2.3.12 Research Area “Design of Nanostructured Materials with High Surface Area for Photo-Electrochemical Water Splitting”

(H. Tüysüz)

Involved: G. Dodekatos, T. Grewe, X. Deng

Objective: In this ongoing and planned research project, a systematic and integrated approach encompassing materials synthesis, *in-situ* structural and electrochemical characterization, as well as catalytic and photocatalytic evaluation particularly for water splitting, which is one of the appealing reactions toward development of sustainable energy sources, is carried out. The main goals of this research are design and development of highly active nanocrystals and ordered mesoporous composite (binary and ternary) electro- and photo-catalysts with heterojunctions by using templating processing and post-treatment, in addition to establishment of design rules in terms of particle size, morphology, pore volume and size, surface area, crystallinity and composition for engineered ordered mesoporous photocatalyst materials, and the study of individual effects of material’s properties that are responsible for the effective charge separation and catalytic activity.

Results: Even two decades after the discovery of ordered mesoporous materials (OMMs), there is still a great interest in design of OMMs and improvement of synthetic approaches. This class of material supplies many fascinating properties that make them outstanding in a range of applications, in particularly in heterogeneous catalysis as support and catalyst.[32] Some of our efforts are devoted to better understanding of the nanocasting methodology and development of novel functional high surface area materials based on transition metal oxides[4,20,28]. A significant effect has been discovered for the replication of ordered mesoporous Cr_2O_3 and iron doped Co_3O_4. In contrast to the published studies, when cubic ordered mesoporous KIT-6 with 100°C aging temperature is used as a hard template, a cubic ordered mesoporous Cr_2O_3 replica with an uncoupled sub-framework structure that possesses an additional (110) reflection and reduced symmetry is obtained. Furthermore, it is noticed that the structure, morphology and symmetry of the Co_3O_4 replica can be tuned by iron doping during the nanocasting process. A small addition of iron during the impregnation forces Co_3O_4 to develop only in one pore system of the double gyroid silica template in some regions of the parent template, resulting in a replica with lower symmetry, higher pore volume and bi-modal pore size distribution. These findings demonstrate for the first time that the growth mechanism of metal oxides in the channels of the gyroid silica is not only related to the interconnectivity of the silica template, it also depends on the type and nature of the metal oxide precursor.

We aim to develop novel ordered mesoporous composite materials and examine them as photo and electro-catalyst for water splitting. We initialized our first electrochemical study on ordered mesoporous Co_3O_4.[85] A series of Co_3O_4 with different morphologies, symmetries, surface areas and particle sizes has been prepared by changing the textural parameters of the silica hard template via nanocasting. These materials were tested as electrocatalysts for water splitting. The highest catalytic activity was achieved in a more concentrated alkali solution with Co_3O_4 that has an open sub-framework structure and high surface area. Co_3O_4 with the highest surface area has much better activities than its bulk counterpart and slightly higher activity than material with nanoparticle morphology. The nanocast Co_3O_4 has excellent structural stability that is retained during the electrolysis of water. This material holds promise as a cheap anode for overall water splitting.[85]

