

Recent Advances in Nanoparticle Shape and Composition Regulation Based on Galvanic Replacement for Cancer Treatment

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Abstract

Owing to their unique physicochemical properties, nanoparticles are used in a variety of ways in the field of cancer treatment, including imaging, drug delivery, and photothermal and photodynamic therapies. The fascinating properties of nanoparticles are determined by their size, morphology, and constituent elements, and various synthetic methods and post-synthetic techniques have been applied to control these factors. Herein, we present examples of shape and composition control through galvanic replacement, a technique that exploits redox potential differences between elements to induce spontaneous ion-exchange and highlight its specific contributions to cancer treatment applications. The present article identifies the recent advances in nanoparticle formation techniques and discusses the future outlook of the field.

1. Introduction

Cancer is regarded as one of the most critical diseases because of the few early signs and metastasis to other organs. Therefore, its prevention and early diagnosis are very important academically, socially, and economically [1-7]. Unfortunately, cancer has a poor prognosis and it is difficult to diagnose early, except through regular health checkups [8-12]. Thus, effective and successful treatment of cancer has long been established as a more practical and essential research field. As conventional cancer treatments, surgery and chemotherapy are the most representative and widely used treatment strategies. In the case of surgery, effective treatment, even for mid-

and late-stage cancer, is possible through cancer tissue extraction, but this strategy presents numerous drawbacks, including its very invasive nature and the risks during surgery [13]. Chemotherapy can also be used in conjunction with surgery or long-term medication, but the high cost, severe side effects of anticancer drugs, and sequelae are problematic [14-16]. Accordingly, several new cancer therapies have been developed, including controlled drug delivery [17-20], photothermal therapy [21-24], and photodynamic therapy [25-28], and these strategies are attracting considerable attention as promising cancer therapies.

These next-generation cancer treatment techniques are being implemented using various nanoparticles to maximize the treatment efficiencies. The term “nanoparticles” generally refers to small metal or non-metallic objects with diameters in the 1–1000 nm range [29,30]; diameters within 200 nm are generally required for biomedical applications such as drug delivery and photoinduced therapies [31-35]. Such nanometer-scale materials exhibit physicochemical properties that are very different from those exhibited by everyday materials. For example, Au is a glossy metallic substance as a bulk material, but Au nanoparticles have various colors owing to surface plasmon resonance [36,37] caused by the quantum confinement effect [38-40]. Numerous studies have been performed in the field of cancer treatment using nanoparticles because of the dependence of their unique characteristics and efficiencies on their shape [41-45], size [46-50], and composition [51-54]. Among them, Au nanoparticles have been established as the most effective and promising nanomaterials for many decades owing to factors such as biocompatibility [55-60], colloidal stability [61-64], and drug loading capacity [65-67], which are essential criteria for therapeutic applications.

In this review, we introduce recent research trends and achievements in the regulation of nanoparticle shape and composition, which present new possibilities in nanoparticle-based cancer treatments that depend on nanoparticles of definite compositions and shapes.

2. Galvanic replacement

Galvanic replacement, first reported by Xia's group in 2003, involves spontaneous metal element exchange reactions between sacrificial nanoparticle templates with lower standard reduction potentials and metal cations with higher standard reduction potentials [68]. Generally, Ag [69-85], Cu [86-91], and Ni [92-95] are used as template nanoparticles, and Au, Pt, and Pd are used as replacing cations by selecting the appropriate reduction potential difference. During the galvanic replacement reaction, the replacing metal cation approaches the template

surface and triggers a spontaneous redox reaction to achieve reduction and deposition on the external surface of the template. As a counter reaction, the template elements are oxidized and dissolved into solution maintaining stoichiometric electron balance. Since core-shell or hollow nanoshell structures can be selectively synthesized by exploiting the stoichiometric electron balance, galvanic replacement is regarded as suitable for the formation of specific three-dimensional (3D) nanostructures [96-103]. However, there are some drawbacks to conventional galvanic replacement. First, excessive replacement causes fragmentation or aggregation because of uncontrollable replacement after the formation of a nanoshell [104,105]. Second, insoluble byproducts such as AgCl are formed by the dissolved template element (Ag^+), and the counter ion of the replacing cation (Cl^-) is deposited on the surface of the particles, reducing colloidal stability [106-108]. Recently, research into galvanic-replacement-mediated nanostructure formation has been performed extensively in order to overcome these shortcomings and increase the pool of applicable elements.

