

Heterogeneous Catalysis

Chain Mail for Catalysts

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chain-mail catalysts · electron transfer ·
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Abstract: Encapsulating transition-metal nanoparticles inside carbon nanotubes (CNTs) or spheres has emerged as a novel strategy for designing highly durable nonprecious-metal catalysts. The stable carbon layer protects the inner metal core from the destructive reaction environment and thus is described as chain mail for catalysts. Electron transfer from the active metal core to the carbon layer stimulates unique catalytic activity on the carbon surface, which has been utilized extensively in a variety of catalytic reaction systems. Here, we elaborate the underlying working principle of chain mail for catalysts as well as the key factors that determine their catalytic properties, and provide insights into the physicochemical nature of such catalyst architectures for further application of the strategy in rational catalyst design.

Reaction-oriented catalyst design is flourishing both theoretically and practically. Balancing catalytic activity and durability is one of the significant challenges to achieve a better performance, because they are both important properties but usually limit each other. Researchers mainly focus on engineering the electronic structures of active centers or the composition of a catalyst to tune the catalytic activity and durability. Here we describe an innovative strategy for designing a catalyst and tailoring its properties: Chain mail for catalysts.

The term chain mail for catalysts comes from an analogy to a battlefield warrior with chain-mail armor. The chain mail can provide pivotal protection to the body from combat damage and thereby ensure the full fighting capacity of the warrior. A chemical reaction environment, which typically includes reactant molecules in the gas phase or a liquid solution, temperature, pressure, and sometimes light rays, is just like a combat field for the catalyst as it fights with its surroundings. The catalyst on the one hand turns kinetically sluggish reaction into a fast-happening process. On the other hand, it suffers from corrosion or phase change under the fierce attack of molecules, ions, and heat, which leads to deactivation of the catalyst; the situation is even worse in harsh reaction environments. Is it possible to protect a catalyst with chain mail to defend the damage from the environment while keeping its catalytic effectiveness? Such chain mail should not only be a robust material to separate and protect the catalyst from the corrosive environment, but should also be able to deliver the catalytic activity to its outer surface and then take part in catalyzing the reaction.

A catalyst is usually rich in bonding sites and electrons. It works by forming chemical bonds and exchanging electrons with the adsorbates to activate them and then open reaction pathways that are unavailable without the catalyst. Chain mail for catalysts should firstly possess similar properties: being able to form ionic or electronic bonds with the reactant molecules, and the electrons of the inner catalyst can flow through the chain mail to the outer surface and serve as extended hands of the catalyst to grab the molecules and activate them. Secondly, the chain mail should be a robust and flexible material that can fully encapsulate the catalyst nanoparticles and thereby physically isolate them from the reaction environment. Concerning this point, two-dimensional (2D) layered materials emerge as reasonable choices for the chain mail. Graphene-based carbon possesses both good chemical stability and peculiar electronic properties, and is thus a promising candidate. It was found about two decades ago that fullerenes (C₆₀) encapsulated in single-wall carbon nanotubes (CNTs) are detectable from the outer surface of the tube by scanning tunneling spectroscopy (STS), a technique that is sensitive to surface electronic fine structures.^[1] The carbon layer is “transparent” to the substance underneath as a result of a surface charge response to their electronic interactions. Graphene-based carbon is also well-

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known for its high rigidity.^[2] These attributes render it an ideal chain-mail material.

The first chain-mail catalyst in its true concept was reported in 2013.^[3] It was built by encapsulating iron nanoparticles (NPs) in CNTs, with the iron NPs isolated in the channel of the capped CNTs and fully separated from the outside reaction environment. This structure exhibits both good catalytic activity and durability in the acidic electrochemical oxygen reduction reaction (ORR), an important reaction on the cathode of fuel cells. The carbon shell serves as the chain mail that protects the highly reactive iron NPs so that they can survive the corrosive acidic medium and remain intact for more than 200 hours in the reaction medium. The chain-mail catalyst also shows an impressive antipoisoning ability, being tolerant to 30 ppm SO₂ for more than 500 minutes without decay of the activity. The carbon layer plays an excellent role as the chain mail to protect the iron NPs.

