

Visible light production of hydrogen by ablated graphene: water splitting or carbon gasification?

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Supporting Information Placeholder

ABSTRACT: Reduced graphene oxide modified by pulsed laser ablation causes water splitting under visible light illumination (532 nm). When the light source is a pulsed laser, water splitting is accompanied by carbon gasification (CO formation), however conventional (LED) light sources produce water splitting exclusively.

Water splitting under solar, simulated solar, or simply visible light is the subject of a rich stream of contributions to the current literature.¹⁻³ These publications generally fall into one of two groups, those that employ a sacrificial donor and those that do not.⁴ Both generally produce H₂ with a wide range of efficiencies, but when a sacrificial donor is used the formation of O₂ is no longer possible and the reaction is not strictly considered ‘water splitting’.⁵ The sacrificial donor is commonly an easily oxidized molecule, such as an amine or alcohol. For example, in the case of methanol those products are H₂ and CH₂O. In 2013, Schneider and Bahnemann have noted that “measuring H₂ gas formation in such a sacrificial system no longer generates any mechanistic information”.⁵ Nevertheless, to understand how the formation of hydrogen by trapping electrons can be extremely favored in the presence of sacrificial electron donors that scavenge the hole with different efficiencies, gave basic mechanism insights, helping us to design new catalytic systems.

When it comes to systems where a specific donor has not been intentionally added, the current best published result was reported by Garcia and coworkers⁶ using oriented gold nanoplates on graphene, as a visible light photocatalyst and yielding 1.2 mol H₂ per gram of composite per h (the preferred units for these reports). Many other modified carbon materials report water splitting, based on the detection of both H₂ and O₂, with variable degrees of success obtaining the correct H₂/O₂ stoichiometry.^{1,7}

When carbon materials are used for water splitting, one question that is frequently not addressed is whether carbon is effectively acting as a sacrificial reducing agent. A few years ago, Matsumoto and co-workers⁸ suggested that graphene oxide nanosheets can generate H₂ and CO₂ upon photoelectrochemical conditions, using UV-light excitation and, although their electrochemical analysis was very accurate, none of the gases were characterized. A well-established reaction in the petroleum industry, referred as a carbon gasification⁹ and producing *syn-gas* (a mixture of H₂, CO and some CO₂), can be simplistically expressed as in reaction 1 and potentially competes with water splitting, reaction 2.



Reaction 1 is endothermic and requires heat, but this is normally generated by nanomaterials under photoexcitation, where most of the radiant energy is transformed to heat, reaching high local temperatures. For example, in the case of gold nanoparticles photoexcited at 532 nm, temperatures as high as 500°C have been reported.¹⁰

Although there are some recent reports studying the mechanism of graphene gasification based on metal oxide-doped graphene,¹¹⁻¹² it is difficult to find examples for pristine GO decomposition. Ermakov and co-workers¹³ have found that blue laser (10 mW and 500 nm spot) was able to burn up graphene layer-by-layer, and a nice computational study shows that the formation of CO would be favorable upon incomplete combustion. Garcia et al.¹⁴ have demonstrated that H₂ and CO can be formed upon 532 nm laser irradiation of a GO suspension in 10% methanol aqueous solution. Although they relate the CO formation to structural changes on the GO, the role of the methanol in the process of CO formation remains unclear. However, to the best of our knowledge, no experimental detection of *syn gas* involving undoped carbon materials has been reported. We here out-

line two important discoveries that would help, not only the applications in H_2 but also on the CO production: 1) we show that visible light laser ablation of reduced graphene oxide (rGO) can generate *syn gas*; 2) the ablated rGO can lead to water splitting under 532 nm visible light illumination, following laser ablation treatment.