2.1. Conventional shape control by galvanic replacement

Since the development of galvanic replacement, its most common application has been the formation of hollow nanocages with interior vacancies. Hollow nanocages exhibit fascinating characteristics, in that their localized surface plasmon resonances (LSPRs) shift to the near-infrared (NIR) wavelength region owing to the narrowing of the energy gap between the anti-symmetric anti-bonding resonance modes and the symmetric bonding resonance modes depending on shell thickness and diameter [109-118]. These high-extinction features in the NIR region induce strong exothermic phenomenon caused by the surface plasmon oscillation through laser irradiation in the corresponding wavelength range, which is often referred to as photothermal conversion [119-133]. In cancer treatment, photothermal conversion is highly efficient in killing cancer cells vulnerable to hyperthermia. Furthermore, the NIR-region absorbance endowed by the hollow nanocage structures corresponds to the photothermal therapeutic wavelength window, which does not overlap with the light absorbing region of substances in the body such as hemoglobin, fat, and water. Since the tissue penetration of NIR light is superior to that of visible light and ultraviolet rays, it presents huge advantages when combined with hollow nanoparticles [134-143].

2.1.1. Hollow nanoshells

To maximize NIR absorption characteristics, template nanoparticle morphology control has been achieved to obtain hollow nanoshells of various shapes. Since the first report of Au nanocages synthesized from Ag nanocubes, various hollow Au nanoshell structures have been prepared using Ag nanospheres [144-155], Ag nanorods [156-159], Ag nanowires [160], and even Ag islands on two-dimensional surfaces as templates [161]. The LSPR red-shift due to the formation of a hollow nanostructure leads to efficient photothermal conversion under laser irradiation, which is observed to be excellent for all these hollow structures. By applying the same galvanic replacement method to different templates, hollow nanocages, hollow nanoshells, hollow nanorods, hollow nanowires, and even hollow dendritic structures can be obtained very easily. Furthermore, this technique is not limited to Au. Of course, hollow Au nanostructures are used for various biomedical applications including cancer treatment because of their high biocompatibility and excellent LSPR efficiencies, but it can also be applied to Pt [162-166] and Pd [167-170], which have higher reduction potentials than the template Ag. In addition to these widely used photothermal therapies, bioconjugation and optical contrast agents for bioimaging have been studied as applications of hollow Au nanostructures. Along with the primary formation of simple hollow nanoshells, various post-synthetic processing techniques have been developed to improve optical efficiency and control the absorption wavelength range, making it more suitable for use. One of the most interesting approaches is the formation of hollow multi-shell structures through repetitive galvanic replacement using the preferentially formed hollow nanoshell itself as a secondary template, rather than simply controlling the size or thickness of the nanoshell. The surface of the formed initial structure is coated with an Ag shell through reduction of Ag cations by a reducing agent, and then galvanic replacement is performed to form a hollow nanoshell [171]. This process can be repeated as many times as desired to form a multi-shell structure, and additional LSPR shifting with optical density enhancement can be achieved based on the difference in electron distribution inside and outside the nanoshell. Thus, more optical efficiency can be expected from the same number of particles. Furthermore, such multi-shell structures exhibit high applicability. However, relatively few practical studies on such systems have been conducted due to the inconvenience of repeated syntheses and purification.

2.1.2. Nanoframes

A nanoframe is a type of skeletal nanostructure based on galvanic replacement and is often distinguished from hollow nanostructures. This category includes not only 3D skeletal nanostructures that are structurally similar to nanocages but also annular planar nanostructures. Planar nanoframe structures that are distinct from the

previously described nanocages can be achieved through essentially the same galvanic replacement, but they are specific nanostructures that are only obtained from specific types of Ag nanotemplates. Theoretically, a 3D template with a height dimension along with a basal plane forms a cage-like structure including hollow nanoshell derivatives. However, templates with relatively short height that do not tolerate structural transformation during galvanic replacement form edge-replaced and basal-plane-dissolved nanostructures, which are often referred to as ring-shaped nanostructures. The most commonly used templates are round-shaped Ag nanodisks [172-175] and Ag nanoplates [176-179] or nanoprisms [180-185], which form nanorings and nanoframes, respectively. Although there are various types according to shape, they all have in common excellent NIR photothermal conversion efficiencies, which is advantageous for *in vivo* cancer treatment, and are easy to load with relatively bulky cargoes both inside and outside due to their surface opened skeletal nanostructures. In addition, unlike hollow nanoshells, which are formed from the dissolution of relatively large amounts of template Ag, unintended cytotoxicity derived from dissolved Ag and reactive-oxygen-species generation are minimized. Therefore, nanoframes are more suitable for *in vivo* biomedical applications owing to their higher biocompatibility. However, research into the general application of nanoframes is still in its initial stages because precise reaction conditions are required for their synthesis. Currently, nanoframes themselves are used as templates to provide desired functionality and characteristics by secondary growth or transformation.

