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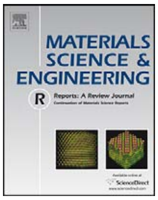

Engineering the properties of metal nanostructures via galvanic replacement reactions

Claire M. Cobley, Younan Xia *

Department of Biomedical Engineering, Washington University, St. Louis, Missouri 63130, USA

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ABSTRACT

In this review, we will bring the reader up to date with recent advances in the use of galvanic replacement reactions to engineer highly tunable nanostructures for a variety of applications. We will begin by discussing the variety of templates that have been used for such reactions and how the structural details (e.g., shape, size, and defects, among others) have interesting effects on the ultimate product, beyond serving as a simple site for deposition. This will be followed by a discussion of how we can manipulate the processes of alloying and dealloying to produce novel structures and how the type of precursor affects the final properties. Finally, the interesting optical properties of these materials and some innovative applications in areas of biomedical engineering and catalysis will be discussed, completing our overview of the state of the art in galvanic replacement.

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* Corresponding author. Tel.: +1 314 935 8328; fax: +1 314 935 7448.
E-mail address: xia@biomed.wustl.edu (Y. Xia).

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1. Introduction

Metallic nanostructures have been extensively studied in recent years for applications in catalysis [1–4], plasmonics [5–8], sensing [9–13], and biomedicine [14–18]. In order to further enhance the performance of these materials, there has been a strong effort in developing new methods for precisely engineering the structures and properties of these systems [2,19]. Of the many techniques that have been demonstrated, galvanic replacement is particularly interesting due to its high tunability and the possibility to study the intricacies of alloying and dealloying in metallic nanostructures [20,21]. Galvanic replacement occurs spontaneously when the atoms of one metal react with ions of another metal having a higher electrochemical potential in a solution phase. The metal atoms are oxidized and dissolved into the solution, while the metal ions are reduced and plated on the surface of the metal template. This simple reaction can be used with a wide variety of metal templates and salt precursors and is limited by little more than the requirement of an appropriate difference in the electrochemical potentials between the two metals. Based on fundamental chemistry, this reaction provides a straightforward and versatile route to a broad range of simple and complex structures including hollow nanocrystals, alloyed nanostructures with controllable elemental compositions, and nanoparticles with tunable optical properties [20,21].

The most important factor in controlling the morphology of the final structure in a galvanic replacement reaction is the shape or morphology of the starting template [22]. As the newly formed metal atoms will deposit on the surface of the template, the final structure should closely resemble the original template. In a typical galvanic replacement reaction, the final structure is a hollow shell with a shape similar to that of the template and slightly larger dimensions [22]. Yet as with many areas, some of the most interesting observations come from the exceptions. In the first part of this review article, we will discuss the galvanic replacement reaction with a number of different types of templates, and highlight some of the engineering strategies that have come out of these comparisons.

The alloying and dealloying processes involved in a galvanic replacement reaction also have a strong impact on both the structures and properties of the final products [20,21]. After a brief introduction to relevant processes such as atomic diffusion, we will discuss some of the ways in which these processes affect the morphology and properties of nanostructures synthesized using this approach. We will also discuss the effect that the choice of a salt precursor has on the evolution of a galvanic replacement reaction, as different morphologies have been observed when switching between a Au(III) salt and a Au(I) salt.

Finally, we will discuss some of the interesting optical properties and promising applications of structures fabricated using the galvanic replacement method. Due to the interaction between the plasmons of the inner and outer surfaces of a hollow structure, it is simple and convenient to tune the localized surface plasmon resonance (LSPR) peaks into the near-infrared (NIR) region for nanoparticles synthesized using the galvanic replacement reaction [23,24]. Structures with strong optical absorption in this region are ideal for a number of biomedical applications, as NIR light can penetrate significantly deeper into soft tissue than visible light [14–18,25–27]. Particles with thin walls can also show more sensitivity to their dielectric environment, an ideal property for sensing applications [24,28,29]. Though it is also possible to create hollow nanostructures with some of these properties by depositing small metal particles on the surface of a dissolvable template, this method is often limited by the difficulty of creating smooth, continuous shells with controllable thicknesses below 10 nm [30,31]. The resulting shells are typically less robust than those synthesized with the galvanic replacement reaction due to their polycrystallinity, and in some cases require additional synthetic steps, such as dissolution of the template [32].

In addition to biomedical applications, alloyed nanomaterials such as those generated with a galvanic replacement reaction also show great promise for catalysis—it has been shown that bimetallic nanostructures can be superior to their individual components for certain catalytic applications [4,33–36]. Galvanic replacement offers a simple and controllable way to produce multi-component nanostructures with enhanced porosity and surface area, and is thus well-suited for such applications [37–39]. Furthermore, some reports have shown enhanced catalytic capabilities with hollow nanoparticles, likely due to the high surface areas. For example, Pd nanoshells were shown to retain their catalytic ability for multiple cycles, unlike their solid counterparts, for organic reactions such as Suzuki coupling [40,41].

2. Template effects

2.1. Galvanic replacement between Ag nanocubes and $HAuCl_4$

A galvanic replacement reaction can be split into two half reactions, the oxidation/dissolution of a metal at the anode, and the reduction/deposition of the ions of a second metal at the cathode. For this reaction to occur, it is critical that the electrochemical potential of the metal ions is higher than that of the solid metal. The relevant equations for a typical reaction between Au and Ag are shown below:

Half reactions:

$$Ag^{+}{}_{(aq)} + e^{-}{}_{(aq)} \rightarrow Ag_{(s)} \qquad (0.80\,V\ vs.\ SHE) \tag{1}$$

$$Au^{3+}{}_{(aq)} + 3e^{-}{}_{(aq)} \rightarrow Au_{(s)} \qquad (1.50\,V\ vs.\ SHE) \tag{2}$$

Combined reaction:

$$Au^{3+}{}_{(aq)} + 3Ag_{(s)} \rightarrow Au_{(s)} + 3Ag^{+}{}_{(aq)} \tag{3}$$

The electrochemical potentials of a number of commonly used metals are shown in Table 1. Note that the potentials listed here are for ideal reactions at 25 °C and 1 atm, and that the elevated temperature of this reaction (100 °C), the presence of Cl^- ions, and other non-standard conditions can all affect the actual potentials [42,43].

In recent years, the synthesis of solid metal nanocrystals having a wide variety of shapes and sizes has been achieved through careful control of the reaction conditions such as temperature, the concentrations of trace ions, and surfactant choice [19]. Many of these nanocrystals can be used as templates for galvanic replacement reactions, making it possible to use this technique to synthesize hollow nanostructures with well-defined and controllable sizes and shapes. A typical example can be found in the reaction between Ag nanocubes and $HAuCl_4$. This reaction is

Table 1
Electrochemical potentials of relevant species relative to the standard hydrogen electrode (SHE).

Half reaction	E°/V vs. SHE[a]
$Ag^{+} + e^{-} \rightarrow Ag$	0.80
$Au^{3+} + 3e^{-} \rightarrow Au$	1.50
$Au^{+} + e^{-} \rightarrow Au$	1.69
$Pd^{2+} + 2e^{-} \rightarrow Pd$	0.95
$Pt^{2+} + 2e^{-} \rightarrow Pt$	1.18

[a] For ideal reactions at 25 °C and 1 atm. Elevated temperatures, the presence of ions, and other non-standard conditions can all affect the actual potentials [42].