prepared sample Cu-IM that revealed only few very small Cu-containing agglomerates while the majority of Cu is most probably highly dispersed on the support, though this could not be detected unequivocally by EDX due to the low signal-to-noise ratio (Fig. S3). In contrast, small (oxidic) CuO clusters of about 1-2 nm are already preformed in...
as-prepared Cu-RP which, in the presence of H2O/MeOH, might be reduced to plasmonic Cu0 particles (Fig. S4).

Figure 2. In situ XANES spectra of Cu-RP, Cu/Au-SP and Cu/Au-CP in the dark (black), under H2O/MeOH in the dark (red) and under subsequent irradiation with visible (green) and UV light (blue). Dashed lines: spectra of reference materials CuO (black), Cu2O (green) and Cu foil (blue).

In all as-prepared catalysts, the position of the absorption edge is characteristic for CuII, as evident from the superposition with the respective CuO reference. When the catalysts are exposed to the H2O/MeOH mixture still in the dark, fast reduction of CuII to Cu0 occurs in sample Cu-RP, while Cu in catalysts Cu/Au-SP and Cu/Au-CP remains essentially divalent. A reason may be that the higher electron affinity of Au in comparison to Cu hampers the reduction of CuII to Cu0 in the absence of UV-vis irradiation.

Upon analyzing the catalysts under the same conditions by in situ UV-vis spectroscopy, additional information about the formation of plasmonic metal particles has been obtained (Fig. 3). The spectra of the as-synthesized samples Cu/Au-SP and Cu/Au-CP (black) contain a weak SPR absorption band of Au nanoparticles around 550-555 nm, which are probably too few to be detected by XANES. Upon suspending in H2O/MeOH (red), no significant spectral changes were observed for sample Cu/Au-SP (Fig. 3b). In contrast, under the same conditions, a clear shift of the SPR absorption maximum from 555 to 570 nm, i.e., a position in between those of the SPR bands of pure Au and Cu (λ = 580 nm[12], is evident for catalyst Cu/Au-CP (Fig. 3a, red). This suggests that mixed Cu-Au particles might have formed. This band still increases in intensity under irradiation but does not change its position (Fig. 3a, blue line).

Differently, SPR bands of pure CuII appear under irradiation in Cu/Au-SP (Fig. 3b, blue line). Upon comparison of samples Cu/Au-SP and Cu/Au-CP it is readily evident that the reductive precipitation protocol has an important impact on the nature of the formed metal particles and in turn on the H2 evolution activity (Table 1). Therefore, detailed investigations by TEM, in situ XANES and in situ EPR spectroscopy have been performed on both Cu/Au catalysts to derive structure-reactivity relationships in hydrogen generation.

