

## Hydrogen Evolution Reaction

## Cobalt-Embedded Nitrogen-Rich Carbon Nanotubes Efficiently Catalyze Hydrogen Evolution Reaction at All pH Values\*\*

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**Abstract:** Despite being technically possible, splitting water to generate hydrogen is still practically unfeasible due mainly to the lack of sustainable and efficient catalysis for the half reactions involved. Herein we report the synthesis of cobalt-embedded nitrogen-rich carbon nanotubes (NRCNTs) that 1) can efficiently electrocatalyze the hydrogen evolution reaction (HER) with activities close to that of Pt and 2) function well under acidic, neutral or basic media alike, allowing them to be coupled with the best available oxygen-evolving catalysts—which also play crucial roles in the overall water-splitting reaction. The materials are synthesized by a simple, easily scalable synthetic route involving thermal treatment of Co<sup>2+</sup>-embedded graphitic carbon nitride derived from inexpensive starting materials (dicyandiamide and CoCl<sub>2</sub>). The materials' efficient catalytic activity is mainly attributed to their nitrogen dopants and concomitant structural defects.

As being the cleanest of all fuels, hydrogen has long been expected to play a pivotal role in our energy landscapes by mitigating, if not completely eliminating, our reliance on fossil fuels.<sup>[1]</sup> However, this hype has so far been elusive, mainly because: 1) molecular hydrogen does not exist naturally on earth, 2) the production of molecular hydrogen from water—the most abundant and renewable hydrogen source—by the water-splitting reaction is inherently quite difficult, and 3) there is a lack of sustainable catalysts composed of inexpensive and earth-abundant elements that can efficiently

catalyze the half reactions involved in the water-splitting reaction.<sup>[2]</sup>

The water-splitting reaction can be viewed as a combination of two half reactions: the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER).<sup>[2]</sup> To conduct electrochemical water splitting, voltages above the thermodynamic potential values corresponding to the intrinsic activation barriers present in both half reactions (also known as overpotential,  $\eta$ ) must be applied. Hence, reduction of both overpotentials using HER or OER catalysts, respectively, is essential to make the water-splitting reaction less energy-intensive. Unfortunately, it is difficult to find suitable HER and OER catalysts that can work well in the same pH range to be coupled together and make the overall water-splitting reaction more energy-efficient. Whereas almost all the best OER catalysts (especially those synthesized from earth-abundant elements) work well only in neutral or basic media,<sup>[3–5]</sup> most of the recently developed HER catalysts function well only in acidic media (except for very few that can work in neutral and basic media, see Tables S1–S3 in the Supporting Information).<sup>[6–23]</sup> Finding competent HER catalysts that can operate in a wide pH range (and hence have the potential to work well with the best OER catalysts regardless of pH) may address one of the major issues currently plaguing the water-splitting reaction, especially when OER catalysts that can work in a wide pH range are relatively rare.

Although Pt-based catalysts are known to efficiently catalyze HER almost irrespective of pH, their widespread use has been limited by their low earth-abundance and high cost. Hence, the development of HER catalysts that are composed of inexpensive and earth-abundant elements and can catalyze HER has been one of the main targets in renewable energy research in recent years. Some of these efforts have already led to some notable noble metal-free or transition metal complex-based HER catalysts (e.g., Ni/Co macrocycles and Ni diphosphine complexes)<sup>[24]</sup> however, most of such homogeneous catalysts were shown to only work in organic media. This problem has been circumvented for some of these catalysts by supporting them on HER-inactive carbon nanotubes (CNTs), which yielded heterogeneous catalysts that catalyze HER in aqueous acidic solutions.<sup>[27]</sup> Recently, some solid-state non-Pt-based systems have also emerged as efficient HER catalysts under various conditions, which include 1) metal sulfides, nitrides, borides and phosphides (e.g., MoS<sub>2</sub> and Ni-Mo-N) in acidic solution<sup>[6–23]</sup> and 2) metal, metal alloys and metal oxides/sulfides (e.g., Ni, Ni-Mo alloy, CoO<sub>x</sub>, PO<sub>4</sub> and Co-S) in neutral or alkaline media (Tables S1–S3).<sup>[25–28,29]</sup>

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