Semiconductor Photocatalysis of Bicarbonate to Solar Fuels: Formate Production from Copper(I) Oxide

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Supporting Information

ABSTRACT: Copper-oxide-based photocatalysts, micron- and nanosized, and silver nanoparticle–copper oxide nanocomposites (Ag/Cu2O) were characterized and evaluated for the first time in the application of bicarbonate conversion to formate. The Ag/Cu2O nanocomposite yielded considerable production improvement over pure copper oxides due to the role of silver as a plasmonic sensitizer. We attribute these marked production improvements to plasmon-induced electron transfer from metal to semiconductor. These photocatalysts were studied in two different hole scavenger solvents (2-propanol and glycerol) using a solar simulator with air mass coefficient 1.5 and 0 (AM 1.5, AM 0) filters. Formate production increased significantly with AM 0 solar irradiation due to inclusion of the ultraviolet portion of the solar spectrum, and nanoparticulate Cu2O showed improved photocatalysis relative to micron Cu2O. Green chemistry solvent, glycerol, proved to be a far superior hole scavenger in comparison to 2-propanol.

KEYWORDS: solar fuels, formate, silver nanoparticles, plasmonic sensitizer

INTRODUCTION

Despite growing public awareness, concentrations of anthropogenic carbon dioxide (CO2) continue to increase unabated. As the most abundant greenhouse gas, efforts to mitigate this trend have focused on conversion of CO2 to value-added chemicals or automotive fuels such as formate or methanol, respectively.1–3 Ideally, CO2 is photochemically converted without the use of additional CO2-generating power sources via solar energy. “Photons to formate” presents an economical strategy toward converting this waste gas to a value-added product such as formate which is a key intermediate toward formic acid, which is a high-energy density hydrogen source. Several applications of the “methanol economy”, championed by Chemistry Nobel laureate George Olah, has been highlighted as an alternative to compressed or adsorbed hydrogen since methanol has a higher energy density than hydrogen, and is renewable, readily transportable, and compatible with our existing infrastructure.5

A number of metal oxides and sulﬁdes have been previously reported as semiconductor photocatalysts for CO2 reduction. For sulﬁdes, ZnS and CdS are the two most widely studied sulﬁdes. ZnS (Eg = 3.87 eV)6 has been utilized because of its strongly reductive conduction band (Ecb = −1.85 V versus NHE), which lies above the lowest unoccupied molecular orbital (LUMO) energy value of CO2 at −0.61 eV. Due to the efficient electron transfer from Ecb of ZnS to the LUMO of CO2, ZnS has been reported to successfully reduce CO2 to formate.7 Henglein8 and Yoneyama9 were among the first to study micron-sized ZnS particles, and to study the size effect and other factors that influence photocatalysis rate. Both hypothesized that smaller ZnS particles will be more efficient due to their larger band gap and higher surface area. The hypothesis regarding improved production yields correlating to higher surface area was later confirmed by our group, where the photocatalytic differences of sphalerite and wurtzite were compared via size, crystal structure, surface area, and band gap of ZnS for the reduction of bicarbonate. This work resulted in the highest quantum yield of 3.2%.10 Other studies involving ZnS to produce formic acid, formaldehyde, and methanol resulted in quantum yields of 0.02%,11 0.24%,12 and 32%,13 though incredibly high, the last quantum efficiency was determined at 280 nm, a high-intensity monochromatic wavelength that can significantly boost product yield. Kuwabata and colleagues applied microcrystalline ZnS in the presence of methanol dehydrogenase to reduce CO2 directly to methanol.14

Though there are only a handful of sulﬁdes studied, oxides have been more widely used in CO2 reduction, and these include TiO2, WO3, SrTiO3, BaTiO3, K2Ti6O16, InTaO4, Zn2GeO4, and Ga2O3. TiO2 (P-25, Evonik) is the most widely known and used semiconductor for CO2 reduction, and its efficiency can be increased by a positive hole scavenger such as isopropl alcohol.15–17 Previous studies and reviews discussing CO2 reduction with Cu2O or copper-oxide-derived species18,19

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include photocatalytic, electrochemical, and photo-electrochemical methods. Recently, Lee et al. reported a Ag–Cu2O electrode to reduce CO2 to ethanol. The addition of Ag into Cu2O suppressed hydrogen evolution, thus enhancing the product selectivity toward ethanol. Given these successful catalytic applications involving copper(I) oxide and because the conduction band (CB) of Cu2O is comparable in energy to the LUMO of bicarbonate, this Earth-abundant, nontoxic material appears appropriate for bicarbonate reduction.