Two sources of rGO, namely rGO(1) and rGO(2), were used getting similar results. In a typical experiment a rGO aqueous suspension (0.8 mg/mL) was treated by a laser drop ablation setup using a 532 nm Nd-YAG laser (see SI).¹⁵ Different numbers of shots per drop (1-20 shots for drops of 7-10 μ L) were used to analyze the effect of the light on the rGO sheets. The solutions were collected in vials after irradiation and analyzed. Figure 1 shows the change in color of the samples collected after irradiation and the corresponding UV-Vis spectra. Increasing the number of shots per drop leads to a variation of the rGO suspension color from dark black (initial suspension) to clear grey (after 20 shots/drop); similar to changes observed in other carbon materials upon pulsed laser exposure.¹⁶⁻¹⁷ Note that at 532 nm only a small fraction of the laser pulse is absorbed by the suspension. We noticed that all the energy/power values reported refer to energy delivered, only a fraction being absorbed. Videos of the irradiated drops show the formation of gas bubbles that contain predominantly hydrogen gas (*vide infra*).

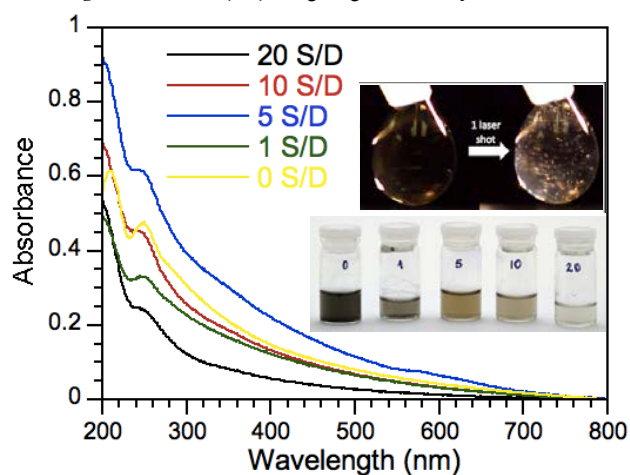


Figure 1. UV-Vis spectra of rGO(1) solutions after various exposures. Insets: *top*: drop suspension before (left) and after (right) several laser shots (the Teflon tube above the drop is 1.6 mm in diameter); *bottom*: Graphene solutions before (left) and after laser irradiation (532 nm laser, 45 mJ/pulse).

TEM pictures of the samples before and after ablation were collected, showing a dramatic change in morphology of the rGO flakes (Figure 2 and SI). Before laser irradiation, the electron microscopy reveals the classical graphene-like sheet conformation, no particular shape is observed, other than possible overlapping of the planes. After laser treatment, spherical shape graphene features can be detected together with the classical sheets. Increasing the number of the laser shots enhance the appearance of sphere-like morphologies. The two sources of rGO show similar behavior (Figure S3): just after one shot, the sample appears to have a spherical shape. By increasing the number of shots per drop, we observed a progressive decrease in the sizes of the spherical structures. A high surface resolution can be obtained by Second Electron imaging (SEI), which confirms the conformational change of the ablated rGO(1) flakes (Figure S4).

Raman spectra were recorded before irradiation and after different numbers of shots/drop rGO, showing a slight variation in the ratio between the D and G bands.¹⁸ Indeed, before ablation the intensity of the two bands are comparable ($G/D \sim 1.08$), while after laser treatment the intensity of the G band increases, compared to the D band ($G/D \sim 1.13-1.25$), indicating morphological changes in the structure, as seen in TEM images (see SI). As the D band is associated to defects and the presence of $C sp^3$, the laser irradiation seems to contribute to a “healing” process of the rGO, possibly related to CO formation from rGO defects (*vide infra*).

The laser ablation can be also performed by using 1 mm thin cuvette, where 0.3 mL of the rGO solution was inserted and irradiated for 30 min, using the same 532 nm laser and maintaining the same laser power (45 mJ per pulse). After irradiation, the solution presented some bubbles inside the solvent and as expected the color was much clearer than the original solution. SEM pictures revealed that in this case, as in the case of the laser drop system, spherical features were obtained. For comparison, the same rGO suspension was irradiated for 2h using a quad of four 532 nm LEDs; no change in the absorbance nor in the rGO morphology was observed by UV-Vis and SEM analysis, respectively.

The results obtained clearly indicate that the changes in rGO structure are directly correlated to the use of lasers and it does not occur if the light at the same wavelength is generated from LEDs.

