

## Cu NPs-doped perovskite for the photo-catalytic valorization of CO<sub>2</sub>

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### Abstract

Carbon capture and usage (CCU) technologies are amongst the alternative strategies aiming at buffering the environmental threaten posed by the increasing amounts of CO<sub>2</sub> in the atmosphere [1]. Due to the energetic inputs, CO<sub>2</sub> sequestration and conversion is still costly and therefore not yet industrially feasible [2]. Photocatalysis involves the use of light as energy source to enable a redox reaction via electronic excitation and consequent formation of electron-hole couples and, in this context, it could enable CO<sub>2</sub> conversion without additional energy and pollution [3]. Strategies such as doping, scaffolding or introduction of a co-catalyst often aim at reducing recombination and improve both selectivity and photo-responsiveness, which often limit the overall catalytic performance [4]. Although TiO<sub>2</sub> is on the most studied photo-active materials, low selectivity and yields still prevent its industrial application [5]. Alkaline-earth-metal-based perovskites have recently emerged as versatile photocatalysts, owed to the possibility to tune both their structure and stoichiometry [6]. Moreover, the intrinsic basicity of alkaline-earth-metal-based perovskites could favour CO<sub>2</sub> adsorption, thereby potentially improving the overall selectivity towards C-based products. CuO was extensively studied for the CO<sub>2</sub> reduction, and also proved to improve selectivity towards C-based products [7]. In this work, BaTiO<sub>3</sub> perovskite and CuO NPs were synthesized via hydrothermal method. Both BaTiO<sub>3</sub> and CuO-BaTiO<sub>3</sub> were tested for the photo-conversion of CO<sub>2</sub> into valuable products and their yields compared to a TiO<sub>2</sub> benchmark. Ambient pressure near edge X-ray absorption fine structure (AP-NEXAFS) investigation in *operando* conditions aimed at monitoring the electronic structure modifications occurring at the sample surface by addition of CuO nanoparticles (NPs). In fact, the formation of redox couples in +2/+1 in Cu co-catalyst is thought to participate to CO<sub>2</sub>-direct reduction and therefore to increase the selectivity towards C-based products [7]. Moreover, the formation of heterojunctions in the CuO-TiO<sub>2</sub> and CuO-BaTiO<sub>3</sub> interfaces is proposed to play an important role in both a) the initial oxidation state of Cu and b) the photo-mediated inter-states charge exchange. As an in-depth understanding of the p-n junction behaviour in a CuO-BaTiO<sub>3</sub> system has not yet been achieved with regard to photocatalysis, the outcomes were related to the photocatalytic activity and to changes in the local chemical environment and oxidation state of the catalyst active sites, to obtain clues on the reaction mechanism.

Keywords: *photo-reduction, nanomaterials, perovskites, CO<sub>2</sub>, p-n junction*

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