Reduced graphene oxide and metal-organic frameworks composites for photocatalytic water oxidation

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Reduction of non-renewable resources as well as increase of green-house gas in atmosphere has become serious issue and prompted research in environmentally friendly fuel production with low carbon impact. Green reactions such as water splitting and CO_2 fixation, also called artificial photosynthesis, have already been recognized as promising solutions. However, the most difficult aspect of those two reactions, that is the water oxidation reaction (WOR), is still challenging as it requires a high oxidative potential and 4 holes to occur.

α-Fe_2O_3 is a well-known photocatalyst for WOR due to its good band gap and valence band position, whose properties motivated us to apply Fe-based metal-organic frameworks (MOFs) with similar properties such as MIL-101 (Matériaux de l'Institut Lavoisier) for WOR. Thanks to its highly ordered porous structure, we hypothesized that mass diffusion problems would be lowered as water could react directly onto the trimeric Fe^{3+} octahedral clusters composing the nodes of the molecular array. This arrangement would also lessen the high recombination rate of photogenerated carriers observed in α-Fe_2O_3 thanks to the reduced migration distance [1].

As expected, O_2 evolution reaction catalyzed by MIL-101 from silver nitrate aqueous solution was confirmed with efficiency higher than α-Fe_2O_3 under visible light irradiation. To assess the photocatalytic reactivity in detail, action spectrum measurements were carried out and proved that MIL-101 could oxidize water with a maximum accessible wavelength of 600 nm (**Figure 1**).

Other Fe-based MOFs with different structures were also inquired such as MIL-88 and MIL-126. Because they also showed activity under visible light irradiation, trimeric clusters and large pores were considered as important traits for application as WOR photocatalyst.

With the purpose of increasing the photocatalytic activity of MOFs, reduced Graphene Oxide (rGO) was introduced as a cocatalysts. Uses of rGO as electron mediator or cocatalyst has greatly increased recently thanks to its attractive properties in terms of electron mobility which facilitate separation of carriers. Composites of MOFs and rGO were synthesized by mixing graphene oxide and Fe^{3+} ions before solvothermal synthesis. The resultant composite, MIL-126/rGO, showed higher activity than pristine MOFs, up to 3 times more O_2 was asserted. This hybridization method is the most appropriate to create a good interface between both materials. For comparison, physical mixing was used as another pathway, and the composite (MIL-126 + rGO) led only to a moderate increase in the amount of O_2 analyzed showing lower interfacial contact (**Figure 2**).

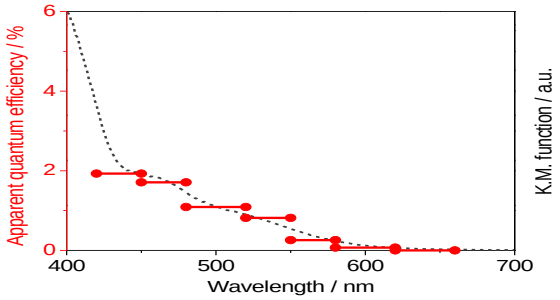

Figure 1 Action spectrum of MIL-101(Fe) for photocatalytic water oxidation in 0.1 M $AgNO_3$ aqueous solution.

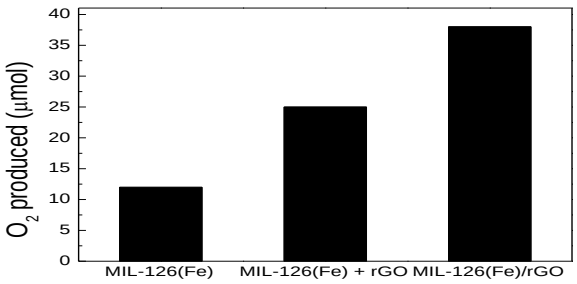

Figure 2 Photocatalytic water oxidation using MOFs composite in 0.05 M $AgNO_3$ aqueous solution.

REFERENCES

[1] M. Matsuoka *et al.*, Chem. Commun., 2016, 52, 5190