2.2. Extended shapes by modified galvanic replacement

Beyond the drawbacks in nanostructure formation by conventional galvanic replacement, such as nanostructural collapse and aggregation under stoichiometric overdose, template surface poisoning by precipitation of insoluble adducts, and the limited number of element pairs suitable for spontaneous redox reaction, numerous efforts are underway to address the current limits. The introduction of new nanostructures suitable for cancer treatment through galvanic replacement has been achieved through these various attempts, and several chemical principles and possibilities are discussed herein.

2.2.1. Porous nanostructures

Porous nanoparticles of metal oxide nanomaterials such as mesoporous silica (SiO₂) [186-193], and mesoporous titania (TiO₂) [194-199] have been extensively studied owing to their facile template assisted

formation. In the case of noble metal nanoparticles, no methods for the controlled synthesis of porous nanostructures have been established owing to the need for reducing-agent-mediated synthetic strategies and the importance of crystallinity. Nonetheless, because of the extremely high surface-to-volume ratios and structural advantages of porous nanostructures, the development of new synthetic methods for noble metals has been a subject of increasing interest [200-211]. The synthesis of porous Au nanoparticles using Ag nanospheres was first achieved through an extended synthetic strategy called inhibitory galvanic replacement. In inhibitory galvanic replacement, the formation of the AgCl adduct, which is a byproduct of conventional galvanic replacement, is intentionally maximized through a low-temperature reaction in order to partially block the replacement reaction [212]. Then, the embedded Au structures are revealed through the addition of excess hydrogen peroxide, which is an effective etchant for Ag and AgCl. As a result, spherically clustered porous Au nanostructures are obtained and, because of their partially connected clustered structures, an entire LSPR band in the visible-NIR range that is suitable for photothermal cancer treatment appears. In porous Au nanoparticles synthesized by inhibitory galvanic replacement, nitrogen adsorption analysis reveals a pore diameter of ≈ 3.4 nm, which implies that oligonucleotides can be effectively loaded and delivered. Porous Au nanoparticles exhibit significantly enhanced gene delivery efficiency compared that of hollow Au nanoshells, which have been used in conventional studies, in the loading and delivery of the small anticancer compound doxorubicin and fluorescently labelled oligonucleotides. This represents the conversion of AgCl adduct precipitation, which is regarded as a drawback of conventional galvanic replacement, to a positive phenomenon, and it is expected that various further applications of the advanced nanostructures formed will be possible.

Structural transformation can vary widely depending on the type of template nanostructure employed and can lead to dramatic differences for flat-surface containing nanostructures such as nanocubes and nanoplates with a high surface-to-volume ratio that enables rapid galvanic replacement. An example of nanoplate-based porous nanostructure formation and cancer treatment is provided by a new synthetic method that is an improvement of conventional galvanic replacement [213]. Conventionally, galvanic replacement of nanoplates is known to result in nanoframes or nanorings, in which all internal spaces are removed, rather than hollow nanoshells, and excessive cation addition causes fragmentation, as in other cases. The disadvantage of spatial structures can be overcome by regulating the competition between replacement and regrowth rate through the addition of various reducing agents, such as L-ascorbic acid, during the galvanic replacement process. The galvanic replacement takes precedence over the initial high concentration of replacing cations, forming a

nanoframe-shaped secondary template, and the depletion of the replacing cation through galvanic replacement shifts the reaction equilibrium to regrowth, resulting in surface growth from the secondary template. This surface growth is attributed to the fact that the reducing agent in the solution forms a partially reduced replacing cation species, which can lead to nondestructive structural transformation, even in excess conditions. This reducing-agent-assisted galvanic replacement forms porous Au nanoplate structures, which exhibit high absorption in the NIR region. Through the optical properties of porous Au nanoplates and the high affinity between thiolated cargoes and the Au surface, thiolated-oligonucleotide loading/releasing and photothermal cancer treatments based on NIR laser irradiation have allowed combinational gene-thermo cancer therapy to be accomplished with excellent efficiency.