HR-STEM images of sample Cu/Au-SP (Fig. 4) combined with EDX analysis (Fig. S5, S6) revealed Cu agglomerates of 1–2 nm size (Fig. 4c) separated from slightly larger Au particles (2–5 nm, Fig. 4a) which contain traces of Cu, too. These Cu agglomerates are oxidic in the as-prepared catalyst (Fig. 2) and get reduced to plasmonic Cu0 particles during irradiation with UV-vis light, giving rise to the SPR band at 580 nm (Fig. 3b). When Cu and Au were precipitated simultaneously in the Cu/Au-CP catalyst, well ordered mixed Cu-Au nanocrystals of 4–8 nm size are formed (Fig. 4b and d, Fig. S6). Moreover, the presence of Cu without obvious agglomeration has been detected by EDX in any support area analyzed, suggesting a more or less uniform distribution of highly dispersed Cu on the support surface. Possibly, a part of this Cu diffused into the subsurface of the support where it is not accessible by XPS anymore. This is suggested by the much smaller surface Cu content in sample Cu/Au-CP compared to Cu/Au-SP. Under ambient air, the mixed Cu-Au particles might contain copper in its oxidized form, which is reduced to Cu0 only in the presence of H2O/MeOH, as seen from the red-shift of the SPR absorption maximum for Cu/Au-CP (Fig. 3a, red).[13]
The different mutual arrangement of Au and Cu in the bimetallic catalysts also influences the reducibility of Cu, as evident from the XANES spectra (Fig. 2). The results are compared with those obtained for the monometallic sample Cu-RP. Addition of H$_2$O/MeOH to this latter sample led to the reduction of Cu$^+$ to Cu$^0$, but did not affect the position of the absorption edge in both Cu/Au catalysts (Fig. 2, red lines). With evidence from the weak SPR band in the UV-vis spectrum (Fig. 3a), the number of metallic Cu-Au particles in sample Cu/Au-CP (Fig. 3a) might be too small to be reflected by the XANES spectrum. Subsequent irradiation with visible light (green lines) caused reduction of Cu$^+$. However, while this reduction stops at Cu$^+$ in sample Cu/Au-SP, metallic Cu$^0$ is formed under the same conditions in the Cu/Au-CP catalyst which showed much higher H$_2$ generation under pure visible light. The different reduction behavior of both Cu/Au catalysts can be clearly distinguished by the shape of the pre-edge feature of the absorption edge. In sample Cu/Au-SP a clear maximum is observed at 8980 eV, which is typical for Cu$^+$. In sample Cu/Au-CP this maximum is missing. Instead, the pre-edge resembles that of the Cu$^0$ reference. Additionally, a maximum at 9020 eV for metallic Cu can be seen in this sample, which was not found in Cu/Au-SP.

This, once again, verifies that it is the metallic plasmonic state of coinage metals that is crucial for proton reduction under visible light rather than the oxidized metal species such as CuO or CuO$_2$, despite the fact that CuO is known as a visible light absorber as well.\cite{14} In contrast to the mixed Cu-Au particles in sample Cu/Au-CP, visible light alone cannot reduce oxidic Cu to its metallic state when the latter is spatially separated from Au in the Cu/Au-SP catalyst. In this case UV light is necessary to form Cu$^+$ (Fig. 2, blue) that then occurs as a consequence of charge separation within TiO$_2$ followed by electron transfer to the CuO$_2$ species. The high dispersion of very small metal centers all over the support in Cu/Au-SP (Fig. 4a and c) is especially beneficial for H$_2$ generation mediated by UV-light, since in this case TiO$_2$ valence-band electrons are excited and transferred to the metal particles. The smaller the metal particles, the more active sites can trap electrons and reduce protons. This is confirmed by the markedly higher H$_2$ rate under UV light for Cu/Au-SP (Table 1).

Besides XANES and UV-vis spectroscopy we have used in situ EPR as a third complementary method able to selectively monitor the behavior of Cu$^0$ species during formation of the active catalyst from the precursor state (Fig. 5). The spectra of both samples Cu/Au-SP and Cu/Au-CP in the presence of H$_2$O/MeOH in the dark contain characteristic signals of Cu$^0$ in axial geometry (d$^9$, S = 1/2). The hyperfine structure (hfs) arising from the coupling of the electron with the nuclear spin of $^{63}$Cu and $^{65}$Cu (I = 3/2, natural abundance 69.09 and 30.91 %, respectively) is poorly resolved, due to dipolar magnetic interaction between neighboring Cu$^0$ sites, which leads do line broadening. A more detailed evaluation reveals that the spectra comprise signals from different Cu$^0$ species (Fig. S7). Signal A with g$_1$ = 2.38, A$_1$ = 80 G and g$_1$ = 2.05 is similar to the one previously observed from Cu$^0$ located in Ti vacancies of the support surface.\cite{15} Signal B (g$_1$ = 2.25, g$_2$ = 2.05, unresolved hfs) shows a more pronounced line broadening, which is due to strong dipolar interactions between Cu$^0$ ions in oxidized Cu clusters.\cite{15} This kind of Cu species dominates in the spectra of both bimetallic catalysts. Upon irradiation with visible light, the signal of Cu$^0$ decreases since
these species are reduced to EPR-silent CuI and CuII. Since sample Cu/Au-SP contains almost all the copper in the form of highly dispersed CuI species, the initial signal intensity is higher and the decline is faster than in sample Cu/Au-CP in which most of the Cu forms mixed particles of larger size with Au and is therefore less dispersed. It is evident from XANES (Fig. 2) and UV-vis spectroscopy (Fig. 3) that switching to UV light causes further reduction to CuII. In sample Cu/Au-CP, this leads to a further drop of the CuI signal while, surprisingly, it increases in Cu/Au-SP despite ongoing formation of EPR-silent CuII. The reason may be that these CuII species reduce dipolar interactions between the fewer remaining CuI species, which leads to line narrowing and increase of the signal amplitude. In any case, the behavior of the CuII signal in both catalysts parallels the results of in situ XANES and in situ UV-vis measurements and reflects the facilitated reduction of Cu to the metallic state in the most active catalyst Cu/Au-CP.