In seeking to optimize copper(I) oxide as a photocatalyst, we also considered that the noble metal nanoparticles of Ag, Au, and Pt have been implemented as plasmonic sensitizers for semiconductors in plasmonic photocatalysis. Plasmonic photocatalysis makes use of the fact that metallic nanoparticles exhibit strong features in their extinction spectra in the visible range. This phenomenon, termed surface plasmon resonance (SPR), occurs when the incident radiation of a particular region of wavelengths resonates with the collective oscillations of the electrons in the nanoparticle. This excitation results in energetic electrons on the surface of the nanoparticle that drive photocatalytic transformations. When nanoparticles are in contact with a semiconductor, a Schottky barrier can form that leads to prolonged charge separation, and can also boost the generation of electrons and holes in semiconductors. Recently, Ag-loaded TiO2 nanocomposites demonstrated better photocatalytic conversion of CO2 to methanol than pure titanium oxide due to the synergistic effect between UV light excitation and SPR. Therefore, another strategy to enhance semiconductor photocatalysis involves construction of a hybrid particle consisting of metal and semiconductor (Ag/Cu2O). The advantages of using a hybrid system include maximized metal–semiconductor interaction, as opposed to semiconductors doped with nanoparticles. We hypothesized that such features would facilitate plasmon-induced electron transfer from metal to Cu2O semiconductor.

This study will present the first of its kind by using Cu2O as a semiconductor photocatalyst for formate production. The parameters of our investigation include copper(I) oxide size and the effects of silver nanoparticles toward catalytic efficiency. We will also demonstrate how the Ag/Cu2O hybrid particle acts to significantly increase formate production through plasmon-induced electron transfer from noble metal to the semiconductor. Perhaps overlooked as an emerging and novel semiconductor interaction, as opposed to semiconductors doped with nanoparticles. We hypothesized that such features would facilitate plasmon-induced electron transfer from metal to Cu2O semiconductor.

**EXPERIMENTAL SECTION**

**Materials.** Polyn vinylpyrrolidone (PVP; MW 40,000), micron and nano copper(I) oxide (Cu2O), sodium citrate (TSC), silver nitrate (AgNO3), sodium borohydride (NaBH4), ascorbic acid, 2-propanol, glycerol, sodium bicarbonate (NaHCO3), copper(II) chloride (CuCl2), sodium dodecyl sulfate (SDS), sodium hydroxide (NaOH), hydroxyamine hydrochloride (NH2OH·HCl) were all purchased from Sigma-Aldrich and used without further purification.

**Synthesis of PVP-Coated Silver Nanoparticles.** Preparation of the Silver Seeds. A 20 mL volume of aqueous solution containing AgNO3 (2.9 × 10−4 M) and TSC (2.5 × 10−4 M) was prepared and cooled in an ice-bath. To this mixture was added an aqueous solution of NaBH4 (0.1 M, 0.6 mL) dropwise with vigorous stirring. The solution became bright yellow immediately. The seeds were then stored in the dark and aged for 2 h prior to use.

**Synthesis of Ag/Cu2O Nanocomposites.** Synthesis of AgNP. The Ag NPs with an average size of 5 nm were prepared by sodium citrate reducing AgNO3 aqueous solution. A 150 mL portion of 1 mM AgNO3 was heated to the boiling point, and then 10 mL of 1 wt % sodium citrate was quickly added. The mixture was then kept at boiling for 0.5 h, yielding the gray yellow Ag NPs.

**Synthesis of Ag/Cu2O Nanocomposites.** A 1.0 mL portion of as-prepared 1 mM AgNP solution was added into 5 mL of Cu2+ solution containing 0.1 M CuCl2 and 0.0338 M sodium dodecyl sulfate (SDS) with shaking. Next, 0.15 mL of 1 M NaOH and 0.25 mL of 0.2 M NH2OH·HCl were added with shaking for 10 s. The mixture was aged for 2 h and centrifuged to separate the nanocomposites. Varying amounts of AgNP (0.2–3 mL) were added to test for differences in catalytic efficiency.

**Semiconductor Characterization.** UV–Vis Spectroscopy. UV–vis spectra of the particles were obtained using a Varian Cary 50 Scan UV–vis spectrophotometer, with wavelength ranging from 800 to 200 nm. Cu2O samples were dispersed in ethanol, while the AgNP and Ag/Cu2O samples were dispersed in Milli-Q water.

