

Advance in Synthesis of High Surface-to-Volume Gold Nanoparticles

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The synthesis of gold nanostructures with high surface-to-volume ratio has gained increasing interest for their high potential advantages in improving the efficiencies of drug delivering, biosensing, and catalyzing chemical reactions. To this end, researchers developed synthetic strategies to prepare nanoparticles with rough surface morphologies or hollow nanoshells through electrochemical methods, including layer-by-layer adsorption and subsequent removal. Among them, galvanic replacement was one of the most preferred and effective methods.¹

Galvanic replacement—first applied in the synthesis of gold nanostructures by Xia and coworkers in 2002—has been a promising synthetic method to prepare a variety of hollow-shell structures, including nanospheres, nanocubes, nanoprisms, and others.² A galvanic replacement reaction can be simplified as a simultaneous exchange between sacrificial inorganic nanocore templates (Ag, Ni, Cu, etc.) and metal cations of interest (Au, Pd, Pt, etc.), based on the differences in their standard reduction potentials. Albeit all the efforts to afford an easy solution-phase procedure for synthesizing high surface-to-volume nanoparticles, there still exists a problem: insoluble bi-products are formed from dissolved template metal cations and counter anions in replacing salt, and they cover the surface of forming nanostructures irregularly, which causes differences in relative diffusion rates of the ion species, and in turn interrupts the formation of mono-disperse and homogeneous hollow nanoshell structures.³

To improve the typical hollow nanoshell structures, many challenges have been recently tried to get more sophisticated functional structures, such as clustered, porous, anisotropic, and combination of them based on the galvanic replacement reaction. One of the hottest approaches was performing a galvanic replacement in the presence of surfactant molecules, such as cetyltrimethylammonium halides and polyvinylpyrrolidone (PVP). These types of controlled galvanic replacement have been recently reilluminated, and the mechanism and the driving force of them were reported as local quenching and a diffusion interruption by the surfactant molecules. In these reports, the formation of well-controlled core-shell structures⁴ or anisotropic high-ordered nanostructures including heterodimer,^{5,6} multimer,^{6,7} popcorn-shaped exterior surface growth and rough surface morphologic hollow

structures⁸ were achieved by a kinetic control or competitive galvanic replacement under the existence of surfactants, respectively.

Although all these approaches are indeed helpful to prepare anisotropic and functional nanostructures, they require delicate control and a stoichiometric reaction condition to prepare the desired structures. In addition, using cytotoxic surfactant can be potentially problematic in their bio-applications.

Recently, Jang and Min reported the robust and facile synthesis of spherically clustered porous gold nanoparticles by using an inhibitory galvanic replacement reaction of PVP-coated silver nanoparticle (AgNPs) with tetrachloroaurate anion (AuCl_4^-) and a subsequent etching process (Figure 1(a)).⁹ Here, PVP contributed the polyol synthesis of sacrificial AgNPs and further acted as a surface protecting polymer shell against the formation of insoluble sediment on the template surface during the galvanic replacement reaction. They carried out the replacement reaction at an unpreferably low temperature, at which the deposition of insoluble AgCl actively occurred onto Ag surface near the reaction region, which locally quenched the replacement reaction by competing with it. The spherically clustered porous gold nanoparticle was finally prepared by a subsequent etching process for revealing embedded spherically clustered nanostructure through the dissolution of remaining Ag and AgCl sediment (Figure 1(b)).

The spherically clustered porous gold nanoparticles exhibited several distinct physical properties originated from their structural features. For instance, nitrogen adsorption measurements showed that the averaged surface area and the volume of pores were around threefold larger than those of the conventional hollow nanoshell structures with the same diameter (Figure 1(c)). Because of their porous but packed configuration, spherically clustered porous gold nanoparticles presented a large red-shift (around 826 nm) in surface plasmon resonance spectra, which was consistent with other hollow or anisotropic nanomaterials. This red-shifted absorption band could arise from the partially linked and clustered nano-network, like other similar cluster-structured plasmonic nanoparticles.¹⁰ The near infrared absorption feature made it possible to apply the spherically clustered porous gold nanoparticles in heat generation mediated by photo-thermal conversion for various biomedical applications