![Figure 1](image)

**Figure 1.** In situ EPR spectra of Cu/Au-SP and Cu/Au-CP under H2O/MeOH in the dark (red) and subsequent visible- (green) and UV-light irradiation (blue). Insets: signal intensity as a function of irradiation time.

**Conclusions**

H2 production from H2O/MeOH mixtures by monometallic Cu-TiO2, as well as bimetallic Cu/Au-TiO2 catalysts depends crucially on the nature of the metal particles which itself is governed by the synthesis procedure. Thus, Cu species deposited on TiO2 by reductive precipitation (Cu-RP) are easily reduced in situ to plasmonic CuI particles under photocatalytic conditions, while this is much more difficult for a catalyst prepared by impregnation (Cu-IM), in which no clear metal particles but highly dispersed Cu species are formed. This leads to an almost threefold H2 production rate of Cu-RP under pure visible light (despite an only half as high metal content as in Cu-IM). This shows clearly that it is the plasmonic CuI particles that boost visible-light activity.

The mixed Cu/Au-SP catalyst prepared by sequential reductive precipitation of 1) Cu and 2) Au did not improve H2 production under visible light in comparison to Cu-RP, since both metal components are separately present, whereby Cu is more highly dispersed on the support surface than Au (reflected by the XPS surface ratios). This Cu dispersion is highest in sample Cu/Au-SP, which leads to a doubling of the UV-light-driven H2 production rate compared to Cu-RP. This is due to the different mechanism which implies charge separation within TiO2 followed by electron trapping at surface Au and Cu sites, the latter being most abundant in catalyst Cu/Au-SP.

When Cu and Au are deposited on TiO2 simultaneously by reductive co-precipitation (Cu/Au-CP), mixed plasmonic Cu-Au particles of 4-8 nm size are formed, which boost the H2 production rate under visible light by a factor of almost 3, compared to the monometallic Cu-RP counterpart, despite the fact that the total metal content in Cu/Au-CP is lower by one third. Obviously, the tight mixing of Cu and Au in the oxidic precursor species raises the reduction potential of Cu and facilitates reduction to plasmonic metal particles that are essential for visible-light-driven H2 generation. Remarkably, visible-light driven H2 production with this catalyst is almost as active as our most active monometallic 1% Au/P25 catalyst, despite the lower total metal content of only 0.4 % and the lower lamp output used in the present work. This opens new opportunities to replace noble Au by less expensive Cu in such photocatalysts without loss in activity.

