

Abstract

The generation of green hydrogen as energy carriers has been considered as one of the most promising solutions for energy storage. However, the high cost of metal catalysts has become the biggest obstacle for further implementation. There has been immense research dedicated to the development of downsizing metallic catalysts to improve its surface-to-volume ratio for a better utilisation of materials which is critical to large-scale industrial production. Since 2011, single atom catalysts on solid supports have attracted significant attention due to their unique characteristic exhibiting a high efficiency and selectivity as homogeneous catalysts. To synthesize single atom catalysts on solid support, nitrogen, oxygen, and phosphorus are common π -donors introduced onto the substrate surface to capture metal ions from the metal salt solution forming a coordination environment to anchor the metal atoms. By this technique, the use of expensive metal in the production of green energy carrier can be significantly reduced which will directly impact the price. Thus, there is a great importance to develop a low-cost and straightforward method with low energy consumption to accelerate the transition towards sustainable energy. This thesis is devoted to the development of single atom catalysts on solid supports. This is done by diazonium grafting pyridine-type ligands onto carbon cloth surfaces, which can capture metal ions to form single atom catalysts with a structure of carbon-ligand-metal for the application in electrocatalytic hydrogen evolution reaction.

By electrografting of *in-situ* generated diazonium cations, the carbon cloth surface can be modified with a terpyridine layer. These grafted terpyridine ligands are able to capture platinum ions from low-concentration solutions (0.5 ppm Pt^{2+}). The resultant platinum single atom catalysts (PtSACs) exhibit a great hydrogen evolution efficiency, outperforming platinum on carbon coated carbon cloth benchmark catalyst (Pt/C@CC) across the entire applied potential range from 0.235 V to -0.765 V (vs RHE) with a much lower metal loading of 0.26 $\mu\text{g}/\text{cm}^2$. At the low overpotential of -50 mV (vs RHE), the calculated mass activity of this PtSAC achieves up to 83 times higher activity compared to Pt/C@CC. During the chronopotentiometric HER, the metal-free terpyridine ligand can scavenge platinum ions leached from the platinum counter electrode and improves its catalytic performance at the same time.

For the further enhancement in grafting quality and addressing the batch-to-batch variation in the hydrophobicity of carbon cloth, multiple pretreatment methods were introduced and compared with chemical grafting in organic media. The wettability of carbon cloth was improved after treatment with Piranha solution, butane flame, electrochemical oxidation, and air-plasma. Among these pretreatments, air-plasma cleaning is considered the most promising approach as evidenced by the improvement in resultant HER performance. However, this improvement may be attributed to the deposition of platinum particles which results from the interaction between plasma etched layer and platinum ions influencing PtSAC synthesis and the performance evaluation. Thus, chemical grafting

in organic media is regarded as the most suitable procedure to mitigate the hydrophobicity issue which can cause a significant loss of active surface area.

While electrografting terpyridine demonstrates high effectiveness in the synthesis of PtSAC, the higher cost on reagents become the main drawback of this method. Using an alternative ligand, 3-aminopyridine, can significantly reduce the cost. To prevent the hydrolysis of 3-diazopyridinium cations during the grafting, the reaction was carried out chemically in acetonitrile instead of aqueous electrolyte. By immersing CC in 3-diazopyridinium for 3 days, a high 3-pyridyl ligands coverage of 5.48% nitrogen surface content was achieved, which can be further increased to 8.99% by extending the grafting time to 5 days. The resultant pyridine monolayer exhibits excellent coordination capacity enabling the immobilization of platinum from 1 and 10 ppm Pt^{2+} solutions in acidic environment regardless of the possible protonation of the pyridinic nitrogen. The resulting Pt loaded surface (0.182 and 0.380 $\mu\text{g}/\text{cm}^2$) leads to the enhanced hydrogen evolution efficiency of -63.6 and -77.4 mA/cm^2 at -0.765 V (vs RHE), respectively. The calculated mass activities of these two PtSACs outperform Pt/C@CC by more than 15 times in low and high potential region. During the operation, the chlorine co-ligands on the platinum atom in the freshly synthesized PtSAC was substituted with hydroxy co-ligands resulting in promoted HER performance which was supported by the change in hydrogen adsorption energy from -0.540 eV to -0.314 eV calculated, using DFT. In addition, the PtSAC layer on CC also contributes to the improvement in wettability enabling the generated hydrogen bubbles to depart from the catalyst surface with a small size of 70 to 110 μm . The advantageous bubble management prevents the excessive blockage of active site ensuring the stable hydrogen production.

To further expand the applicability of this type of single atom catalysts, different pyridine-type ligands were grafted onto carbon cloth through chemical grafting in organic solution to overcome the wettability. Through the comprehensive comparison of cost, grafting procedure and quality, the 3-diazopyridinium grafted CC presents the best performance among other four ligands mentioned in chapter 7. As a result, the highest platinum loading of 0.386 $\mu\text{g}/\text{cm}^2$ was achieved which leads to the highest hydrogen evolution efficiency of -135.4 mA/cm^2 at -0.765 V (vs RHE). Taking their platinum content into account, the highest platinum mass activity was observed for CC-Phenan-Pt which was followed by CC-4Pyd-Pt attributed their extremely low platinum content. The high stability of covalent bonded platinum-pyridine complexes enables these PtSACs to operate under harsh conditions.