**Size, Crystal Structure, and Surface Area Determination.** Dynamic light scattering (DLS) was performed using a Microtrac Zetasizer particle size analyzer to obtain the hydrodynamic radius of the particles. Crystal structure information was obtained using an X’Pert Pro X-ray diffraction (XRD) instrument. BET surface area measurements were performed on a Micromeritics ASAP 2020 surface area and porosity analyzer, and scanning electron microscopy (SEM) was performed using a Hitachi S-4100 scanning electron microscope. Transmission electron microscopy (TEM) and high-Resolution transmission electron microscopy (HR-TEM) were performed using a JEOL-2010 TEM and JEOL-2010F field emission electron microscope.

**Diffuse Reflectance Spectroscopy (DRS).** Diffuse reflectance spectra were obtained under a Thermo Scientific Evolution 260 Bio UV–vis spectrophotometer with an integrated sphere in order to obtain its absorbance spectra. Dynamic light scattering (DLS) was performed using a Microtrac Zetasizer particle size analyzer to obtain the hydrodynamic radius of the particles. Crystal structure information was obtained using an X’Pert Pro X-ray diffraction (XRD) instrument. BET surface area measurements were performed on a Micromeritics ASAP 2020 surface area and porosity analyzer, and scanning electron microscopy (SEM) was performed using a Hitachi S-4100 scanning electron microscope. Transmission electron microscopy (TEM) and high-Resolution transmission electron microscopy (HR-TEM) were performed using a JEOL-2010 TEM and JEOL-2010F field emission electron microscope.

**Ion Chromatography.** Ion chromatography was performed on a Dionex AS50 IC with a Dionex IonPac AS6 Ion exclusion column and a Thermo Scientific Dionex AMMS-ICE 300 suppressor. The IC instrument is equipped with a Dionex CD2S conductivity detector. Reagents used were 0.4 mM heptafluorobutyric acid as the eluent at a...
flow rate of 1.2 mL/min and 5 mM tetrabutylammonium hydroxide as the regenerant.

Photoexperiments. The reaction matrix was as follows: a buffer made of 0.3 M NaHCO₃, 2 M hole scavenger (2-propanol or glycerol), and Milli-Q water. Cu₂O catalysts were added at an optimized concentration of 1 mg/mL. For catalysts in the solution phase (nanoparticulate Cu₂O and Ag/Cu₂O), 0.5 mL of the catalyst was added. To find the optimal catalyst concentration and optimal rate, the catalyst was first varied from 0.01 to 3 mg/mL as described by Kisch. The optimal catalyst concentration was found to be 1 mg/mL as the rate plateaued with increasing catalyst concentration as seen in the Supporting Information, Figure S1. The matrix was transferred in a quartz tube, sealed, and placed under an ABET Technologies SunLite solar simulator with AM 1.5 (or AM 0) filter for 8 h. The light source was a 1000 W xenon arc lamp with an output of 1000 W/m², the equivalent of 1 sun. A light source providing select wavelengths of 365, 400, 525, and 660 nm was custom-built using a Mouner Electronics LED with fwhm of 15 nm, with the same output intensity as the solar simulator. Aliquots were collected at 2 h increments, and formate concentration was quantified by ion chromatography.

Apparent Quantum Efficiency (AQE). Using an Ophir Photometrics Nova II laser energy meter, the energy output of the solar simulator was measured. This power measurement was converted to moles of photons per second. This photon flux was then used to calculate the apparent quantum efficiency (AQE) of the catalyst using eq 1 and 2.

\[
\text{AQE} = \frac{\text{actual mol formate}}{\text{theoretical mol formate}} = \frac{1 \text{ mol e}^-}{2 \text{ mol photons}} \cdot \frac{2 \text{ mol e}^-}{1 \text{ mol e}^-} = \frac{1 \text{ mol formate}}{100} = \% \text{AQE}
\]

RESULTS AND DISCUSSION

XRD spectroscopy (Supporting Information, Figure S2) shows that both micron and nano Cu₂O have a cubic structure (Table 3). DLS confirms that the particles are fairly monodispersed (Supporting Information, Figure S3), and SEM indicates that the Cu₂O particles are aggregated (Figure 1, top) because nanoparticles are more likely to aggregate in the solution phase. BET surface area measurements (Table 3) showed that nanoparticulates have more surface area than micron-sized particles, as expected for nanoparticles because of their high surface atom to volume ratio. TEM of nanoparticulate Cu₂O (Figure 1) shows that the average size of nano Cu₂O is 30 nm. HR-TEM (Figure 2) further confirms the morphology and composition of the catalysts, showing that in Ag/Cu₂O there are 5 nm silver nanoparticles embedded in Cu₂O. The composition of Ag/Cu₂O was further confirmed by energy dispersive X-ray spectroscopy (EDS; Supporting Information, Figure S4).