As discussed above, additional reaction modulation factors such as temperature, post-synthetic etching, and reductive additives have allowed the formation of porous Au nanostructures that could not be synthesized with conventional galvanic replacements. Porous Au nanostructures have a higher surface-to-volume ratio because of surface roughness compared to similar structures having smooth surfaces, leading to enhancement of the overall absorbance characteristics in the UV-Vis-NIR region by their networked substructures. As a result, it is possible to induce the photothermal conversion effect by light irradiation of various wavelengths, and it is advantageous to selectively apply an NIR wavelength suitable for photothermal cancer treatment. Moreover, based on their structural specificity, they are more appropriate for gene delivery than Au nanorods or nanocages, which have been the most common candidates for cancer treatment. The only disadvantage of these porous nanostructures is the difficulty in quantifying the number of nanoparticles in solution. Replacement and regrowth have been competitively accomplished to form monodisperse but irregular nanostructures, meaning that accurate quantification techniques have not been developed, unlike for well-ordered nanospheres, nanorods, and nanocubes. It has been assumed that the Ag template used is completely transformed into the desired nanostructure without disappearing during galvanic replacement, and its concentration has been quantified. Further studies on this will provide major contributions to biomedical applications that have large concentration effects. Despite these present disadvantages, porous nanostructures have received a great deal of attention recently in many research fields owing to their extremely high surface-to-volume ratios and unique physicochemical properties, and the same is true for cancer treatment.

2.2.2. Anisotropic nanostructures

Anisotropic metal nanoparticles are considered to be of interest in variety of applications because of their various physicochemical properties resulting from their structural specificity, which is also a key feature in cancer treatment. The most common examples are nanostars, sea-urchin like nanoparticles, and nanoworms, and various functionalities such as photothermal therapeutics, surface enhanced Raman scattering (SERS), and magnetic resonance (MR) imaging are possible depending on the constituent metal elements [214-221]. In general, the synthesis of anisotropic nanoparticles is controlled by regulatable molecules including solvents, surfactants, peptides, and polymers through diffusion rate and growth kinetics modulation. Here, we introduce the synthesis and cancer-treatment applications of anisotropic nanoparticles formed by galvanic replacement.

Because galvanic replacement is a reaction based on spontaneous element exchange and growth in heterogeneous systems, the diffusion and approach of metal cations, which can affect these factors, is regarded as a major concern. In this regard, a rough mechanism has been revealed through various structure formation tendencies depending on pH, temperature, and additives. However, because of the contribution of numerous critical factors, it is difficult to develop a precisely designed synthetic method. According to Zhang et al., the interaction between a Cu template and the replacing Pt can be confirmed by the fact that the size and number of hollow voids, which are the most important features of nanostructures formed through galvanic replacement, can be varied depending on pH and the presence of the surface-stabilizing polymer PVP [222]. These adjustments result in the formation of nanoboxes, heterodimers, multimers, and popcorn-shaped hollow voids. These are interpreted as a result of diffusion rate control, which affects the redox reaction between the template and the replacing cation. Although the nanoparticles formed are not utilized in practical biomedical applications, approaches based on the diffusion rate as a core mechanism from the viewpoint of functionally enhanced nanoparticle formation encompass several possibilities. Diffusion contributes to the number of collisions between metal elements for replacement, but it also has an important effect on the directionality of the structure being formed and extended. This is related to the Kirkendall effect at the interface between the formed metal and the alloy. Depending on the geometry of the voids formed and the contact type, the formation of porous or rough surfaces or the formation of conventional nanocages are determined. Furthermore, it is possible to confirm that a dendritic nanostructure is formed through position-limited diffusion control where the replacing cation contacts for replacement. However, if the focus is on the physicochemical and optical properties to be derived, these kinds of structures may be more suitable for biomedical applications than conventional hollow nanostructures.

Another interesting approach to the manufacture of anisotropic nanoparticles for cancer treatment is

partially polymer-coated Au nanoworms [223]. The nanostructures formed by the excessive galvanic replacement of a Ag nanoparticle template coated with the biocompatible polymer dextran are formed in a way by which the whole connection structure is maintained but the spherical structure is destroyed. This non-conservative replacement forms a complex nanostructure that is partially covered with a dextran shell with the remainder being an exposed bare Au surface. The independent structures of the bare Au surface and partial dextran shell can be applied to chemotherapy separately. Chemical affinity-based loading of a thiolated-cargo on the exposed Au surface and chemical bonding-based loading exploiting the abundant hydroxyl functionality of dextran allows the simultaneous loading of two different therapeutic cargos onto the nanostructure. In addition, NIR plasmonic photothermal conversion by the anisotropic nanostructures results in excellent efficacy in combinational cancer treatment using hyperthermic therapy.