How does catalysis work on the surface of the chain-mail carbon layer? Metal NPs are always highly reactive owing to the large number of free electrons and dangling bonds on their surfaces. In the above system, the iron NPs inside the CNTs can form covalent bonds with carbon by overlapping of the Fe 3d and C 2p states. The bonding between Fe and C brings two effects: 1) it disturbs the local π bonding system of the carbon network and thereby destabilizes the 2p states of the carbon in the contact area, and 2) facilitates the transfer of free electrons from the iron NPs, which have lower electron work functions, to the carbon layer and thereby enriches the carbon surface with electrons. These two effects lead to an increased electronic density of states (DOS) of carbon at the Fermi level as well as a reduced work function of the carbon layer covering the iron NPs, and this had been confirmed by both density functional theory (DFT) calculations and experimental spectroscopic characterizations.^[3,4] In simple terms, the chain-mail carbon layer is activated by the electronic interactions between the inner iron NPs and the carbon as well as the induced charge redistribution. This results in the carbon layer becoming a part of the catalyst,

where the adsorption and dissociation of O₂ is facilitated and the ORR is initiated (Figure 1).

What are the factors that determine the catalytic properties of a chain-mail catalyst? A chain-mail catalyst consists of two parts: the chain-mail layer and the encapsulated metal NPs. The catalytic activity arises from perturbation of the local electronic states of the chain-mail layer and transfer of electrons from the metal NPs to the outer surface. The catalytic durability depends on the intrinsic stability of the chain-mail material. Thus, the physicochemical properties of the two parts have major effects on the catalytic properties. In the following, we analyze separately the key factors relevant to these two parts.

The surface of the chain mail is where the catalytic reaction takes place. The catalytic activity depends on how much the surface is activated by the encapsulated inner NPs and also how much the surface is enriched with electrons coming from the inner NPs. This is strongly related to the thickness of the chain-mail layer. The surface of an over-thick chain-mail layer is barely affected by the inner NPs. A simple DFT calculation of the thickness effect of a graphene-like carbon layer showed that the electrons of the inner NPs can traverse up to three carbon layers before the effect becomes too weak (Figure 2).^[5] Thus, the chain-mail surface is not likely to be activated if the layer number is greater than three. A better choice is to reduce the thickness of the chain mail to below three layers to make it more “transparent” to the inner NPs. After a series of research efforts, the controllable synthesis of such chain-mail catalysts with specific carbon layer numbers (single layer or double layer) has been realized, so that the catalytic activity can be more effectively enhanced.^[5b,6] However, if the chain-mail layer is too thin it may also bring the risk of low catalytic durability in harsh reaction environments. In such cases, a double-layered carbon chain mail would provide a good balance of the catalytic activity and durability.

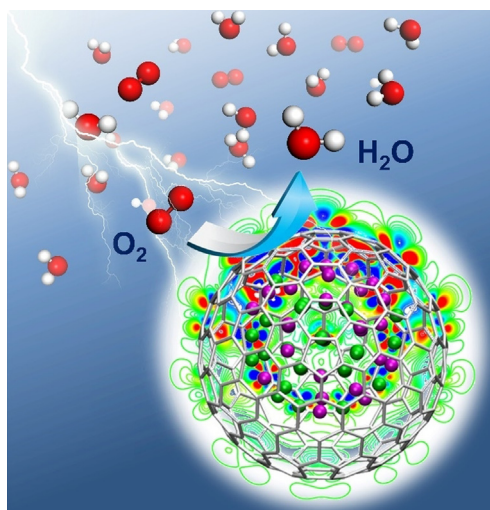


Figure 1. A schematic representation of the ORR process on the surface of a chain-mail catalyst with graphene encapsulating CoNi metal clusters.

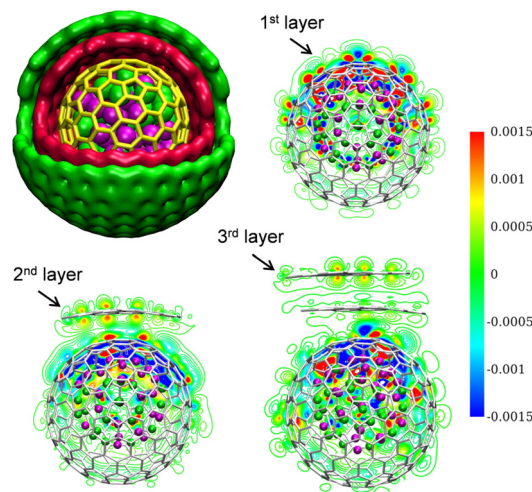


Figure 2. Differential charge densities of chain-mail catalysts with one, two, and three carbon layers encapsulating CoNi alloy nanoparticles, showing the traversing of electrons from the inner core metal to the outer surface through up to three layers.^[5b]