UV-vis spectra of Cu₂O taken in the aqueous phase (Supporting Information, Figure S5) do not show any strong absorption. Absorbance spectra are much more prominent when using DRS (Figure 3). Silver nanoparticles (AgNPs) display a plasmon band at 425 nm which is also apparent in Ag/Cu₂O (Figure 4). To obtain the band gap data, DRS was used, and corresponding absorbance plot and subsequent conversion to Kubelka–Munk plot are shown in Figure 3. From DRS, it was determined that the band gap energies for Cu₂O micron size and Cu₂O nanosize were 1.9 and 2.3 eV, respectively. Cyclic voltammetry was used to place band gap values on an absolute NHE scale. It was found that nanosized Cu₂O has a slightly larger band gap than micron-sized Cu₂O due to quantum confinement (Table 1; Supporting Information, Figure S6). Since a Ag/AgCl reference electrode was used, eq 3 is used to convert to normal hydrogen electrode (NHE) values.

\[
E(\text{NHE}) = E(\text{Ag/AgCl}) + 0.197 \text{ V}
\]

With the particles fully characterized, photoexperiments were conducted to test for formate production. Based on previous studies, it was found that formate production is pH-dependent. At a pH of 8.5, HCO₃⁻ is the predominant species present, and is therefore expected to be the species undergoing reduction.

Table 2 and Table S1 (Supporting Information) show the boost in formate production under air mass coefficient 0 (AM 0) as opposed to air mass coefficient 1.5 (AM 1.5) solar simulation irradiation. Metal oxide semiconductors are primarily photoexcited by UV radiation, but the AM 1.5 filter blocks much of the higher-frequency UV radiation between 300 and 400 nm. Under both AM 1.5 and AM 0 conditions, nanoparticulate Cu₂O yielded a higher formate production than micron-sized Cu₂O (Figure 8; Supporting Information, Figure S8), with respective productivities of 0.76 and 0.37 mmol formate/(gcat h) in IPA, and 1.99 and 0.93 mmol formate/(gcat h) in glycerol (Figure 8, Table 2; Supporting Information, Table S1). To the best of our knowledge, these are the highest production levels reported for CO₂ conversion to formate using Cu₂O as a photocatalyst. With (Cu₂O)* as the photoexcited semiconductor, the proposed redox mechanism of Cu₂O semiconductor photocatalysis is shown in Figure 5a and Scheme 1. After photoexcitation and the generation of electrons and holes, subsequent reduction of HCO₃⁻ to HCO₂⁻ and finally to HCO₂⁻ takes place. The other half reaction takes place when 2-propanol scavenges photogenerated holes and undergoes oxidation to acetone. For confirmation of the reaction mechanism in Figure 5, acetone was detected and quantified by a gas chromatograph (GC). A linear increase of acetone was observed between 0 and 8 h (Supporting Information, Figure S7).

Studies have shown that plasmon-excit excit nanoparticles can create hot electrons with energies between the vacuum level and the work function of the metal. These hot electrons arise from plasmon decay and, in this transient state, can transfer charge into other species to catalyze chemical reactions. With AgNPs we observe formate production comparable to that of a semiconductor (Figure 9), with respective productivities of...
0.053 mmol formate/(g_{cat} h) in IPA and 0.75 mmol formate/(g_{cat} h) in glycerol (Table 2). Ag/Cu_{2}O showed the highest productivity in glycerol of 2.76 (AM 1.5) and 3.41 (AM 0) mmol formate/(g_{cat} h) (Figure 10, Table 2; Supporting Information, Table S1). In IPA, this nanocomposite catalyst had much lower productivity of 0.066 (AM 1.5) and 0.091 (AM 0) mmol formate/(g_{cat} h) (Table 2; Supporting Information, Table S1).