As the series of examples above shows, studies on the formation of anisotropic Au nanostructures and sophisticated Au nanostructures using modified galvanic replacement have been actively conducted. Based on the physicochemical properties derived from the structures, various application techniques have been devised that are significantly different from those available with conventional hollow nanoshell or nanocage structures. The synthetic advantage of being able to form high-order nanostructures without the use of toxic surfactants facilitates their application in numerous application fields. Many cancer-treatment studies have been conducted based on their excellent photothermal conversion and therapeutic cargo payload capabilities.

3. Composition control by galvanic replacement

Research on the synthesis of nanoparticles of various shapes and compositions has attracted much attention because composition contributes to the physicochemical properties of the particles as much as morphology. However, the synthesis of nanoparticles with the same morphology and size but with different constituent elements cannot be achieved easily because of various factors such as the crystal structure, atomic size, and electron configuration of each element. Galvanic replacement has been widely applied to the formation of such nanoparticles owing to its template-based elemental replacement reaction manner.

3.1. Platinum-group elements

In general, Ru, Os, Rh, Ir, Pd, and Pt are referred as platinum-group elements. Ag is most commonly used as a template for galvanic replacement because it forms various structures easily and is cheap. Only Au, Pd, and Pt can be applied under ambient conditions for voluntary redox replacement of Ag. However, in order to provide more scope for structural formation and the applications of galvanic replacement, there is a need to expand these element pairs, and the most important candidate is the platinum group source used in various fields, including catalysis. Because platinum-group nanoparticles are known to exhibit UV-restricted LSPR spectra and are relatively expensive and toxic compared to Au-based nanoparticles, their application to biomedical applications is relatively restricted. However, some recent studies have reported interesting properties in the case of porous Pt and Pd nanoparticles, such as efficient light absorption in the visible and NIR wavelength region. This suggests that new possibilities for platinum-group elements may be developed if systematic and quantitative research is supported. Recently, quantitative comparisons of these possibilities have been made through the formation of porous Au, Pt, and Pd nanoplates through reducing-agent-assisted excessive galvanic replacement [224]. For example, Kang et al. compared the cytotoxicities, gene loading efficiencies, photothermal conversion efficiencies, and combinational cancer treatment applicabilities of porous nanoplates composed of Au, Pt, and Pd with similar sizes and morphologies prepared using the same Ag nanotemplate. Interestingly, Pd was superior to Au, which was previously considered to be superior in all ways. Even in terms of price, Pd is cheaper than Au, which means that in future cancer treatment research based on nanoparticles, more attention should be paid to new element-based approaches beyond established norms.

Another example of the galvanic replacement of Ag templates by platinum-group elements is the specific response of Rh. Since Rh^{3+} exhibits a lower standard reduction potential than that of Ag, conventional galvanic replacement cannot occur under ambient conditions. However, in two recent cases, Cu template mediated galvanic replacement [225-228] and a spontaneous response was derived using Nernst-equation-based reasoning by controlling the temperature and concentration so that the whole cell voltage was positive [229]. This approach allowed the formation of hollow Rh nanoshells, Rh nanoframes, and porous Rh nanoplates, respectively. Furthermore, the biomedical potential for Rh nanoparticles, which is widely used in conventional hydrogen generation catalyst applications, has been demonstrated. It is important that there are no biological study results regarding the cytotoxicity of Rh owing to the current limitations of its application. According to *in vitro* and *in vivo* analyses, Rh nanoparticles formed through inverse galvanic replacement showed biocompatibility and photothermal conversion efficiency comparable to those of Au [229]. In actual cancer treatment applications,

photothermal therapy was performed after conjugation with TAT, which is a cell-penetrating peptide, allowing introduction into cells and cancer tissues. Although there has been no application to actual cancer treatment, galvanic replacement with other platinum-group elements has received some attention recently. However, only galvanic replacement of Ru, Os, and Ir using a Cu template because of their low reduction potentials is known, and physicochemical characterization and potential verification of these are currently insufficient. As in the case of Rh, the application to biomedical applications, including cancer treatment, of platinum-group elements has tremendous possibilities [230-235]. Consequently, a suitable synthetic platform and systematic analysis are urgently required.