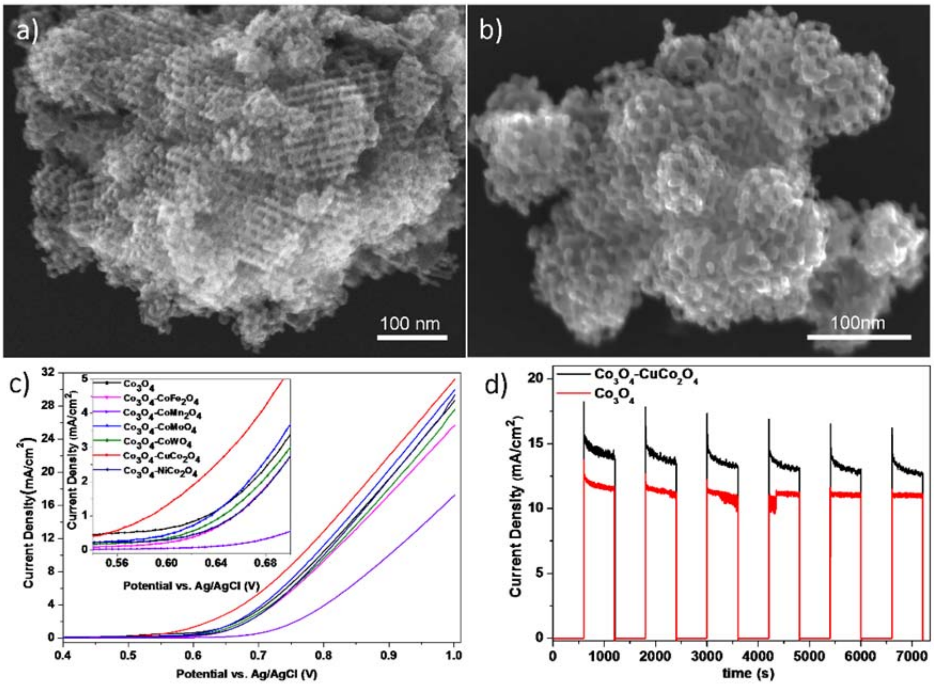

Figure 1. HR-SEM images of ordered mesoporous Co_3O_4 (a) and Co_3O_4-$CuCo_2O_4$ (b) that has been prepared via nanocasting by using silica as hard template. Oxygen evolution currents of as-made Co_3O_4, Co_3O_4-CoM_2O_4 (M= Fe, Mn), Co_3O_4-$CoMO_4$ (M = Mo, W) and Co_3O_4-MCo_2O_4 (M = Cu, Ni) composites dispersed on glassy carbon electrode in 0.1 M KOH electrolyte (c), the inset figure shows the current increment in a narrow voltage range (0.54 ~ 0.70 V vs. Ag/AgCl). Chronoamperometric measurement of Co_3O_4 and Co_3O_4-$CuCo_2O_4$ under a bias of 0.8 V vs. Ag/AgCl for 6000 sec (d) indicating stability of the materials.

Our further study was on enhancement of the electrocatalytic activates of nanocast Co_3O_4. The second generation electrocatalysts are based on binary mixed ordered mesoporous oxides. The surface of nanocast Co_3O_4 could be successfully modified by a solid-solid reaction with various transition metal salts [24]. The novel method that we develop provides a blueprint for the production of composite materials based on ordered porous oxides that could have interesting physical and chemical properties (Figure 1a-b).[49]

The catalytic activity of the composite materials was studied in electrochemical water splitting, and the Co_3O_4-$CuCo_2O_4$ was found to be most active, with a lower onset potential and higher current density than pure Co_3O_4 (Figure 1c-d). This work opens up new possibilities in developing functional materials with ordered structure and high surface area based on non-precious metal catalysts.[46] A further study concerning the combination of this anode material with a high surface area semiconductor material for photo–electrochemical water splitting is in progress.

The design of third generation electrocatalysts will be based on ternary mixed metal oxides. A study concerning the fabrication of novel ordered mesoporous metal oxide/alloys is in progress as well. In particularly, Co_3O_4/CoPt, CuO/CuPt materials are thought to be remarkable as electrocatalyst based on the previously obtained results. Besides the synthesis and catalytic investigation, a study concerning the conductivity and charge transport on the prepared materials is planned to be carried out to understand the main reason for the catalytic enhancement. For that purpose, there will be an external collaboration with Dr. Steven J. Konezny (Yale University, USA).

Some part of our research is also focused on development of semiconductor nanostructured materials where the effects of junctions between two crystal structures for photocatalytic hydrogen production is studied. A project in collaborating with Prof. C. Chan (Arizona State University, USA) has been started on sodium tantalum oxide based materials since they are among the most stable and active photocatalysts. By a novel method, precisely controlling the reaction parameters, we could fabricate amorphous porous $NaTaO_x$, crystalline $NaTaO_3$ and crystalline $Na_2Ta_2O_6$ with morphologies that consist of a porous structure with interconnected nanoparticles or nanoparticles only. The photocatalytic investigation for overall water splitting indicated that catalytic activity highly depends on the crystal structure and morphology of the samples, with a maximum catalytic activity obtained for crystalline $Na_2Ta_2O_6$ with a nanoparticle and porous matrix structure. It seems that the junctions between two phases or morphologies of sodium tantalum oxides have an important effect on the material's catalytic behavior.[86]

