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Carbon Nanoparticles as Visible-Light Photocatalysts for Efficient CO₂ Conversion and BeyondLi Cao,[†] Sushant Sahu,[†] Parambath Anilkumar,[†] Christopher E. Bunker,^{*,†} Juan Xu,[†] K. A. Shiral Fernando,[§] Ping Wang,[†] Elena A. Gulians,[§] Kenneth N. Tackett, II,[†] and Ya-Ping Sun^{*,†}[†]Department of Chemistry and Laboratory for Emerging Materials and Technology, Clemson University, Clemson, South Carolina 29634, United States[‡]Propulsion Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio 45433, United States[§]Sensors Technology Office, University of Dayton Research Institute, Dayton, Ohio 45469, United States

ABSTRACT: Increasing atmospheric CO₂ levels have generated much concern, driving the ongoing carbon sequestration effort. A compelling CO₂ sequestration option is its photocatalytic conversion to hydrocarbons, for which the use of solar irradiation represents an ultimate solution. Here we report a new strategy of using surface-functionalized small carbon nanoparticles to harvest visible photons for subsequent charge separation on the particle surface in order to drive the efficient photocatalytic process. The aqueous solubility of the catalysts enables photoreduction under more desirable homogeneous reaction conditions. Beyond CO₂ conversion, the nanoscale carbon-based photocatalysts are also useful for the photogeneration of H₂ from water under similar conditions.

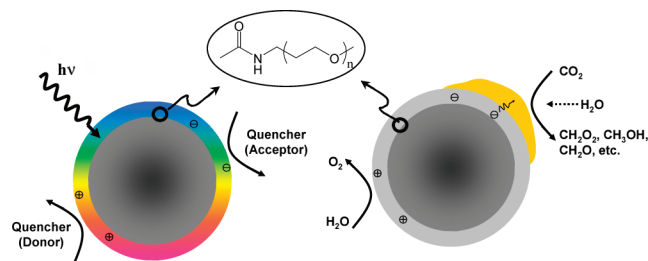


Figure 1. Aqueous soluble PEG-functionalized carbon nanoparticles before (left, fluorescent) and after (right, photocatalytic for CO₂ reduction in aqueous solution) coating with metal.

The significant rise in atmospheric CO₂ levels due to the combustion of hydrocarbon fuels has generated much concern. Among various CO₂ sequestration options, a compelling approach is photocatalytic conversion to recycle CO₂ back to hydrocarbon fuels, for which the use of solar irradiation may represent an ultimate solution. However, there are major challenges in finding potent photocatalysts for such a task.^{1–3} Nanoscale wide-band-gap semiconductors such as titanium dioxide (TiO₂) and cadmium sulfide (CdS) were originally used and have since been quite popular in CO₂ photoreduction and related photocatalytic reactions,^{1–4} but their limitations in terms of the requirement for UV excitation and generally low conversion efficiencies have also become evident.^{2,3} Various improvement strategies, including the use of TiO₂ nanotubes and dye sensitization to extend the absorption of the photocatalysts into the visible region, have been developed.^{5,6} Here we report a new approach involving the use of surface-functionalized small carbon nanoparticles to harvest visible photons for subsequent charge separation on the particle surface in order to drive the photocatalytic process. The aqueous solubility of the catalysts enables photoreduction under essentially homogeneous reaction conditions. Beyond CO₂ conversion, the nanoscale carbon-based photocatalysts are also useful to the photogeneration of H₂ from water under similar experimental conditions.

It is now known that small carbon nanoparticles can be covalently functionalized to give them strong absorption and

emission in the visible spectral region that may also extend into the near-IR.^{7,8} The fluorescence emissions are attributed to radiative combinations of electrons and holes confined on the carbon nanoparticle surface (Figure 1),^{7,9,10} phenomenologically resembling those found in nanoscale semiconductors. In this study, the carbon particle surface was also doped with gold or platinum to concentrate the photogenerated electrons to enable more efficient CO₂ reduction.