3.2. Other transition metal elements

Unlike general galvanic replacement, which requires a metal templates such as Ag, Cu, and Ni, a new approach using metal oxides as a template was first reported in 2013 by Hyeon et al [236]. In this pioneering work, a hollow bimetallic oxide nanoparticle was produced by post-synthetic transformation using the oxidation-reduction reaction between oxidized water, taking into account that the transition metal may have various oxidation forms. Although not directly applicable to biomedical applications, Mn and Fe used in the study have potential as MR imaging contrast agents and magnetic properties that allow site-specific concentration *in vivo* [237-242]. Based on the myriad of transition-metal nanoparticles present in the form of metal oxides and the ability to mass-synthesize them, this approach is an example of extended galvanic replacement and can be viewed as a new and feasible approach for the future.

4. Conclusion

Synthesis of various interesting nanostructures through galvanic replacement and cancer treatment based on drug delivery and plasmonic photothermal therapy have been introduced. The development of methods for structurally and compositionally regulated nanoparticle synthesis is regarded as a key element for future nanotherapeutics and improving the safety and efficiency of nanoparticle mediated cancer treatments. To this end, galvanic replacement, which is used to synthesize complex structures via an environmentally friendly and convenient procedure, has reached beyond what was thought possible through continuous improvement. Many of the metal elements that form nanoparticles are not being exploited in biomedical applications because of factors

such as high-price, toxicity, and instability. However, by introducing the possibility of overcoming these general disadvantages through the regulation of structure and composition, we believe that continuous interest and research will bring new vitality to the field of biological research including cancer treatment.

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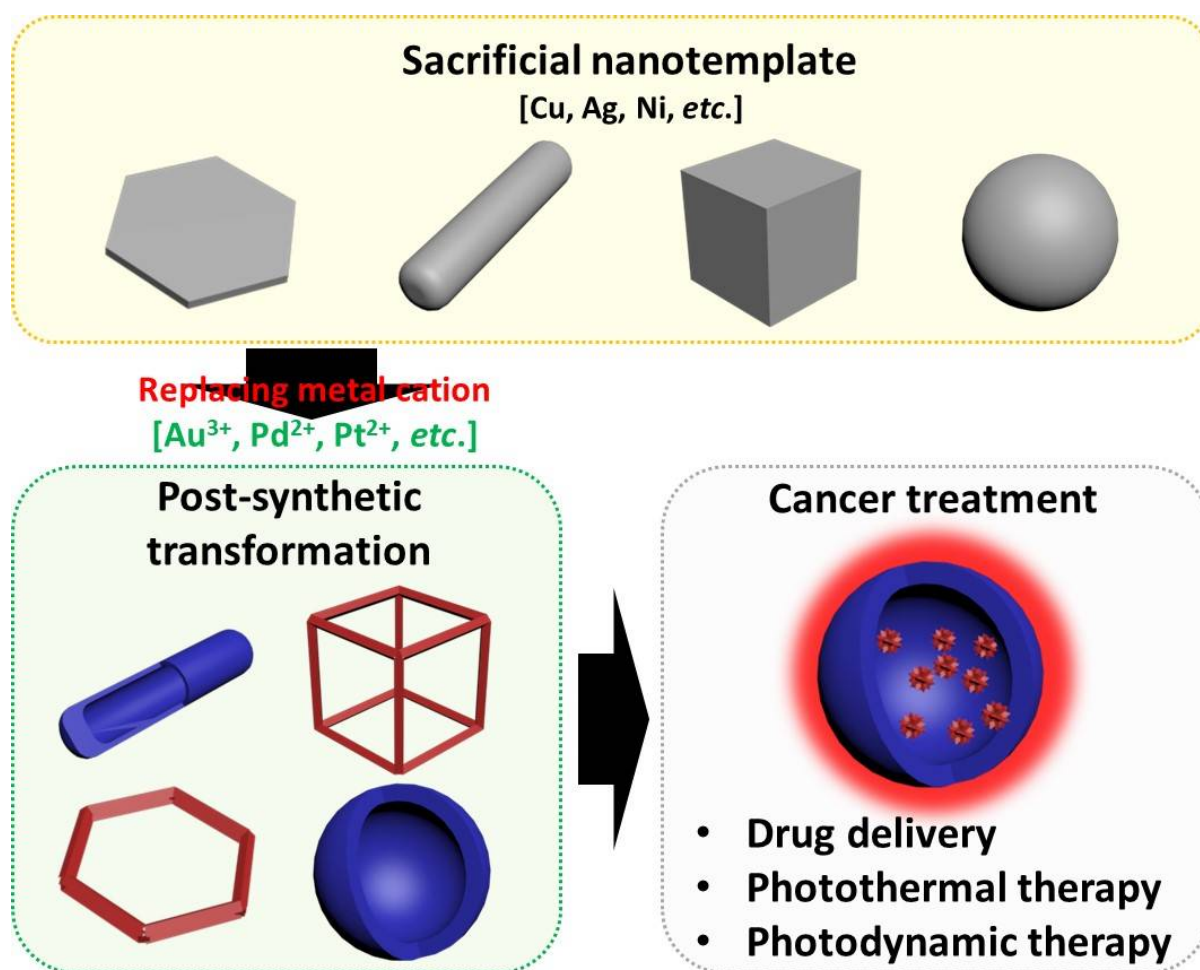


