Quantification of active site density and turnover frequency: from single atom to bulk metal catalysts

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Turnover frequency (TOF) is a key descriptor of the catalysts for a valid comparison of their intrinsic activities. Since reaction rate depends on the TOF and the catalyst concentration, much effort has been made to maximize catalytic performance via increasing active site density (ASD) as well as TOF. In electrocatalysis, a special concept of electrochemically active surface area (ECSA) has been alternatively used to calculate the ASD of electrocatalytic materials due to their very complex local environments. Unfortunately, this in situ voltammetric protocol is restrictively applicable to bulk platinum group metals, while measurements of ECSA or ASD (and consecutive TOF) are still challenging for other promising electrocatalytic materials. Here, a versatile in situ method for ASD quantification will be introduced, enabled by adopting a cyanide anion as a probe molecule. Importantly, this analytical strategy demonstrates its scalable generality to access a variety of the electrochemical conditions and of the electrocatalytic materials from a series of single atom to conventional bulk metal catalysts.