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Development of photoelectrochemical devices for photovoltaic and artificial photosynthesis

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Photovoltaic and artificial photosynthesis are a key research fields, because they will have a huge beneficial impact on a future post-carbon energy area, since sunlight is a gigantic green and renewable energy resource. Photoelectrochemical cell is an attractive solution to convert solar energy into either electricity (photovoltaic) or into storable chemical fuels or to produce chemicals for industry (artificial photosynthesis). It is composed of semiconductors functionalized with dyes and/or catalysts and immersed in an electrolyte containing a redox mediator or reactants. However, as far as the stability is concerned, the desorption of the dyes or of the dye-catalyst assembly from the metal oxide surface in electro- and photo-electrocatalytic systems still represents an important issue, which is far from being solved. Therefore, there is a real need for new approaches to improve the stability and lifetimes of photoelectrochemical systems. Towards this objective, we will report a crosslinking approach based on thermally induced Huisgen 1,3-dipolar cycloaddition click reaction between an electron deficient alkyne and azide (Figure).



Figure. Schematic representation of the copper free click chemistry methodology to crosslink the dyes over a mesoporous film (left) and of a CIGS based photocathode (right).

We will show that thermal copper free Huisgen reaction is a very simple and versatile reaction, which can be directly conducted on the dyes already anchored to functionalize nanocrystalline film of a TiO_2 or NiO. The crosslinked photoelectrodes kept their initial photoelectrochemical properties and, more interestingly, the desorption of the molecular components is heavily reduced. In the second part of the talk, we will present the development of photoelectrochemical photocathoded based on copper indium gallium (di)selenide (CIGS) semiconductor functionalize with a molecular catalyst to reduce CO_2 to CO, thereby providing a strategy for generating economically valuable products at both electrodes with sunlight with unprecedented efficiency.