AgNPs have been shown to enhance photocatalysis because these nanoparticles scavenge *OH radicals. The scavenging of *OH radicals is expected to increase formate production because *OH radicals are detrimental to formate production. *OH radicals can react with both bicarbonate and formate, hence the deleterious effect on overall formate production (eqs 4–6). Since previous experiments have used plasmonic metallic nanoparticles as a sensitizer for TiO\textsubscript{2} and have successfully demonstrated electron and resonant energy transfer from nanoparticles to semiconductor, we attempted to apply AgNPs as a sensitizer for Cu_{2}O.

In a control experiment, silver nanoparticles added to Cu_{2}O (i.e., Ag/Cu_{2}O) showed no enhancement in formate production (Supporting Information, Figure S9), with productivity of 0.37 (AM 1.5) and 0.93 (AM 0) mmol formate/(g_{cat} h) when added to micron Cu_{2}O and 0.66 (AM 1.5) and 2.78 (AM 0) mmol formate/(g_{cat} h) when added to nanoparticulate Cu_{2}O in glycerol. This observation is expected due to the incompatibility of the VB and CB energies of Cu_{2}O and the Fermi level of silver nanoparticles. Since the valence band and conduction band energies for Cu_{2}O do not allow for the generation of *OH

| Table 1. Valence Band, Conduction Band, and Band Gap Values\(^a\) for Cu_{2}O |
|---------------------------------|-----------------|-----------------|
|                                | Cu_{2}O (eV)    | literature\(^1\)  |
|                                |                 | experimental     |
| VB                              | 1.3             | 1.067 (nano)     |
|                                 | 1.3             | 1.01 (micron)    |
| CB                              | −0.7            | −0.89 (nano)     |
|                                 | −0.7            | −0.87 (micron)   |
| band gap                        | 2.0             | 1.96 (nano)      |
|                                 | 2.0             | 1.88 (micron)    |

\(^a\) Experimental values are obtained from cyclic voltammetry.

| Table 2. Productivity [mmol Formate/(g_{cat} h)] of Cu_{2}O, AgNP, and Ag/Cu_{2}O in IPA and Glycerol\(^a\) |
|-------------------------------------------------|-----------------|-----------------|
| particle population                             | productivity in IPA AM 1.5 | productivity in glycerol AM 1.5 |
| Cu_{2}O micron                                  | 0.067 ± 0.007   | 0.47 ± 0.008    |
| Cu_{2}O nano                                    | 0.37 ± 0.02     | 0.93 ± 0.04     |
| Ag/Cu_{2}O                                      | 0.66 ± 0.0007   | 2.78 ± 0.1      |
| Ag                                              | 0.053 ± 0.0002  | 0.75 ± 0.03     |

\(^a\) All reported values are from triplicate measurements.
radicals, adding AgNP to Cu2O does not increase formate production.

Interestingly, the nanocomposite Ag/Cu2O system shows significant enhancement of formate production. Within a nanocomposite system, there are different mechanisms in which the plasmonic metal can enhance the performance of the semiconductor. The photoexcited plasmons in the metal can decay radiatively re-emitting photons and concentrate electromagnetic field at the molecular scale. Surface plasmons at the metal can also relax nonradiatively creating a transient population of nonequilibrium (hot) charge carriers or by releasing thermal energy. The hot electrons can be transferred to the conduction band of the semiconductor. The localization of electromagnetic fields close to the metal–semiconductor interface and the enhanced supply of electrons to semiconductor conduction band can improve the overall photocatalytic efficiency of the system. Figure 5b illustrates both direct electron transfer and plasmon energy transfer from metal (represented by silver spheres) to semiconductor (represented by red rectangles); both are responsible for the enhanced performance of the semiconductor through LSPR-induced charge separation in the semiconductor.