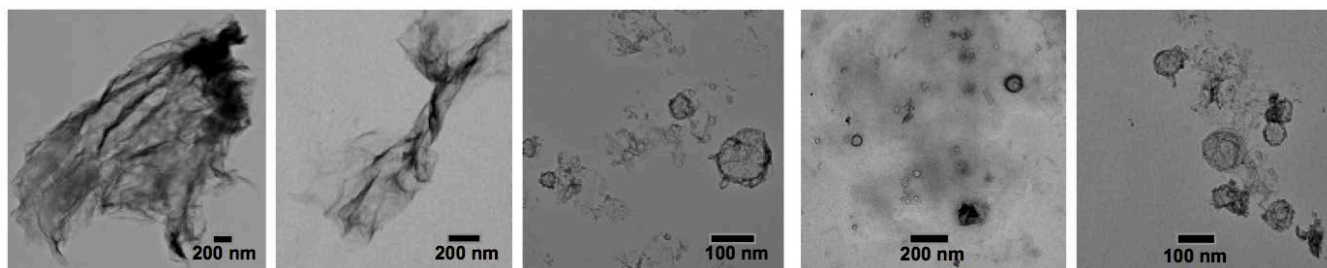


Figure 2. TEM pictures of rGO(1) solutions before (left) and after 1, 5, 10, 20 shots per drop (left to right).

The formation of bubbles inside the solvent can be readily observed by recording videos of the drop during the laser irradiation (inset Figure 1), or simply after irradiation of the sample in a sealed cuvette, Figure 3. In order to identify what gas was being formed, an aliquot of the reaction headspace was taken after the irradiation and injected into a gas chromatograph equipped with a packed column and a universal thermal conductivity detector (TCD), utilizing Ar as gas carrier. Analysis at the GC-TCD revealed that hydrogen gas was produced in the sample following 90 min of rGO irradiation. Thus, approximately 63 mmol H₂ per gram of rGO are produced per h upon pulsed laser exposure. We note that under these conditions it is difficult to quantify the formation of O₂, although a slight increase in the O₂/N₂ ratios was consistent with the production of oxygen from water splitting (eq. 2) as further discussed in the results from partial pressure experiments (*vide infra*).

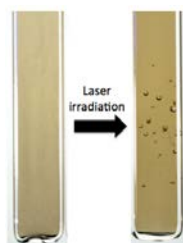
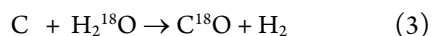


Figure 3: Picture of the graphene solution inside the 1 mm thick cuvette before and after 30 min of LED irradiation. The formation of bubbles inside the solution was observed in both LED and laser experiments.

Two potential events could be responsible for the generation of H₂: the splitting of H₂O or the degradation of the graphene structure, equations 1 and 2. In the case of reaction 2 the emission of H₂ is accompanied by the production of O₂. On the other hand, the evolution to form *syn-gas* may result from graphene degradation (reaction 1), in such a way that H₂ is accompanied with the formation of CO or CO₂. In this case, the carbon in rGO behaves as a sacrificial donor, the same way that amines or alcohols do in many reports on water splitting. Such ‘assisted’ water splitting does not conform to the basic chemistry and stoichiometry of reaction 2.

Several attempts have been made to determine which of the two reactions was responsible for the H₂ formation, the most successful being the use of ¹⁸O isotopically labeled water. The idea behind this experiment was to monitor the release of ¹⁸O₂ or CO/CO₂ containing ¹⁸O, as in reactions 3-5.



For this purpose three solutions of rGO in H₂¹⁸O were prepared in a long neck cuvette and purged with Ar for 45 min. The samples were subjected to different treatments,

namely rGO modification and water splitting using different light sources. The samples headspaces were then analyzed using a customized quadrupole mass spectrometer. First, a sample was irradiated with a 532 nm laser for 1 h (2 in Figure 4); second, a different sample was irradiated for 1 h with 532 nm LEDs (3 in Figure 4); and finally, the third sample was prepared and irradiated for 30 min with 532 nm laser. After the laser irradiation, the third sample was purged for another 45 min with Ar to make sure that any possible gas detected after the second step was not already produced during the laser irradiation. Finally, the LED irradiation was performed for 1 h (4 in Figure 4). Figure 4 summarizes the results found after mass analysis of the 3 samples headspace. The first sample showed the presence of ¹⁸O₂ and some labeled C¹⁸O, but no labeled CO¹⁸O. Particularly, 532 nm laser irradiation generated a mixture of gases containing 22:78 C¹⁸O:¹⁸O₂.

