

Oriented Cu_2O nanoplatelets supported on few layers graphene as efficient visible light photocatalyst for overall water splitting

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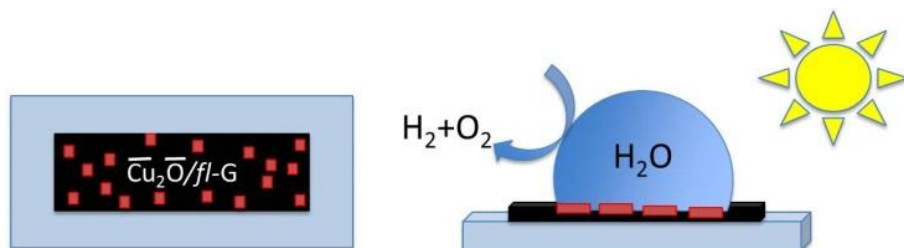
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There is much current interest in the photocatalytic generation of hydrogen from H_2O using sunlight. Although the number of photocatalysts and reports are quite large, there is still room for much improvement, particularly for developing materials able to perform the overall water splitting into H_2 and O_2 in the corresponding stoichiometric amounts in the absence of any sacrificial agent.^[1, 2] Cu_2O has been reported as visible-light semiconductor for overall water splitting,^[3, 4] although it suffers from a low stability and it undergoes photocorrosion as consequence of the accumulation of an excess of positive charges during the operation of the semiconductor that leads to an irreversible oxidation of Cu^+ to Cu^{2+} . There is, therefore, much interest in increasing the stability of Cu_2O under photocatalytic conditions. In this regard, it has been reported that graphene in a few weight percent increases the efficiency of a semiconductor by favoring charge separation accepting electrons from the semiconductor valence band. It is also clear that the preparation procedure of the semiconductor-graphene should play a crucial role by increasing the interfacial contact between the semiconductor and graphene.^[5]

In this contribution, a new preparation procedure of Cu_2O /graphene hybrid material as nanometric films based on the pyrolysis at 900°C under inert atmosphere of chitosan films containing adsorbed a Cu^{2+} salt result in phase separation of copper and graphene and a strong grafting between the two components. This Cu_2O -graphene interaction is manifested by: i) a relatively small average Cu_2O particle size, ii) a morphology of Cu_2O as nanoplatelets wetting the graphene surface, iii) a shifting in the binding energies of Cu 2p orbitals measured by XPS, and iv) facet orientation exhibiting predominantly the 220 facet as revealed by XRD of thicker films.

This Cu_2O -graphene films exhibit a remarkable photocatalytic activity for the overall water splitting in the absence of any sacrificial electron donor agent, as illustrated in Scheme 1.



Scheme 1. Pictorial representation of a frontal view of films of oriented Cu_2O nanoplatelets (small orange squares) supported on few-layers G (black large rectangle) deposited on a quartz substrate (light blue rectangle) and the process of photocatalytic H_2 and O_2 evolution

from pure, liquid H₂O without stirring using the $\overline{\text{Cu}_2\text{O}}/\text{fl-G}$ film on quartz (presented in a lateral view) illuminated with UV-Vis light.

Figure 1 shows the temporal profile of H₂ and O₂ evolution upon simulated sunlight irradiation. The photoresponse spectrum indicates that the photocatalytic overall H₂O splitting occurs also under visible light (<420 nm) irradiation, although with slower efficiency than under UV excitation. Importantly prolonged irradiation (days) indicates that the photocatalytic activity of Cu₂O does not decay and characterization by SEM shows that the Cu₂O have changed morphology due to the photocatalytic stress, but has maintained the average particle size.

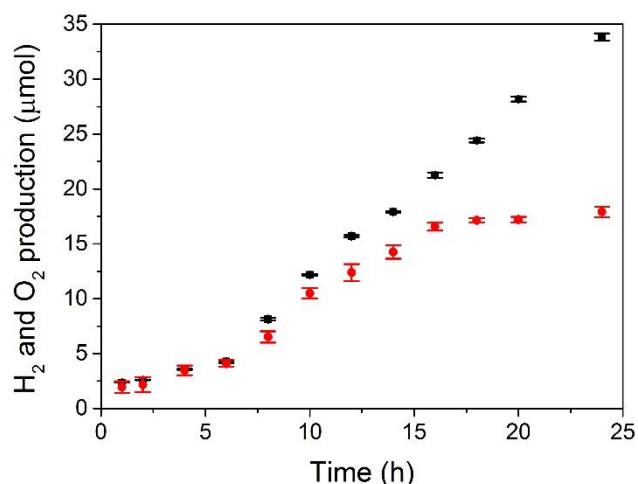


Figure 1. Raw H₂ (black squares) and O₂ (red dots) production from $\overline{\text{Cu}_2\text{O}}/\text{fl-G}$ film (12.5 cm²) as function of time upon UV-Vis light irradiation from a 300 W Xe lamp. The productivity data correspond to 19.5 mmol/g_{Cu+G} · h.

Considering the minute mass of Cu₂O present on the films, the specific H₂ production rate is remarkable (see Figure 1 caption) and much higher than that reported for Cu₂O and also than that measured by us for commercial Cu₂O. In addition, these controls undergo photocorrosion as expected for this photocatalyst. These comparison show the unique properties of the Cu₂O-graphene hybrid derived from the preparation procedure.

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