

Galvanic deposition of subnanometric Os particles on TiO₂ nanotube arrays: Boosting the electrocatalytic hydrogen evolution performance

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Proton exchange membrane water electrolysis (PEMWE) powered by renewable energy sources is seen as the most promising technology for high-rate production of green hydrogen. The acidic environment of PEMWE systems requires the use of efficient, but expensive platinum group metal (PGM)-based catalysts for the cathodic hydrogen evolution reaction (HER), which limits the prospects for wider commercialization of this technology. One of the main research directions today is designing stable and interactive substrates and facile methods for dispersing PGMs in order to reduce their content in HER cathodes and improve their utilization in the reaction. Our previous work showed that galvanic deposition of PGM nanoparticles on self-ordered TiO₂ nanotube (TNT) arrays can produce highly active composites with low PGM loading [1,2]. In this study, we extend the galvanic displacement approach to depositing osmium particles on hydrogenated “nanogross”-covered TNT array substrates [3]. Structural characterizations show that Os particles deposited by this procedure are mainly at the sub-nanometric level and entirely cover the inner tube walls. Our systematic investigations reveal the influence of galvanic deposition conditions (OsCl₃ concentration/temperature/duration) on the HER overpotential and mass activity of resulting Os@TNT composites. An optimum Os@TNT composite, achieving a balance between apparent and mass activity, is prepared at 3mM/55°C/30min and contains ~12 μg_{Os} cm⁻². It exhibits a low overpotential of 61 mV at a current density of 100 mA cm⁻², a high mass activity of 20.8 A mg_{Os}⁻¹ at an overpotential of 80 mV, and a durable performance in 1 M HClO₄. Density functional theory (DFT) calculations suggest that the hydrogenation degree of the TiO₂ surface does not only have a large impact on the dispersion and size of deposited Os particles, but it also affects their adsorption properties. The electronic interactions between the hydrogenated TiO₂ surface and small Os clusters may weaken the strong Os–H* binding characteristic for bulk Os and thus boost the intrinsic HER activity of Os sites.

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