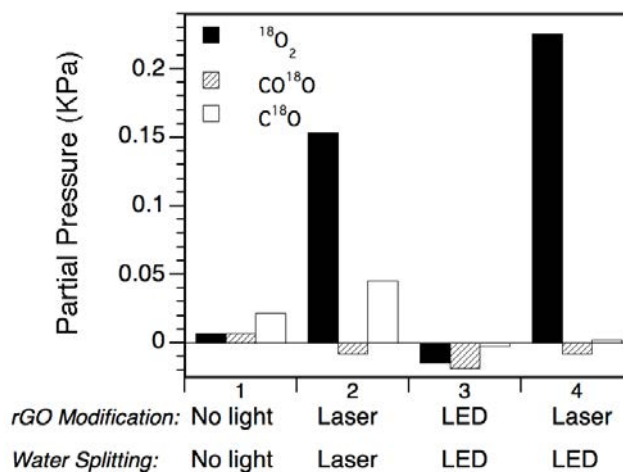


Figure 4: Comparison between ¹⁸O₂ (black), C¹⁸O (line) and CO¹⁸O (white) partial pressures of an air sample (1) and the reaction head sample of an argon purged rGO(2) dispersion in H₂¹⁸O obtained after different treatments: 532 nm laser irradiation (2), after 532 nm LED irradiation (3), and 532 nm laser irradiation followed by 532 nm LED irradiation. The values are obtained comparing the areas of traces referred to each gas detected to the area of the trace relative to water vapor and multiplying the value obtained for the water partial pressure (3.2 KPa) at 25°C. Negative values are within experimental error of typically ±0.02.

The key observation in Figure 4 is that laser irradiation leads to concurrent water splitting and *syn-gas* formation; thus reactions 3 and 5 occur under laser irradiation, with reaction 5 being favored; no indication for reaction 4 was observed. We note that while H₂ was detected in the Laser/Laser and Laser/LED experiments in Figure 4, quantification was very challenging in these experiments, but such quantification was already achieved in the work with H₂O (no ¹⁸O). While LED exposure of rGO did not yield any products, LED irradiation of laser pre-treated rGO (45 mJ

pulses for 45 minutes as indicated above) led to significant water splitting with no *syn-gas* generation. This could account for some reports on H₂ generation induction period;¹⁴ the restructure rGO is likely responsible for the H₂ formation and therefore some time is needed for the restructuring of the rGO flakes before H₂ is formed. Quite clearly under these conditions rGO is not a sacrificial reductant and water splitting is the only process observed. These results prove that our structural modification of the graphene sheets to spheres (see Figure 2 and SI), using laser irradiation, is promising as a method to produce catalysts for the splitting of water. This morphological modification is convenient since it occurs with visible light, in water at room temperature and can be readily controlled by the energy delivered (number of laser shots per drop).

Conclusions

There are numerous reports of solar-induced water splitting in the literature. Much has been learned from what is best described as ‘assisted’ water splitting, in which a sacrificial donor or reductant is employed; such systems produce hydrogen, but are not strictly water splitting, as they do not obey the chemistry or stoichiometry of reaction 2.⁴⁻⁷ While heavily criticized in a recent ‘Commentary’, it is clear that such approach was useful as a learning tool as science progressed towards true water splitting. Today’s leading catalysts^{1, 19} are in many instances carbon-based and while they have hydrogen production as a common characteristic, they usually do not test for carbon gasification (i.e., generation of CO or CO₂) and those that have tested for oxygen generation have frequently faced challenges reconciling the observed H₂/O₂ stoichiometry. To the extent that our observations can be generalized, our results show that carbon gasification may be a concern under conditions of pulsed laser irradiation, but that conventional sources (visible LED light in our case) do not cause carbon gasification and that therefore rGO (and probably other graphene-like materials) do not behave as sacrificial reductants in these systems. Indeed, a reassuring observation given the growth in carbon-based water splitting photocatalysts.

ASSOCIATED CONTENT

Supporting Information. Details of methods and materials, spectroscopic data, SEM images and LED emission spectrum. The Supporting Information is available free of charge on the ACS Publications website.

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