Control experiments were performed under dark conditions for 8 h for both Cu2O and Ag/Cu2O nanocomposites (Supporting Information, Figure S10). In both cases the production of formate was negligible confirming the importance of their photocatalytic effect. For confirmation of the plasmonic effect of silver, wavelength-dependent experiments were performed at four select wavelengths of 365, 400, 525, and 660 nm for micron Cu2O, nano Cu2O, and Ag/Cu2O composites. The wavelength of 365 nm is the absorption maximum for Cu2O, but the plasmonic effect of silver is not very pronounced at this wavelength. As expected, at this wavelength an increase in formate production is observed with
both micron and nano Cu$_2$O, and minimal enhancement with Ag/Cu$_2$O is observed (Figure 6, left). Near the plasmonic peak of Ag nanoparticles at 400 nm, a significant enhancement in the production of formate is observed with Ag/Cu$_2$O composites (Figure 6, right), which is attributed to the plasmonic effect of Ag nanoparticles. At the 400 nm wavelength the absorbance of Cu$_2$O is negligible; the observed improvement cannot be solely explained by increased light absorption on Cu$_2$O due to plasmon-induced resonance energy transfer from Ag to Cu$_2$O. Plasmonic heating cannot be the main reason for the observed enhancement effect either, since CO$_2$ to formate requires the energy of 0.61 V, which is higher than the thermal energy generated by plasmonic heating under solar irradiation. The Fermi level of Ag is $-4.2$ eV, with an interband transition of 3.8 eV ($\sim 330$ nm). The energy gap between the conduction band of Cu$_2$O and the Fermi level of Ag is 1.1 eV. Any light absorbed above 330 nm is expected to promote electrons from the Fermi level of Ag nanoparticles to the conduction band of Cu$_2$O. Hence, the plasmon-induced hot electron transfer from silver nanoparticles to Cu$_2$O seems to play the most important role here. These effects are further confirmed by the action spectra (Figure 7), which study the wavelength dependency of AQE. The AQE is highest at the absorption maximum of Cu$_2$O and plasmonic peak of silver nanoparticles.

Bicarbonate reduction requires a sacrificial agent to fill photogenerated holes, thus reducing charge recombination. As a control experiment, the photocatalytic reaction with Ag was carried out without a hole scavenger, and very low amounts of formate were produced (Supporting Information, Figure S11). Based on earlier work including our own, 2-propanol and glycerol were chosen because they both contain secondary donor hydrides. Glycerol possesses one secondary and two primary alcohol groups available for oxidation, whereas 2-propanol only has one secondary alcohol group. Among the positive hole scavengers compared in this study, 2-propanol is derived from petroleum sources. Glycerol, on the other hand, is...
of interest because it derives from plants, is low-cost, environmentally benign, and relatively abundant. It has been shown in this work, as well as in that of Leonard et al., that glycerol is a more efficient hole scavenger than IPA. This feature derives from the number of available primary hydrides and secondary hydroxyl carbons available in glycerol.\textsuperscript{10} Coupled with these more recent results, use of glycerol is expected to be a far superior hole scavenger than IPA.

Formate production can be quantified in terms of apparent quantum efficiency (AQE), calculated by eqs 1 and 2. Table 3 and Table S1 (Supporting Information) summarize the different forms of Cu\textsubscript{2}O tested. Possessing greater surface area, nanoparticulate Cu\textsubscript{2}O yielded a higher AQE than micron-sized Cu\textsubscript{2}O. Under AM 1.5 conditions, micron-sized Cu\textsubscript{2}O generated an AQE of 0.14\% in IPA and 0.95\% in glycerol; and 0.15\% and 3.65\% in IPA and glycerol under AM 0 conditions. Nanoparticulate Cu\textsubscript{2}O yielded an AQE of 0.74\% in IPA and 1.87\% in glycerol under AM 1.5 conditions; and 1.52\% and 3.99\% under AM 0 conditions. AgNP alone was able to produce an AQE of 0.11\% in IPA and 1.51\% in glycerol. Ag/Cu\textsubscript{2}O in glycerol showed the highest AQE of 5.53\% (AM 1.5) and 6.82\% (AM 0).

**CONCLUSION**

In summary, a new set of nontoxic and Earth-abundant semiconductor materials have shown photochemical efficacy in the conversion of bicarbonate to formate. Micron and nanoparticulate Cu\textsubscript{2}O, nanocomposite Ag/Cu\textsubscript{2}O, and silver nanoparticles added to Cu\textsubscript{2}O were characterized and examined for their photochemical properties. Because of its higher surface area and smaller band gap, as expected, nanoparticulate Cu\textsubscript{2}O proved to be a more efficient photocatalyst than micron-sized Cu\textsubscript{2}O. Although silver NPs have been shown to scavenge *OH radicals, a species deleterious to the bicarbonate/formate conversion, we observed no enhancement in formate production upon the inclusion of AgNP with Cu\textsubscript{2}O. These findings confirm the favorable VB/CB energy levels of Cu\textsubscript{2}O, with regard to their suitability for electron transfer to bicarbonate, but no other reactant or solvent species. Significantly enhanced formate production is apparent with Ag/Cu\textsubscript{2}O due to plasmon-induced electron transfer from Ag to Cu\textsubscript{2}O. The recent developments in nanocomposite architectures such as Ag/Cu\textsubscript{2}O have found an important application here via plasmonic properties of metallic nanoparticles that harness resonant energy to enhance semiconductor efficiency. This study reports the highest quantum efficiency values compared to previous CO\textsubscript{2} or bicarbonate to formate conversions. Future studies include the use of other semiconductors, with similar nanocomposite systems, and the use of ultrafast spectroscopy to further elucidate charge carrier dynamics and the reaction mechanism of plasmon-enhanced photocatalysis.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.7b03244.

