

## Graphdiyne a new 2D material for photocatalytic H<sub>2</sub> generation.

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Graphdiyne (GDY) is an emerging two-dimensional (2D) carbon material composed of sp<sup>2</sup> and sp-hybridized carbon atoms, resulting in a regular and porous structure. GDY, which is rich in  $\pi$ -conjugated electrons, exhibits remarkable properties such as low weight, high mechanical strength, excellent conductivity, and tunable electronic and optical characteristics.<sup>[1]</sup> These outstanding features make GDY an appealing material for various applications, including electronic devices, catalysis and photocatalysis, purification membranes, and energy harvesting.<sup>[2]</sup> Notably, GDY's intrinsic band gap (0.7–1.4 eV) plays a critical role in charge carrier mobility, making it particularly attractive for solar-to-chemical energy conversion.<sup>[3]</sup> Despite its exceptional properties, GDY faces challenges such as low processability and a narrow energy band arrangement, which limit its practical application in photocatalysis. To address these limitations, GDY needs structural modification, such as molecular functionalization, hybridization with metals and metal oxides, and heteroatom doping.<sup>[4]</sup>

In this presentation, we will show how the electronic properties of GDY can be adjusted to reach high solar-to-hydrogen conversion efficiency. We employed different strategies, such as the substitution of the acetylene group by hydrogen, which allows not only an increase in the electronic bandgap of GDY but also reaches optimal charge carrier separation once coupled to an adequate semiconductor. In addition, another approach aims at oxidizing GDY to generate oxygen defects, followed by size reduction to form quantum dots (QDs). The structural properties of GDY, both before and after modification, were characterized using techniques such as high-resolution transmission electron microscopy (HRTEM), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). The experimental and theoretical results demonstrated that introducing oxygen defects or H-substitution induces significant changes in the electronic and optical properties of GDY. The engineered materials exhibited exceptional photosensitization when combined with commercial TiO<sub>2</sub>-P25 for photocatalytic hydrogen generation. Notably, a hybrid material containing 1 wt% defect-rich GDY-QDs achieved a hydrogen evolution rate of 1322  $\mu\text{mol g}^{-1} \text{h}^{-1}$ , five times higher than TiO<sub>2</sub>-P25 alone.

### References

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