Figure 1. Overall scheme of galvanic replacement mediated post-synthetic transformation of nanoparticles and their potential application in cancer treatment by using advantages in drug delivery, photothermal therapy, and photodynamic therapy.

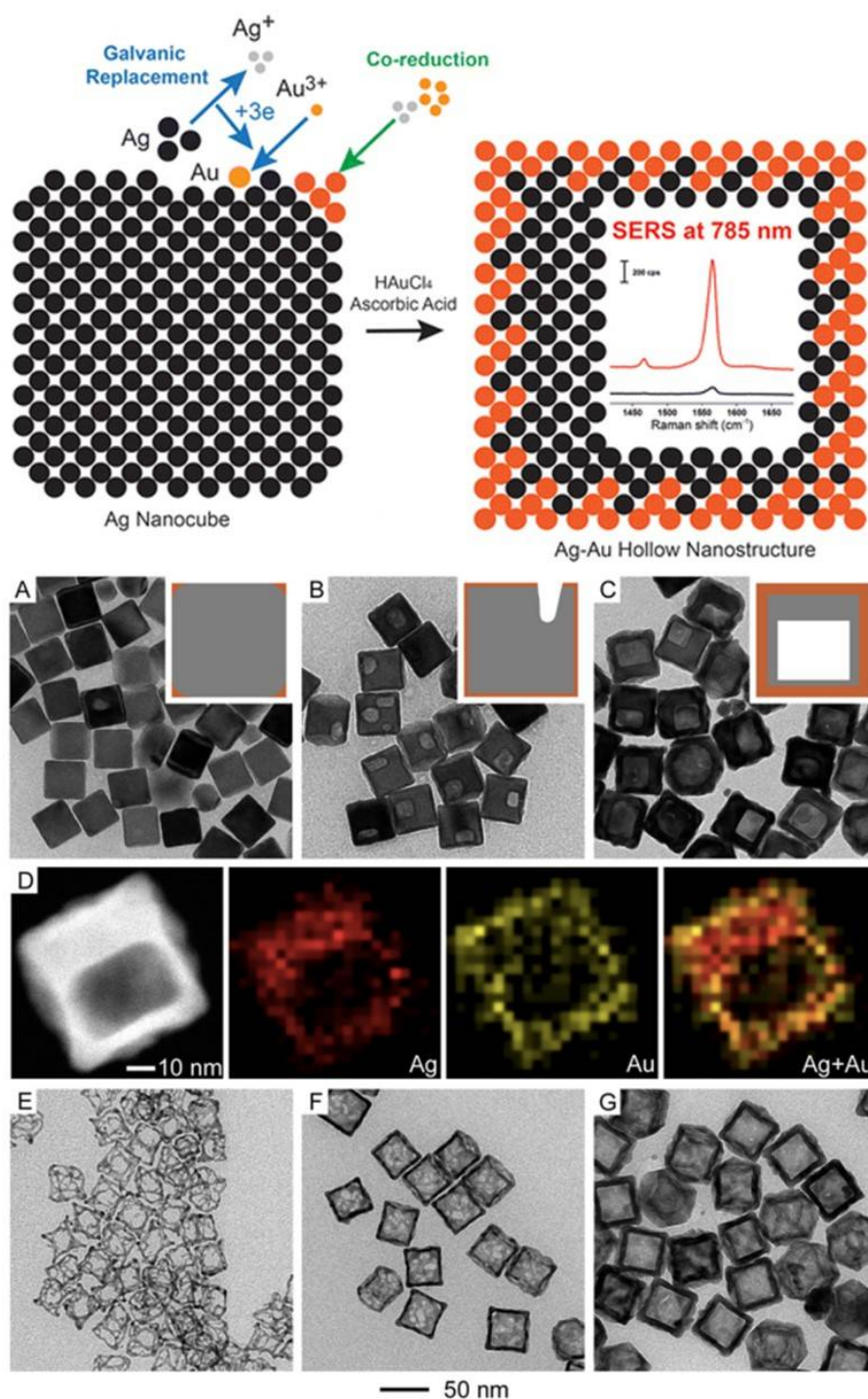


Figure 2. Ag nanocube template based galvanic replacement to manufacture hollow nanocage and nanoframe. Schematic illustration of ascorbic acid assisted galvanic replacement and their potential application in SERS (top). Different volume of replacing Au(III) addition in the presence of ascorbic acid: (A) 0.05, (B) 0.2, and (C) 0.6 mL. (D) HAADF-STEM/EDX mapping of 0.6 mL Au(III) condition. (E-G) TEM