Carbon powders containing sub-10 nm nanoparticles were refluxed in aqueous nitric acid (2.6 M) for 12 h, dialyzed in membrane tubing (pore size equivalent to $M_w \sim 1000$) against fresh water, and then centrifuged to retain the supernatant as an aqueous suspension of small carbon nanoparticles bearing surface carboxylic acid moieties.⁷ The particles recovered from the suspension were functionalized with oligomeric poly(ethylene glycol) diamine (PEG_{1500N}; Figure 1) in a classical amidation reaction that involved the acylation of the particle-surface carboxylic acids in neat thionyl chloride as an intermediate step.^{7,10} The functionalized carbon nanoparticles were readily dissolved in water to form stable aqueous solutions of various concentrations, with solution colors ranging from yellow at low concentrations to black at very high concentrations. A UV–vis absorption spectrum of the solution used in subsequent photolysis for gold coating is shown in Figure 2.

The functionalized particles were coated with gold or platinum by simple solution-phase photolysis, as these metals are known in the literature for their photocatalytically enhanced reduction reactions.^{11–13} The photoexcited carbon particles acted as electron donors to reduce the gold or platinum salt

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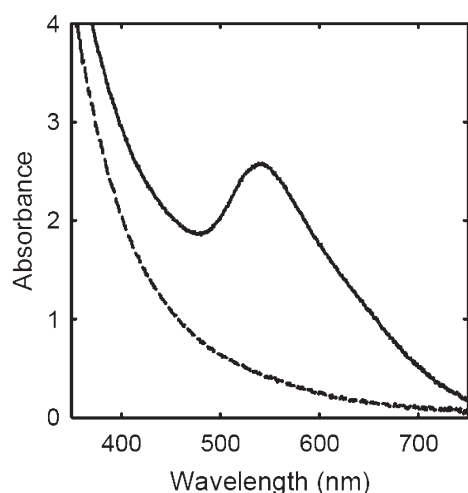


Figure 2. Absorption spectra of the functionalized carbon nanoparticles in aqueous solution before (dashed line) and after (solid line) coating with gold.

(HAuCl_4 or H_2PtCl_6 , respectively) to the corresponding metal on the particle surface, similar to what was observed in the photoreduction of aqueous silver cation into silver metal.⁹ The photolysis conditions were such that only the functionalized particles were allowed to get photons (405–720 nm for gold and 425–720 nm for platinum, to exclude not only the metal salts but also any residual impurities in the salt samples from photo-excitation), thus eliminating the possibility of any “free” (i.e., not associated with carbon nanoparticles) gold or platinum nanoparticles. For gold, the progressive photoreductive coating of the carbon particles was monitored by the emergence and rapid increase of the surface plasmon absorption of the coated nanoscale gold (Figure 2, corresponding to a gold-to-core carbon molar ratio of $\sim 1:38$). No gold formation was found in repeated control experiments in the absence of the functionalized carbon nanoparticles, as expected.

Transmission electron microscopy (TEM) imaging, which took advantage of the high electron density and crystalline fringes of the coated metal, confirmed the gold coating (Figure 3), as did results from energy-dispersive X-ray (EDX) analyses. The average diameter of the gold-coated particles was ~ 9 nm according to statistical analysis of multiple TEM images, and the size distribution standard deviation was ~ 3 nm.

For platinum coating of the functionalized carbon nanoparticles, the convenient monitoring of a plasmon absorption was not possible (such an absorption was absent in the concerned wavelength region; see Figure 4), so the coating was again confirmed by TEM imaging (Figure 4) and the associated EDX results.

The functionalized carbon nanoparticles with gold or platinum coating were used as photocatalysts for the reduction of CO_2 . In a typical experiment, an aqueous solution of the gold-coated particles (corresponding to the UV–vis absorption spectrum in Figure 1) was added to an optical cell in the photolysis setup, after which the solution was purged with CO_2 gas toward saturation at ambient temperature. The resulting solution in the optical cell was photoirradiated with visible light (425–720 nm) for 5 h. As known in the literature, the photoreduction of CO_2 generally yields formic acid as a significant product.^{1–3} In this study, the formic acid formed as a volatile

