Novel design of hydrogen-selective palladium-based composite membranes and sensors

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Hydrogen gas is crucial for upcoming transportation technologies and is a key for many chemical processes. Moreover, hydrogen is considered as one of the best clean energy carriers which could contribute to tackle the major environmental issues our society is facing. Therefore, the development of reliable, fast and efficient means to separate or detect hydrogen gas is of great importance for its production, storage and use.

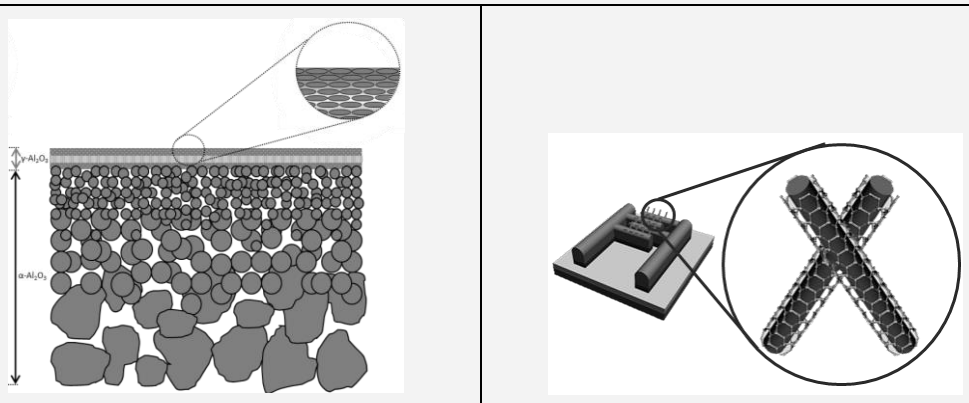
In the case of hydrogen separation, many membrane materials have been designed for selective hydrogen extraction, such as pure inorganic or polymer membranes and their composites, hybrid membranes (Si-based membranes, MOFs), metal alloys etc. In the area of metal-based membranes, palladium (Pd) represents a particularly attractive material thanks to its high selectivity towards hydrogen enabling the production of pure H_2. On the other hand the typically applied (self-supported) Pd membranes are relatively expensive and generally not well adapted for large scale application. Concerning hydrogen detection, the most widely applied sensor materials are nowadays based on semiconductor metal oxides presenting excellent physical and chemical stabilities. However, these sensors typically suffer from a relatively low selectivity. Hence, strong efforts are nowadays required to improve both membrane hydrogen separation efficiency and sensor response intensity/selectivity at acceptable cost.

Herein, we present a novel synthesis strategy based on Atomic Layer Deposition of Pd nanoparticles, which could be advantageously applied at different scales, i.e. macrosystems (membrane separation) [1] and nanosystems (sensors detection) [2]. Indeed, ALD is a very attractive technique allowing the direct preparation of thin films or nanoparticles of a large range of materials on high aspect ratio substrates with precise thickness control, high uniformity and excellent conformality.

As schematically represented in Fig. 1a, embedded Pd nanoclusters confined within the pores of a γ-Al_2O_3 membrane layer were prepared on (tubular) ceramic support. This novel strategy enabled the fabrication of hydrogen selective palladium-alumina (Pd/Al_2O_3) composite membranes featuring hydrogen flux above 1000 GPU and attractive separation factors ($F_{H2/N2}$ ~16 and $F_{H2/CO2}$ ~ 9) at moderate temperatures (188°C). In the case of hydrogen detection, we applied a strategic combination of ZnO nanowires (NWs) decorated with palladium nanoparticles (Pd NPs) and a molecular sieve metal organic framework (MOF) nanomembrane (Fig.1b). Such modification of miniaturized sensor devices enabled the assessment of their performance for H_2 detection at concentrations as low as 10 ppm in the presence of various gases. Remarkably high response signals of 3.2, 4.7 and 6.7 (Ra/Rg) have been measured for H_2 detection at only 10, 30 and 50 ppm have been measured, whereas no noticeable response towards other tested gases was detected.

In conclusion, the presented results demonstrate the proof of concept for the fabrication of new designs of hydrogen selective composite membranes and sensors. Furthermore, this strategy of Pd

ALD could be extended to the design of other gas selective or catalytic membrane materials by a judicious choice of metals and their alloys thus opening a new avenue for the preparation of highly selective separation and sensing devices.



(a) (b)

Fig. 1. Schematic representation of (a) Pd/Al_2O_3 composite membrane (with zoom of γ-Al_2O_3 inner top-layer gradually infiltrated with Pd; (b) Pd/MOF/ZnO gas sensors (with zoom of ZnO nanowires coated with Pd/MOF composite layer.

References

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