



Self-supported electrocatalysts for advanced energy conversion processes

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The biggest challenge in developing new energy conversion technologies such as rechargeable metal-air batteries, regenerated fuel cells and water splitting devices is to find suitable catalysts that can efficiently and stably catalyze the key electrochemical processes involved. This paper reviews the new development of self-supported electrocatalysts in three categories: electrocatalysts growing on rigid substrates, electrocatalysts growing on soft substrates, and free-standing catalyst films. They are distinct and superior to the conventional powdery electrocatalysts, showing advantages in controllable nanostructure and chemical component, flexible electrode configuration, and outstanding catalytic performance. The self-supported electrocatalysts with various architectures like nanowire/plate/pillar arrays and porous films, composed of metals, metal oxides/selenides/phosphides, organic polymers, carbons and their corresponding hybrids, are presented and discussed. These catalysts exhibit high activity, durability and selectivity toward oxygen reduction, oxygen evolution, and/or hydrogen evolution reactions. The perspectives on the relevant areas are also proposed.

Introduction

Nowadays, global concerns have been concentrated on the utilization of clean and sustainable energy as the alternative of fossil fuels due to the aggravating energy crisis and environmental issues. Many advanced devices involving electrochemical processes for clean energy conversion are being extensively investigated by both experimental and theoretical methods [1–4], and their performance is significantly influenced by the kinetics of key electrocatalytic reaction processes, such as the oxygen reduction reaction (ORR), oxygen evolution reaction (OER), and hydrogen evolution reaction (HER) [5–8]. In the past decades, a large variety of highly efficient electrocatalysts have been developed to accelerate the commercialization of these energy conversion devices [9–15], driven by profound understanding on the nature of relevant electrocatalytic processes and by technological advances in the relevant fields. However, the conventional electrocatalysts for ORR, OER and HER, used under experimental conditions and in realistic devices, are usually in the form of fine powders. Electrode fabrication always requires the time-consuming film casting or

coating procedure with assistance of polymeric binders and extra conductive additives, which results in uncontrolled microstructures, limited active surface areas, plenty of dead volumes and undesirable interface that are unfavorable for electron conductance and multiphase reactant/product mass transport [16–18]. Moreover, continuous gas evolution (i.e. H₂, O₂) during such electrocatalytic reactions makes the coated catalysts peel off from electrodes [19,20], which greatly impairs their catalytic activity and lifetime (Fig. 1).

Recently, self-supported electrocatalysts directly growing on conductive substrates or forming free-standing films have attracted tremendous interest [21,22]. This new class of electrocatalysts exhibits outstanding performance for the ORR, OER and/or HER processes with many intrinsic advantages in comparison with their powdery counterparts (Fig. 1). Basically, through different synthetic strategies such as hydrothermal process or electrochemical deposition, electroactive species are able to *in situ* grow on rigid metallic substrates or flexible carbonaceous substrates in the fashion of nanostructured arrays, or form free-standing films with three-dimensional (3D) porous structures [23–26]. The one-pot fabrication protocol without post-coating procedure does not

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<i>Differences</i>	<i>Self-supported electrocatalysts</i>	<i>Powdery electrocatalysts</i>
Electrode preparation	Electroactive species directly grown on rigid (metallic foils, foams, meshes) and soft (carbon fiber paper) substrates; free-standing films	Powdery materials post-coated on glassy carbon and other electrodes
Binder used	Self-supported with no binders	Polymeric binders and extra conductive additives
Electrode configuration	Nanowire/plate/pillar arrays; 3D porous architecture	Uncontrolled microstructure with large dead volumes
Surface area	Large electroactive surface areas	Limited electroactive surface areas
Mass transfer	Easy electrolyte penetration; facile access of reactants to active sites	Restricted mass transfer
Electron conductivity	Efficient electron transfer along nanostructures, between active species and substrates	Inferior conductivity caused by binders used and undesirable interface in the electrode
Stability	Strong adhesion between active species and substrates; enhanced long-term/cyclic stability	Easy peeling of coated materials, especially in multiphase reactions involving gas bubbles (OER, HER)
Prospect	Time-efficient, convenient, highly active and stable, consequently suitable for large-scale industrial applications	Complicated, time-consuming, less active, and unstable

FIGURE 1

A comparison between self-supported and powdery electrocatalysts.

require organic binders. It can lead to the direct contact of the electroactive species with underneath conductive substrates, and the well integrity of the free-standing catalyst films. This may assure the good electron conductivity and favor the high mechanical stability of catalysts for long-term and cyclic usage [27,28]. Also, the complex nanostructures of self-supported catalysts are more effective in enlarging the catalytically active surface areas as compared to conventional planar catalyst coatings, which benefits better exposure and enhanced utilization of electroactive sites [21–24]. Furthermore, the open space within nanostructured arrays or 3D porous films facilitates electrolyte penetration, ion (e.g. OH^- , H^+) diffusion to the electroactive sites, and the fast emission of reaction products (e.g. O_2 , H_2), consequently promoting the reaction kinetics [25,26]. Thus, the self-supported electrocatalysts with time-efficient and convenient preparation procedure as well as excellent activity and stability have shown great potential for direct application in many clean energy devices.

Up to now, there are several comprehensive reviews on the development of electrocatalysts aiming at materials synthesis (mainly in powdery form) and catalytic applications [29–33]. Some reviews also introduce self-supported materials for energy storage in supercapacitors and lithium-ion batteries [34–36]. However, no detailed review focuses on the self-supported materials for electrocatalytic processes. The present review highlights the design and fabrication of various self-supported catalysts for

key electrochemical reactions such as ORR, OER and HER. Three typical categories including electrocatalysts growing on rigid substrates, electrocatalysts growing on soft substrates, and free-standing catalyst films are presented and discussed, revealing the material structure, catalytic performance and their end-uses in practical devices.

Electrocatalysts growing on rigid substrates

Metal foils are the most commonly used rigid substrates to cultivate electroactive species. Various metal oxides have been chosen as the electroactive species, in which spinel-phase cobalt oxides (CoO_x) are widely investigated due to their good catalytic activity and corrosion stability toward electrochemical reactions in alkaline media [37,38]. Initial studies afford irregular nanoparticles dispersed on metal foil surface without specific nanostructures. For instance, CoO_x nanoparticles were grown on different metal foils including Au, Pd, Pt, Cu and Co by a galvanostatic deposition method [39]. The electroactivity toward OER decreased in the order of $\text{CoO}_x/\text{Au} > \text{CoO}_x/\text{Pt} > \text{CoO}_x/\text{Pd} > \text{CoO}_x/\text{Cu} > \text{CoO}_x/\text{Co}$, paralleling to the electronegativity drop of metal foils used. Notably, even without any subtle nanostructure, the turnover frequency (TOF) for OER occurring on CoO_x/Au ($\sim 1.8 \text{ s}^{-1}$) was nearly 40 times higher than that of bulk CoO_x , and three times higher than that of bulk Ir, the state-of-the-art noble metal OER electrocatalyst [40,41], which implies the superiority of self-supporting configurations.

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