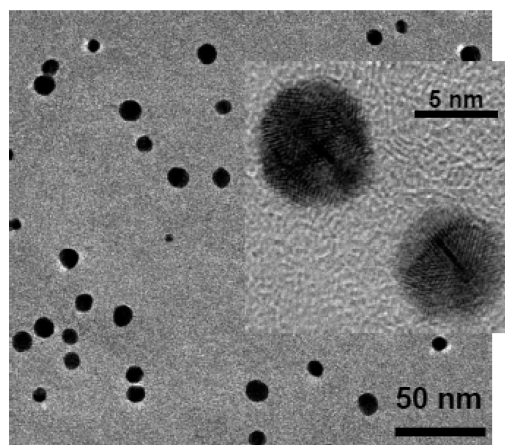


Figure 3. TEM images (inset: high-resolution) of the functionalized carbon nanoparticles with gold coating.

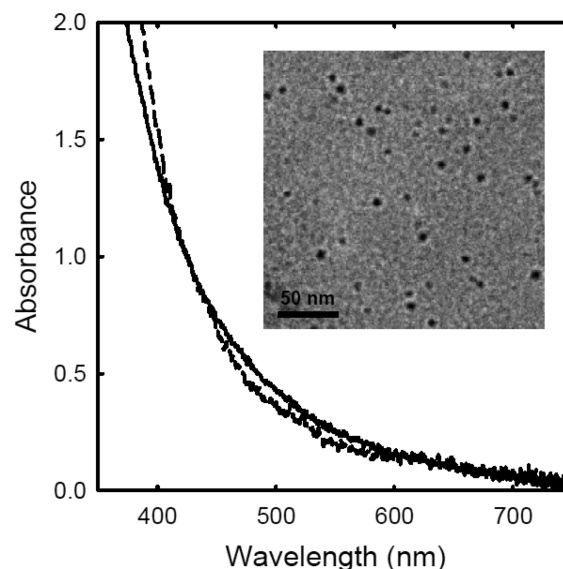


Figure 4. Absorption spectra of the functionalized carbon nanoparticles in aqueous solution before (solid line) and after (dashed line) platinum coating. Inset: TEM images of the coated particles.

photoproduct in the aqueous solution post-photoirradiation was harvested by simple distillation, from which a new aqueous solution containing formic acid was collected and then basified to pH 12 with aqueous NaOH to convert the acid to sodium formate. Upon the evaporation of water, the salt was analyzed by ^1H and ^{13}C NMR spectroscopy to confirm and quantify the amount of formate using sodium acetate as an internal standard (Figure 5).

The formation of formic acid from CO_2 photoconversion was confirmed by ^{13}C -labeling experiments using aqueous $\text{NaH}^{13}\text{CO}_3$ (at the saturated CO_2 -equivalent concentration) as the feed under neutral and acidic pH conditions (mimicking aqueous CO_2). The ^{13}C -labeled formic acid thus obtained from the same photocatalytic reduction was readily detected by ^{13}C NMR spectroscopy with only a few hundred scans (vs $>20\,000$ scans required for regular formic acid from aqueous CO_2 or NaHCO_3).

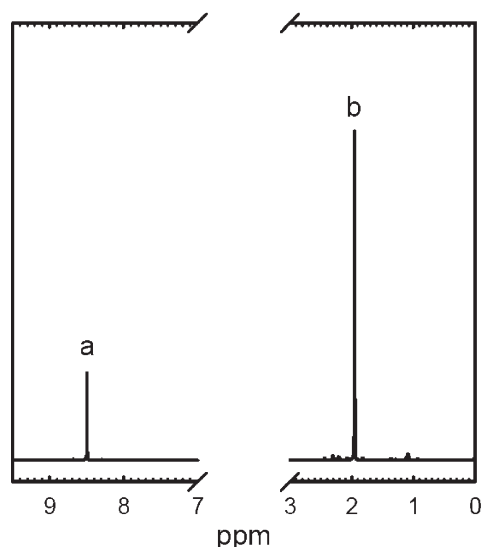


Figure 5. ^1H NMR spectra of (a) HCOONa harvested from the CO_2 photocatalytic reduction and (b) CH_3COONa as an internal standard in D_2O .