Rate vs photocatalyst concentration, XRD spectra, DLS size distribution, EDS results, UV–vis spectra, CV curve, acetone production vs time, formate production vs time, and productivity and AQE values (PDF)

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**Table 3. Summary of Semiconductor Characterization**

<table>
<thead>
<tr>
<th>particle population</th>
<th>crystal type</th>
<th>diameter (nm)</th>
<th>surface area (m²/g)</th>
<th>AQE in IPA (%) AM 1.5</th>
<th>AQE in glycerol (%) AM 1.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu\textsubscript{2}O micron</td>
<td>cubic</td>
<td>&lt;5000</td>
<td>1.27 ± 0.6</td>
<td>0.14 ± 0.01</td>
<td>0.95 ± 0.02</td>
</tr>
<tr>
<td>Cu\textsubscript{2}O nano</td>
<td>cubic</td>
<td>&lt;350</td>
<td>6.48 ± 1.1</td>
<td>0.74 ± 0.03</td>
<td>1.87 ± 0.08</td>
</tr>
<tr>
<td>Ag/Cu\textsubscript{2}O</td>
<td>—</td>
<td>all ~5000 ± 15</td>
<td>—</td>
<td>0.13 ± 0.002</td>
<td>5.53 ± 0.2</td>
</tr>
<tr>
<td>AgNP</td>
<td>—</td>
<td>12.89 ± 1.5</td>
<td>—</td>
<td>0.106 ± 0.0005</td>
<td>1.51 ± 0.07</td>
</tr>
</tbody>
</table>

“*All reported values are from triplicate measurements. \(b\), measurement was not performed (Ag/Cu\textsubscript{2}O and AgNP samples were in aqueous solution, and thus the crystal structure and surface area could not be determined by the instrument)."
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REFERENCES


Since CO₂ can be recovered from a variety of industrial sources and exists in its neutral hydrated form as bicarbonate, the current unabated production of this greenhouse gas makes it a potential feedstock for regeneration via solar fuels. As a potential negative emission technology (NET), the chemical conversion of carbon dioxide and/or bicarbonate to C-1 products such as formate or methanol underscores a second advantage, mainly economic as this greenhouse gas becomes value-added in comparison to being sequestered. As a chemical feedstock, formate or depending on pH, methanoic acid functions in a number of industrial, medical and agricultural applications ranging from preservative, food additive, and antibacterial agent in livestock feed. Methanoic acid can be converted to methanol as a high-octane number end product. This concept of the “methanol economy”, has been highlighted as an alternative to hydrogen fuel because methanol is regenerative via CO₂ and more readily transportable.

In Hanqing Pan’s research, new nanostructures along with their respective chemical components comprise much of her research endeavors. The first aspect involves new fabrication techniques resulting in nanoparticles, nanosheets, nanotubes, nanorods, nanobelts, and nanoflowers with the express intent to afford high specific surface areas. Another parameter, the chemical component, involves optimization of the semiconductor band gap with improvements in metal oxides, metal sulfides, multicomponent oxides, or doping with metal ions, anions or trace amounts noble metals. An additional challenge for consideration of any photocatalyst concerns the matter of utilizing non-toxic and earth-abundant materials toward solar fuel development. Her outstanding scientific research paper in ACS Sustainable Chemistry and Engineering; Impact Factor 5.95 (2015) presents a number of sustainable chemistry findings regarding reduction/oxidation chemistry combined with nanotechnology and one-sun input. Although appearing in print in February 2018, the article was published on the web as an ACS/ASAP in Dec 07, 2017. If this timeline is unacceptable to the committee, an added and earlier paper by Ms. Pan appearing in November 2017 is attached as well.

Hanqing Pan: Publications (10); h-index = 3, Citations (16)