**Experimental Section**

**Catalyst Preparation**

All catalysts were prepared using P25 (Evonik, BET surface area: 50 m²/g) as TiO2 support, which consists of 85 % anatase and 15 % rutile. Monometalic Cu/TiO2 was prepared by two different procedures. a) Impregnation was carried out by suspending 1.0 g TiO2 powder in 300 mL absolute alcohol. An aqueous solution of Cu(NO3)2·3H2O (0.15 mm, 25 mL, Aldrich) was added dropwise. The mixture was stirred for 10 h at 80 °C,
filtered and washed with 500 mL distilled water. After drying at 100 °C for 12 h, the material was calcined at 500 °C (3 K/min) for 3 h in flowing air. The catalyst is denoted by Cu·M. b) Reductive precipitation was carried out by suspending 1.0 g TiO2 in 20 mL H2O. After adding an aqueous solution of Cu(NO3)2·3H2O (0.15 mm, 5 mL, Aldrich), a freshly prepared solution of NaBH4 (0.1 m, 4 mL) was dropped into the suspension. The mixture was stirred for 20 min and the catalyst was filtered, washed, dried at 100 °C for 12 h and denoted by Cu·RP. Mixed CuAu metal catalysts were also prepared via the reductive precipitation method, though with different reaction sequences. c) Stepwise precipitation (denoted by -SP) was carried out by first dropping an aqueous NaBH4 solution (0.1 m, 4 mL) into 20 mL of an aqueous suspension containing 1 g TiO2 and 36 mg Cu(NO3)2·3H2O. After 20 min, 4.0 mg HAuCl4·3H2O (Aldrich) in 10 mL H2O were added dropwise followed by subsequent addition of further NaBH4 solution (0.1 m, 1 mL). After stirring for 10 min, the material was filtered, washed and dried at 100 °C for 12 h. d) Co-precipitation was applied to prepare a mixed CuAu/TiO2 catalyst by adding an aqueous NaBH4 solution (0.1 m, 5 mL) to 50 mL of an aqueous suspension containing 1 g TiO2, 36 mg Cu(NO3)2·3H2O and 4.0 mg HAuCl4·3H2O. The mixture was stirred for 30 min, filtered, washed and dried for 12 h at 100 °C (denotation: CuAu·CP).

Photocatalytic tests

Photocatalytic tests were carried out at 25 °C under argon atmosphere with freshly distilled solvents using 25 mg catalyst in 10 mL MeOH/H2O (vol. ratio: 1/1) and a 2.5 W Hg vapor light irradiation source (Lumatec Superlite 400). Further details on the equipment and the experimental set-up have been published previously.[14] The gas evolution was recorded first under visible light (400–700 nm filter) for ca. 6 h and subsequently under UV-vis light (320–500 nm filter) for ca. 2.5 h. After each reaction, a gas sample was taken for gas chromatography in order to determine the relative composition of the evolved gases (GC HP 6890N, carboxen 1000, TCD, external calibration). The variation of the hydrogen volumes for repeat experiments is between 5–25 %, including the error of the measurement set-up itself as well as the reproducibility of the catalyst preparation method.

Catalyst characterization

UV-vis spectra in reflectance mode were recorded by an Avantes AvaSpec-2048 UV-vis spectrometer with a 45 ° optical probe from catalysts in pure form and suspended in H2O/MeOH (1:1) before and during irradiation with UV-vis light (same irradiation source as used for catalytic tests). The amount of deposited metals was determined by ICP-OES using a Varian 715 (plasmon resonance). The amount of deposited metals was determined by ICP-OES using a Varian 715 ICP spectrometer (EDXS) for chemical analysis. EDX spectra and high-angle annular dark field (HAADF) images were acquired with a spot size of 5c (ca. 0.15 nm) and a 30 μm condenser aperture. Prior to TEM analysis, the dry sample was deposited on a carbon-supported Ni grid.

XP spectra were recorded using a VG ESCALAB 220XI instrument with Al Kα radiation (E = 1486.6 eV). Peaks were fitted by Gaussian–Lorentzian curves after Shirley background subtraction. The electron binding energy was referenced to the Ti 2p3/2 peak of TiO2 at 458.8 eV. For quantitative analysis, the area peaks were determined and divided by the element-specific Socrfield factor and the analyser-depending transmission function.

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Keywords: photocatalysis • in situ spectroscopy • surface plasmon resonance • hydrogen generation • bimetallic catalysts


All that glitters isn’t gold. The impact of different metal deposition methods on light-driven H₂ production is studied. Au/Cu alloy particles formed by coprecipitation evolve much more H₂ under vis light than separate Au⁰ and Cu⁰ particles formed by stepwise precipitation. The opposite is true under UV light.