

Nanostructure Synthesis and Fabrication Room 113-115 - Session NS-TuM

Nanostructures I

Moderators: Seong Keun Kim, Korea Institute of Science and Technology (KIST), Mato Knez, CIC nanoGUNE

10:45am **NS-TuM-12 The Precise Tailoring of Catalyst Interface by Atomic Layer Deposition, Yong Qin**, Institute of Coal Chemistry, Chinese Academy of Sciences, China

INVITED

The active sites of the supported nano-catalysts may include the surface sites of the metal nanoparticles and the interface sites between the metal nanoparticles and the support. The metal-support interfaces considerably affect the catalytic performances, and in many cases, are even more effective than the surface sites. Therefore, the precise tailoring of the surface/interface structure is the most important approach to improve the catalytic performance, especially the selectivity of heterogeneous catalyst. Surface modification and encapsulation of the metal nanoparticles are used extensively for the surface/interface tailoring. In order to obtain highly efficient catalyst and understand the catalytic mechanism, it is critically important to precisely control the particle size distribution, the location and content of the modification materials, and the composition and microstructure of the interface. However, in general, it is difficult to regulate these parameters accurately by traditional methods, such as chemical vapor deposition, sol-gel method, precipitation, impregnation, and so on. Atomic layer deposition (ALD) is an advanced thin-film technology, which possesses thickness control at the atomic level, excellent uniformity and conformality, and good reproducibility. In view of the limitations of traditional methods on the tailoring of the surface/interface structures, we developed new methods for the controllable synthesis of metal nanoparticles, dense/porous oxide films, and carbon films by ALD. Based on these synthesized materials, the tailoring of the surface/interface structure were performed by coating, ultrathin coating, confining in nanospace, ultrathin coating of confined catalyst, and assembling of double-interface structure. These catalysts were characterized and evaluated deliberately, and the mechanisms of how the surface/interface structures affect the catalytic performances were discussed. These results will provide new guidance for the design and synthesis of highly effective catalysts.

11:15am **NS-TuM-14 Improving the Anti-sintering Ability of Au/TiO₂ Catalysts by Constructing Semi-embedded Structure via Selective Atomic Layer Deposition, Yuanting Tang, X Liu, B Shan, R Chen**, Huazhong University of Science and Technology, China

Au nanoparticles are very active for various important catalytic reactions, such as CO oxidation, partial oxidation of hydrocarbons and so on^[1]. However, Au nanoparticles are highly susceptible to sinter at elevated temperature, which leads to serious decrease in catalytic activity. In this work, TiO₂-Au/TiO₂ catalysts are fabricated with semi-embedded structure via area selective atomic layer deposition (ALD). The area selective ALD method is realized through passivation of metal nanoparticles with self-assembled monolayers^[3]. CO oxidation is performed as probe reaction. The results show that TiO₂-Au/TiO₂ catalysts exhibit outstanding room-temperature CO oxidation activity even after calcination. The key feature of the embedded structure lies in its ability to anchor Au nanoparticles and effectively limits the growth of Au nanoparticles via strong metal-oxide interactions, while still leaving active metal facets exposed. The reported method shows great potential for the simultaneous enhancement of thermal stability and activity of precious metal nanoparticles.

[1] Liu X, He L, Liu Y M, et al., *Accounts. Chem. Res.* 2014, 47, 793.

[2] Valden M, Lai X, Goodman D W, *Science*, 1998, 281, 1647.

[3] Liu X, Zhu Q, Lang Y, et al., *Angew. Chem. Int. Ed.* 2017, 56, 1648

11:30am **NS-TuM-15 Tuning of Boron Nitride Nanotubes, Nanopores and Nanoporous Membranes by ALD, Matthieu Weber, B Koonkaew, S Balme**, Institut Européen des Membranes, France; *I Utke*, EMPA, Swiss Federal Laboratories for Materials Science and Technology, Switzerland; *F Picaud*, Université Bourgogne Franche-Comté, France; *I Iatsunskyi, E Coy*, Adam Mickiewicz University in Poznan, Poland; *D Cornu, P Miele, M Bechelany*, Institut Européen des Membranes, France

In this presentation, we report the design and the fine-tuning of boron nitride nanotubes, nanopores and nanoporous membranes by atomic layer deposition (ALD).

First, we developed an ALD process based on the use of BBr₃ and NH₃ as precursors in order to synthesize BN thin films. The deposited films were characterized in terms of thickness, composition, microstructure and mechanical properties.^{1,2}

Next, we report the scalable synthesis of BN nanotubes that can be tuned in terms of diameters dimensions through a novel and easy route combining ALD and annealing steps. Carbon nanofibers templates are used as initial supports. In order to obtain the crystallization of BN and to eliminate the carbon initial supports, the samples were first placed at a temperature of 1350°C in nitrogen atmosphere for 5 hours, and then annealed at 600°C for 4 hours in air. The inner diameter can be controlled by choosing the initial carbon nanofibers supports. High resolution TEM imaging has been carried out to characterize the obtained BN nanotubes. The self-limiting reactions of ALD provide a clear control over the diameter thickness of the BN layer deposited with sub-nanometer accuracy as a steady-state ALD growth of ~0.8 Å/cycle has been observed on all our samples. The self-supported BN nanotubes synthesized present good mechanical properties and are easy to handle. Furthermore, the sorption performances of the BN nanotubes have been assessed, and the results showed that the nanotubes absorb up to 110 times their weight in oil while repelling water. These proof-of-concept results are thus very promising for water purification purposes.

For the first time, this BN ALD process was also used to tune the diameter of fabricated single transmembrane nanopores by adjusting the BN thickness and to enable studies of the fundamental aspects of ionic transport on a single nanopore. At pH=7, we estimated a surface charge density of 0.16 C.m⁻² without slip and 0.07 C.m⁻² considering a reasonable slip length of 3 nm. Molecular dynamic simulations performed with experimental conditions confirmed the conductivities and the sign of surface charges measured.² The high ion transport results obtained and the ability to fine-tune nanoporous membranes by such a scalable method paves the way towards applications such as ionic separation, energy harvesting and ultrafiltration devices.

1 Weber M et al. Boron Nitride Nanoporous Membranes with High Surface Charge by Atomic Layer Deposition,

ACS Applied Materials and Interfaces 9, 19, 16669 (2017).

2 Weber M et al. Mechanical Properties of Boron Nitride Thin Films Prepared by Atomic Layer Deposition. *CrystEngComm*, 19, 6089 (2017).

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