The quantification of the photoproduct was used to estimate quantum yields for photocatalytic reactions of CO_2 under the specific experimental conditions.⁶ For the reduction to formic acid only, the estimated quantum yield was $\sim 0.3\%$, which was likely lower than the overall quantum yield for the CO_2 conversion (because of conversion to other photoproducts such as methanol;¹³ see Figure 1). Nevertheless, even for the production of formic acid alone, the observed quantum yield is already at the higher end of the available literature values for reactions with a variety of photocatalysts under many different conditions.³ As a more direct comparison, the use of suspended TiO_2 nanoparticles (Degussa P25) as photocatalysts with UV light irradiation (through a 350 nm cutoff filter) in the same photolysis setup resulted in quantum yields that were an order of magnitude lower (also for formic acid only).

For the platinum-coated photocatalysts in the CO_2 conversion reaction under otherwise identical experimental conditions, the results were generally similar to those with the gold-coated ones described above, though more quantitative comparisons, including those for effects of varying amounts of metal coating, are still being pursued.

Mechanistically, photoexcitation of the surface-passivated small carbon nanoparticles likely results in charge separation to form surface-confined electrons and holes (Figure 1),^{9,10} on which significant experimental evidence has already become available. For example, the bright fluorescence emissions, which can be attributed to radiative recombinations on the particle surface, could be quenched by both electron donors and acceptors in an equally efficient fashion.⁹ The emissions were also essentially diminished by the gold or platinum coating, as the coated metal was designed to soak up the surface-confined electrons, disrupting the radiative recombinations. Therefore, the functionalized carbon nanoparticles apparently served the function of harvesting visible photons to drive the photoreduction process, with the particle surface defects facilitating the charge separation by trapping the separated electrons and holes, phenomenologically similar to what occurs for metal-coated semiconductor nanoparticles (e.g., platinum-coated CdS or TiO_2).^{11–13} In addition to

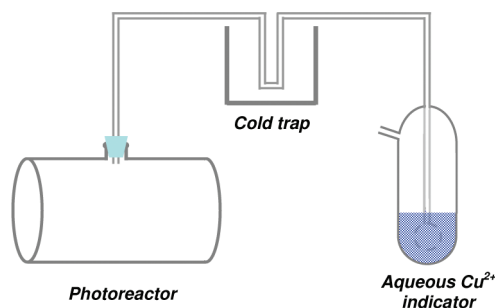


Figure 6. Schematic diagram of the setup used for the detection of photocatalytically generated H_2 .

the obviously important advantage of strong visible absorption, other distinctive features of the nanoscale carbon-based photocatalysts include their aqueous solubility for the photoconversion under homogeneous reaction conditions and the confinement of the photoinduced charge separation to the particle surface, thus facilitating more efficient electron harvesting by the coated gold or platinum as the cocatalyst in the CO_2 conversion.

Beyond CO_2 photoreduction, the same functionalized carbon nanoparticles with gold or platinum coating could be used as photocatalysts for H_2 generation from water.^{4,14,15} Experimentally, the same aqueous solution of the gold- or platinum-coated nanoparticles in the absence of CO_2 was irradiated under the same conditions as those described above. The top of the sealed optical cell for the photoirradiation was connected to a H_2 indicator containing an aqueous CuSO_4 solution (bright blue color) (Figure 6). H_2 generation in the photocatalytic reaction of water was detected by a color change and precipitation in the H_2 indicator (due to reduction of Cu^{2+} to Cu^+ and Cu by H_2 at 30°C). A more quantitative determination of the amount of photogenerated H_2 from water and the associated reaction quantum yields is in progress. According to literature results, there are overlaps in terms of the configuration in photocatalysts for CO_2 reduction and water splitting.^{2–4,12,14} In fact, one of the mechanistic explanations for CO_2 reduction in aqueous solution is based on a two-step process, namely, initial photocatalytic generation of atomic H followed by reduction of CO_2 .¹²

In summary, surface-modified small carbon nanoparticles represent a highly promising new platform for visible-light photocatalysis of CO_2 conversion and beyond. The photocatalysts are stable in the photoreduction reactions. The photoconversion efficiencies likely benefit from the solubility of the catalysts (which allows for homogeneous reaction conditions in solution), surface confinement of the photoinduced charge separation and trapping, and the straightforward doping of metal cocatalysts. There is obviously more room for improvement in the further development of these carbon-based photocatalysts.

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