Developing photocatalytic metal oxide films via Solution Precursor Plasma Spray for Environmental Use

The explosive growth of global energy consumption is leading to massive greenhouse gas emissions causing adverse climate changes, requiring effective and fast responses [1].
To reduce CO_2 emissions, there are several possible approaches:
- One consists in using alternative, carbon-free energy sources, such as solar, wind and tidal energies which are however intermittent and unequally distributed and for which storage is a critical issue.
- A second consists in applying carbon-capture and sequestration technologies; however, this would lead to high increases in energy costs and does not offer a solution to carbon emissions.
- A third, promising route, aims at converting CO_2 into fuels and possibly other economically valuable chemicals. This route involves novel technologies, namely photocatalytic and electrocatalytic conversion and the combined photo-electrocatalytic conversion, which enable the reduction of CO_2 into various useful products, such as carbon monoxide (CO), methane (CH_4), formic acid (CH_3COOH), etc. [2]. These routes can be generically designated as "catalytic conversion techniques". This route should of course be combined to the use of renewable energy input.

Generally speaking, the third approach, turning CO2 into fuel is more attractive, since it will not only decrease the concentration of CO2 in the atmosphere, but also will supply extra energy for consuming. The interest in the photochemical conversion of CO_2 has increased dramatically since the 1970s: various wide-band-gap semiconductors have enabled to produce a mixture of formaldehyde, formic acid, methanol and methane. The photochemical catalytic-CO_2-reduction route can be divided into several steps: (1) adsorption of CO_2 on the surface; (2) generation of photogenerated-electron/hole pairs by absorption of sufficient photon energy; (3) separation and migration of electron-hole pairs on the surface of the photocatalyst; and (4) reduction of CO_2 by a series of elementary chemical reactions [3].

Since photocatalysis is a surface/interface-reaction process, catalysts play an important role in the reactions involving electrons and protons, which yield the conversion into fuels. Many characteristic properties of photocatalysts are believed to influence CO_2 conversion efficiency. So far, the explored semiconductor materials for photocatalytic reduction of CO_2 mainly include metal oxides, metal sulfides, nitrides and phosphides [4]. The candidate metal oxides are able to be further classified into three main groups, including simple metal oxides (such as TiO_2 and ZnO), perovskite type double oxides (such as ABO_3 and $LiTaO_3$) and spinel type ones (such as AB_2O_3, $MnCo_2O_4$ and $MnCo_2O_4$) [5]. In addition, other metal oxide formulations obtained by doping or coupling different metals have been recognized as interesting photocatalysts in this field [5, 6]. Moreover, it should be noted that the CO_2 reduction process is highly endothermic. Therefore, in order to realize sustainable CO_2 conversion, renewable energy - such as solar, wind or wave– shall be used. As such, the previously explored composite metal-oxide semiconductors are deemed capable of absorbing photon energy from sight, an objective that requires narrower energy bandgaps than some common metal oxides (namely TiO_2 and ZnO). Especially, spinel-type materials exhibit narrower energy bandgaps, resulting in higher utilization efficiency of solar light. Furthermore, owing to their low cost, easy accessibility, high stability and efficiency, cobalt-based spinel-type materials, such as Co_3O_4, $ZnCo_2O_4$, and $MnCo_2O_4$ have begun to attract

attention in the photoconversion of CO_2 into fuels [7-9]. Therefore, our primary aim in this study was to focus on two material types: Co_3O_4, representing a relatively simple composition and $ZnCo_2O_4$ representing a classical, binary-spinel material.

In fact, these metal oxides have been intensively prepared by some conventional synthesis routes, such as hydrothermal, sol-gel, and precipitation. As mentioned above, such methods suffer from major deficiencies, such as their multi-steps nature, their long preparation as well as small-scale yields. Therefore, introducing a novel method to fabricate metal-oxide photocatalysts using a rapid, one-step route is of high interest.

Moreover, to the best of our knowledge, there is currently no attempt on performing the photoconversion of CO_2 based on Solution Precursor Plasma Spray (SPPS) process before, except the present cooperation project between LERMPS-UTBM and LEM-Université Paris Diderot. Our primary work (unpublished) about photoconversion of CO_2 starts from SPTS-deposited Co_3O_4 and $ZnCo_2O_4$ catalysts, exhibiting a high photocatalytic activity for turning CO_2 into CO with a yield as high as 13676 μmol g^{-1} h^{-1}. It should be noted that the photoconversion performance developed by our SPTS-deposited catalysts is matching recent state-of-the art publications in the field of heterogeneous catalysis.

All in all, in this thesis, the primary aim is developing more advanced metal oxide films via Solution Precursor Plasma Spray method with enhanced photoconversion performance. The attention might be paid on: 1) synthesizing novel suitable material systems with higher catalytic activities, 2) optimizing surface morphologies with higher surface area, exposing higher activity crystal facets and 3) introducing suitable oxygen vacancies into as-deposited films with narrower bandgap and better separation of holes/electrons. As a result, not only higher yield of reduction products would be required, but also expecting to obtain some more interesting products (i.e. CH_4, CH_3OH).

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