AAP China Scholarship Council - CSC 2024

PROJET DE RECHERCHE DOCTORALE (PRD)

Titre du PRD :

DIRECTION de THESE

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Ecole doctorale de rattachement : ED397 - Physique et Chimie des Matériaux

Nombre de doctorants actuellement encadrés : 1

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Ecole doctorale de rattachement Sorbonne Université : ED397 - Physique et Chimie des Matériaux ou autre :

Nombre de doctorants actuellement encadrés : 0

CO-TUTELLE INTERNATIONALE envisagée : ☐ OUI ☒ NON

DESCRIPTIF du PRD :

*Ce texte sera affiché en ligne à destination des candidates et candidats chinois : il ne doit pas excéder **2 pages** doit être rédigé en **ANGLAIS***

CuxMg1-xO nanoparticles: The interplay between size, composition and crystal structure

I. State of the art

The variety of stable oxidation states found with many transition metals results in corresponding oxides of diverse stoichiometries (for example: Cu2O, CuO; VO, V2O3, VO2 and V2O5 etc.). When reduced in size and dimensionality, these materials exhibit remarkable flexibility in their stoichiometry, atomic structure, and electronic characteristics. This often results in the formation of complex compounds that have no bulk equivalents. Moreover, the multitude of applications of these compounds (photovoltaics, catalysis, photocatalysis, energy storage and harvesting materials, etc.) is closely related to the ability of these metals to exist in multiple oxidation states. This becomes particularly important in surface reactions (adsorptions, interactions with light etc.) where the oxidation state can be changed. Finally, their potential mixed form (where cations of different size, electronegativity and reducibility are combined) provides means for the modification of the parent's oxide structural (mixing, alloying, janus, core-shell), electronic (band gap engineering) and reactivity characteristics. A strong dependence of the mixing characteristics on the size and dimensionality of the objects has been predicted [Goniakowski J. Phys. Chem. C 2019, 123, 7898 and Goniakowski J. Phys. Chem. C 2020, 124, 8186.] whereas the experimental proof is still missing.

II. Summary and objectives of the project

In that context, we propose to study the oxide in which Mg and Cu will be combined. MgO, a model system for surface chemistry studies, was largely studied in our working group, both experimentally and theoretically. This research has yielded a precise atomic description of its surface and manipulation of its optical properties or surface reactivity. Depending on synthesis, this oxide could be synthesized with controlled size and its surface could be decorated with other cations (Ca, Sr, Zn). Interestingly, when mixed with ZnO, an oxide that exhibits the wurtzite crystal structure which strongly differs of that of MgO (cubic), it was shown that on nanometer scale, ZnxMg1-xO adopts uniform, cubic crystal structure in which Mg2+ surface sites of low-coordination are replaced by Zn2+. In that way, MgO was shown to serve as the support on which thermodynamically instable cubic-ZnO structure can be stabilized under normal conditions. Taking this experience into account, in this Ph.D thesis, we offer an multilevel research project that covers: synthetic chemistry, fundamental surface science and photocatalysis. The main goal will be the synthesis of MM′O3 nano-structures (with M=Mg and M′ = Cu) and their characterization in terms of size, shape, surface composition, crystal structure. The aim will be to design CuxMg1-xO nanoparticles at the atomic level as a function of Mg/Cu ratio and to investigate the mixing ability. Indeed, FCC cubic MgO with ionic radius of Mg2+ =72 pm is expected to accommodate on its surface the Cu2+ with 73 pm. However, in this oxidation state, CuO exhibits the monoclinic crystal structure that strongly differs of FCC cubic. The eventual deviation of CuO "natural" crystal form (that is monoclinic) should strongly impact its optical and chemical surface activity. In addition to Mg/Cu ratio, these aspects will be studied as a function of the CuxMg1-xO nanoparticles size. The controlled synthesis of pure and mixed metal-oxide nanoparticles represent strong skills of our research group [Stankic et.al Angewandte Chemie - International Edition, 44 (2005), 4917; Stankic et al.Nano Letters, 5 (2005), 10, 1889, Haque et al., J. Phys. Chem. C (2021), 125, 46, 25841]. The same applies regarding the surface science techniques, especially the XPS which will play a central role in determining the oxidation state of Cu-cation once segregated on the MgO surface.

III. Working program

1) Synthesis.

The multiple synthesis routes will include: i) glove-box metal-combustion (GBMC), ii) metal-organic chemical vapor synthesis (MOCVS); a simultaneous co-evaporation of Mg- and Cu-precursors in reactor and iii) co-precipitation method in liquid form.

2) Characterization

The nano-CuxMg1-xO nanoparticles will be characterized via appropriate characterization techniques: TEM (for size, shape, chemical composition), XRD (for crystal structure), XPS (chemical composition and oxidation state), N2-physisiorption (specific surface area), DR-UV Vis (optical transitions, band gap).

3) Surface reactivity

There is a long tradition of our working group in studying the reactivity of metal-oxide surfaces towards probe molecules [Haque et al., Physical Chemistry Chemical Physics, 19 (2017), 10622, Haque et al., J. Phys. Chem. C, 122 (2018), 17738]. Among several objectives defined, the surface chemistry of CuxMg1-xO nanoparticles will be examined upon adsorbing probe molecules (H2, H2O) and followed via FTIR spectroscopy at liquid He temperature. This will allow for the identification of the specific surface element at which the adsorption occurs at CuxMg1-xO surface (to distinguish between Mg- or Cu-surface site) and to correlate its chemical reactivity to the coordination number of the identified active surface site.

Finally, an advantage will be taken by theoretical modeling that exist within our research team to support the experimental work of the proposed doctoral thesis.

AVIS de l'Ecole Doctorale :

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