Tuning the atomic composition of the chain-mail layer by doping with heteroatoms can influence the charge redistribution as well as the activity of the chain-mail surface. Doping with nitrogen has been found to have a promoting effect on the traversing of electrons from the inner iron NPs through the chain-mail layers to the outer surface, and hence can enhance the catalytic activity.^[3,7] Other properties of the chain-mail layer, for example the curvature and chirality of CNTs, which relate to their electronic features, are also potential factors that may affect the catalytic properties of the chain-mail catalyst. It is worth noting that other types of 2D materials such as boron nitride (BN) and molybdenum disulfide (MoS₂), which have received widespread attention in recent years, may also be good candidates as chain-mail materials.^[8] With BN in particular, as a result of its polarized electronic distribution,^[9] catalyst nanoparticles encapsulated by BN layers could exhibit very different properties compared with those encapsulated by graphene layers. Furthermore, the relatively higher thermal stability of BN could compensate the lower thermal stability of graphene-like carbon under harsher reaction conditions.^[10]

The encapsulated metal NPs are the cores of the chain-mail catalysts, working like a heart pumping out electrons to the chain-mail surface. They are the origin of the reactivity and the source of the redistributed electrons. Thus, their metallicity accounts for the efficacy of enhancing the activity of the chain mail. Non-noble transition metals usually have relatively lower electron work functions compared with noble metals, and thus are very reactive and susceptible to phase changes in oxidative or corrosive environments, so that they are seldom used directly as catalysts. In such cases, it is a good choice for them to “wear” the carbon chain mail, which can not only provide physical protection to them but also help to deliver a better catalytic performance.^[6b,11]

From an overall picture of chain-mail catalysts, we would say it is more than just an approach to boost the robustness of catalysts. The combination of the chain-mail material and the highly reactive metal cores also offers a method to engineer the catalytic activity.^[12] For example, in the case of metal NPs that are over-reactive for a reaction, they will most probably be poisoned by some strongly adsorbed species that is difficult to desorb or convert. Covering the metal NPs with a chain-mail layer and optimizing the layer thickness would allow the activity to be modulated to a moderate level to meet the Sabatier principle, that is, the adsorption should be neither too strong nor too weak to achieve a better catalytic performance. Another aspect is that the combination of the electronic states of the chain-mail layer and the metal cores can also be used to mimic the electronic structures of noble metal catalysts, such as Pt, to achieve their catalytic properties (Figure 3). This has been proved feasible recently, where the activity of the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) could approach or even exceed those of precious metal catalysts, such as Pt and Ir, when using chain-mail catalysts of a few-layer or single-layer graphene shell encapsulating 3d metal NPs.^[5b,6a] This points to a feasible way to search for alternatives to noble metal catalysts in the future.

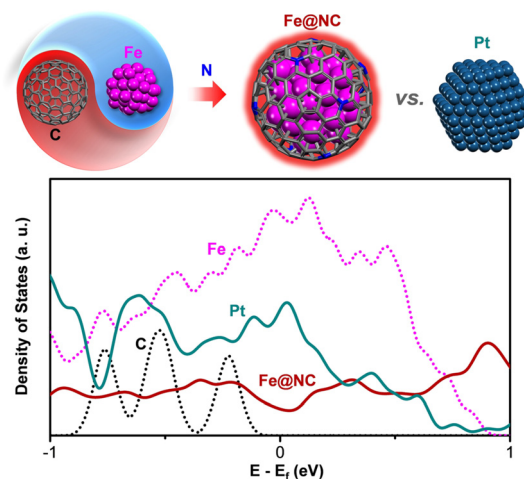


Figure 3. Mimicking the distribution of the electronic density of states of Pt nanoparticles near the Fermi level using a combination of a nitrogen-doped carbon sphere (NC) and iron metal clusters to form a chain-mail catalyst.

In summary, the concept of using graphene or other 2D materials as a chain-mail layer to protect vulnerable transition-metal nanoparticles and modulate their catalytic properties by the redistribution of electrons will undoubtedly receive increasing attention and stimulate more and more academic research. The related studies will potentially be an important branch in the research of nanoconfinement catalysis and provide the theoretical basis for the rational design of novel catalysts in the future.

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Conflict of interest

The authors declare no conflict of interest.

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