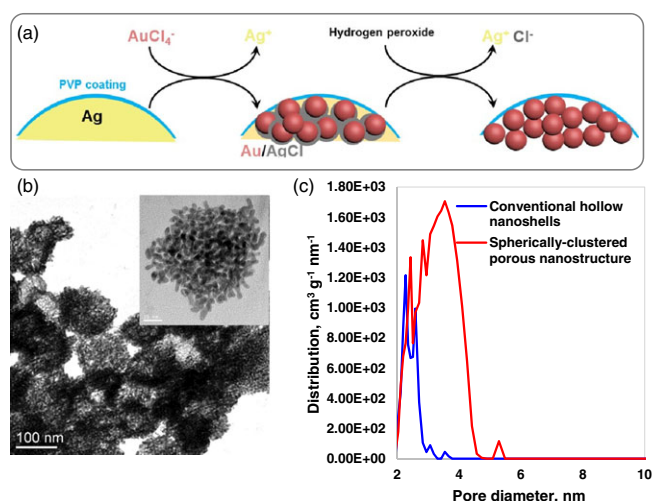


Figure 1. (a) Schematic illustration of the synthesis of spherically clustered porous gold nanoparticles. (b) Transmission electron microscope images showing the porosity of the synthesized nanostructures (the inset shows a lower magnification image). (c) Plot of the pore diameters of previously reported hollow nanoshells and spherically clustered porous nanostructures. Reprinted with permission from Ref. 9. Copyright 2015 American Chemical Society.

including light-triggered cargo releasing and photothermal cancertherapies.

The authors also successfully demonstrated a multiple drug delivery—as a biomedical application of the nanostructures—by using two distinct strategies. One was the delivery of an anti-cancer small molecule doxorubicin by using an acid-triggered breakable imine linkage formed by chemically treating the remaining coated PVP films and the other was the delivery of fluorescently labeled thiolated oligonucleotides (DNAzymes used in this study) by affinity adsorption of functional thiol end-group onto the surface of exposed gold nanopores (Figure 2(a)). Due to the greatly increased surface area and pore volume, the amount of oligonucleotide (a relatively bulky burden) delivered by the spherically clustered porous gold nanoparticles was 10 times larger compared with that of the conventional hollow nanoshells. Using present exceptionally high-payload cargo delivery platform enabled the efficient delivery of oligonucleotides (Figure 2(b)). Combined with the aforementioned photothermal conversion property, spherically clustered porous gold nanoparticle-based chemo-thermo-gene cancer therapy showed a highly efficient ablation of cancer cells.

In summary, robust protective polymer coating of sacrificial nanocore and their taboo low temperature galvanic replacement with subsequent etching enabled the formation of noble high surface-to-volume porous gold nanoparticles. The authors demonstrated a successful application of these nanostructures to drug delivery and cancer therapy. This etching-mediated post-synthetic transformation method

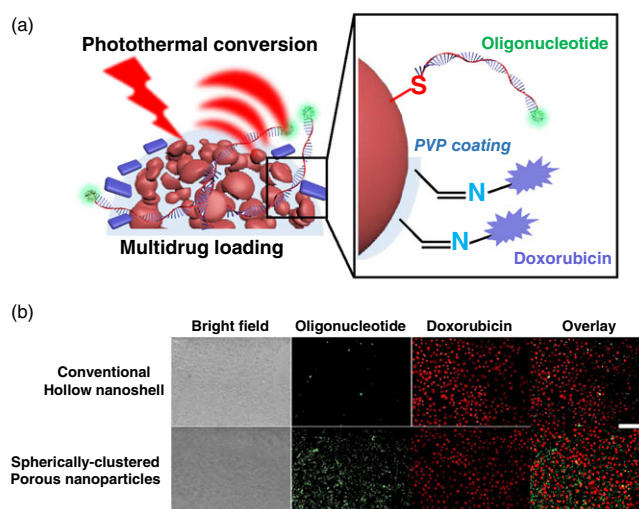


Figure 2. (a) Schematic illustration of a multiple drug loading strategy. (b) Comparison of cargo-delivering abilities against human hepatocarcinoma cells between conventional and the newly synthesized nanostructures. Reprinted with permission from Ref. 9. Copyright 2015 American Chemical Society.

provides a more convenient and facile route to prepare high surface-to-volume gold nanoparticles, and emphasizes the need for reconsidering the importance of embedded nanostructures, which have been regarded “useless” conventionally. The reported porous structures have sufficient nanogaps and clustered conformation, with which we envision their potential to be utilized in various applications including surface-enhanced Raman spectroscopy and gold nanocatalysts.

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