Following this observation, a novel series of sodium tantalum oxide is fabricated to investigate the junctions between two different sodium tantalates.[87] It was shown that the crystal structure, band gap, morphology and textural parameters of sodium tantalates can be controlled via a feasible hydrothermal route by changing the pH and reaction time. $Na_2Ta_2O_6$ with pyrochlore-type structure, that has an average particle size of around 27 nm, is synthesized at low alkali concentration. By slightly increasing the alkali concentration, another $Na_2Ta_2O_6$ sample with an average particle size of 15 nm and higher surface area is prepared (Figure 2a). Further increasing the alkali concentration results in a series of composite materials based on a mixture of $Na_2Ta_2O_6$ and $NaTaO_3$ (Figure 2b-c). In addition, large $NaTaO_3$ cubes are prepared at very high alkali conditions (Figure 2d). The catalytic activities of the prepared samples are investigated for photocatalytic hydrogen production and their efficiencies are correlated to the composition, surface area and junction between the two crystal structures of the materials (Figure 2e). The highest photocatalytic activity is achieved with $Na_2Ta_2O_6$ nanoparticles with the highest surface area. It is noticed that the hydrogen production rate is not only correlated to the high surface areas of the materials, an enhanced H_2 production is obtained for composite materials that is attributed to junctions between the pyrochlore and perovskite phases of sodium tantalite.[87]

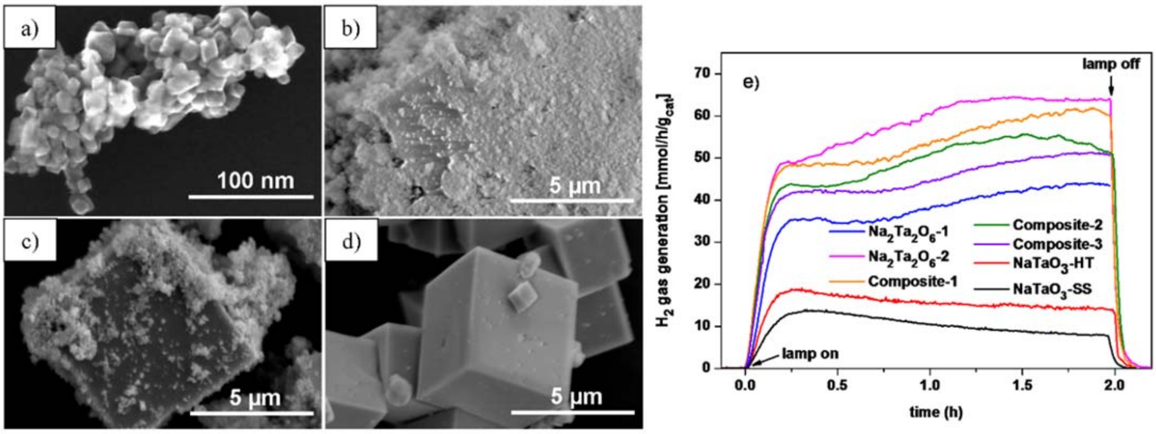

Figure 2. SEM images of $Na_2Ta_2O_6$-2 (a), Composite-2 (b), Composite-3 (c) and $NaTaO_3$-HT (d). Hydrogen production rate of the sodium tantalates prepared by hydrothermal route and the reference material $NaTaO_3$ produced via a solid-solid state.

The above investigations have proven that there is a clear effect of the junctions between two crystal phases of sodium tantalum oxide, which is mainly due to the better charge transfer and separation of electron and holes. A better junction may affect photocatalytic activity of the material even stronger. In order to study that, systematic studies on design of nanocrystals that have two crystal phases in the same particle are in progress. In addition, a composite material in an ordered mesoporous form might provide much better catalytic activity due to the distinctive material properties like high surface area (provides higher catalytic site), tailored porosity and narrow pore size distribution (allow preparation of composite structure with high heterojunction area and incorporation of catalytically active and selective species such as co-catalysts or plasmonic nanoparticles), controllable composition and crystallinity (provide flexible composition and crystallinity control that affect material’s physical properties including light absorption efficiency and charge transfer). For this purpose, a study related to the preparation of ordered mesoporous composite tantalum oxide and sodium tantalum oxide is in progress as well.