images of nanostructures from subsequent etching with H_2O_2 . Reprinted with permission from ref.70. Copyright © 2014, American Chemical Society.

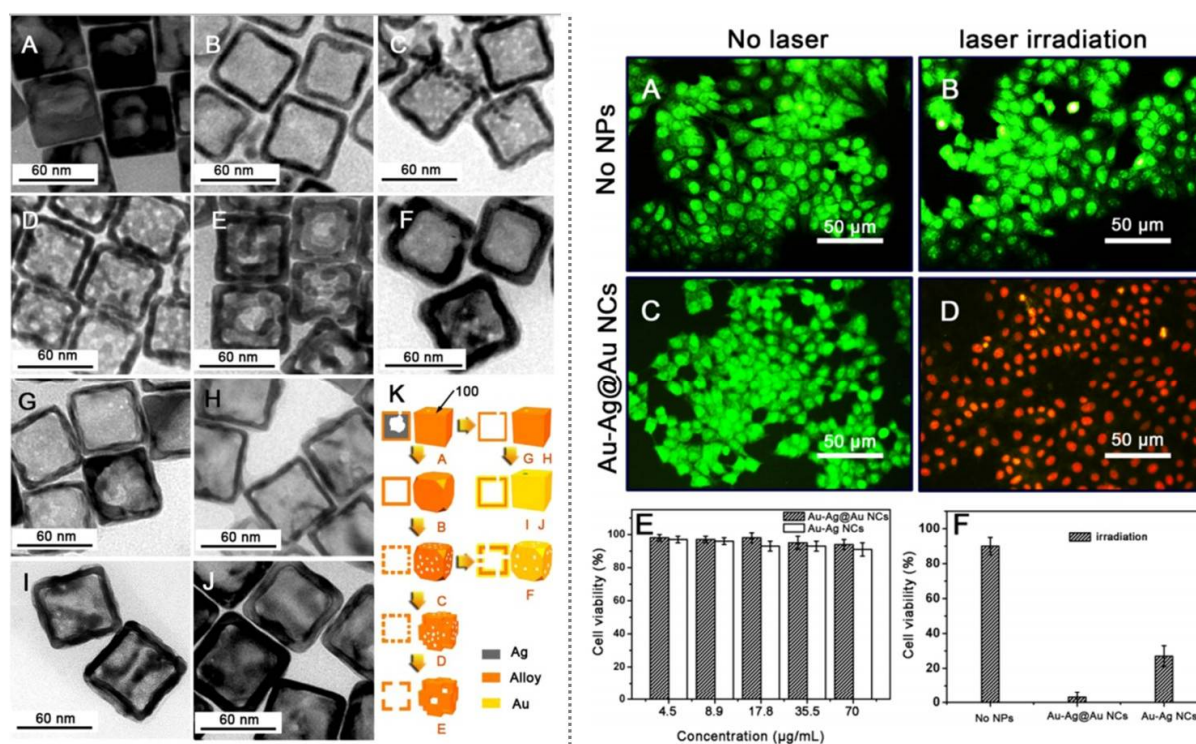


Figure 3. TEM images of Ag nanocubes after reaction with different volumes of Au(III) with their schematic illustration (left from dotted line). Comparison of photothermal destruction of MCF-7 breast cancer cells without (A,B) and with (C,D) the incubation of PEGylated nanoshells. (E) cell viability of MCF-7 cells after incubation with nanoshells and (F) with laser irradiation (right from dotted line). Reprinted with permission from ref.121. Copyright © 2015, American Chemical Society.

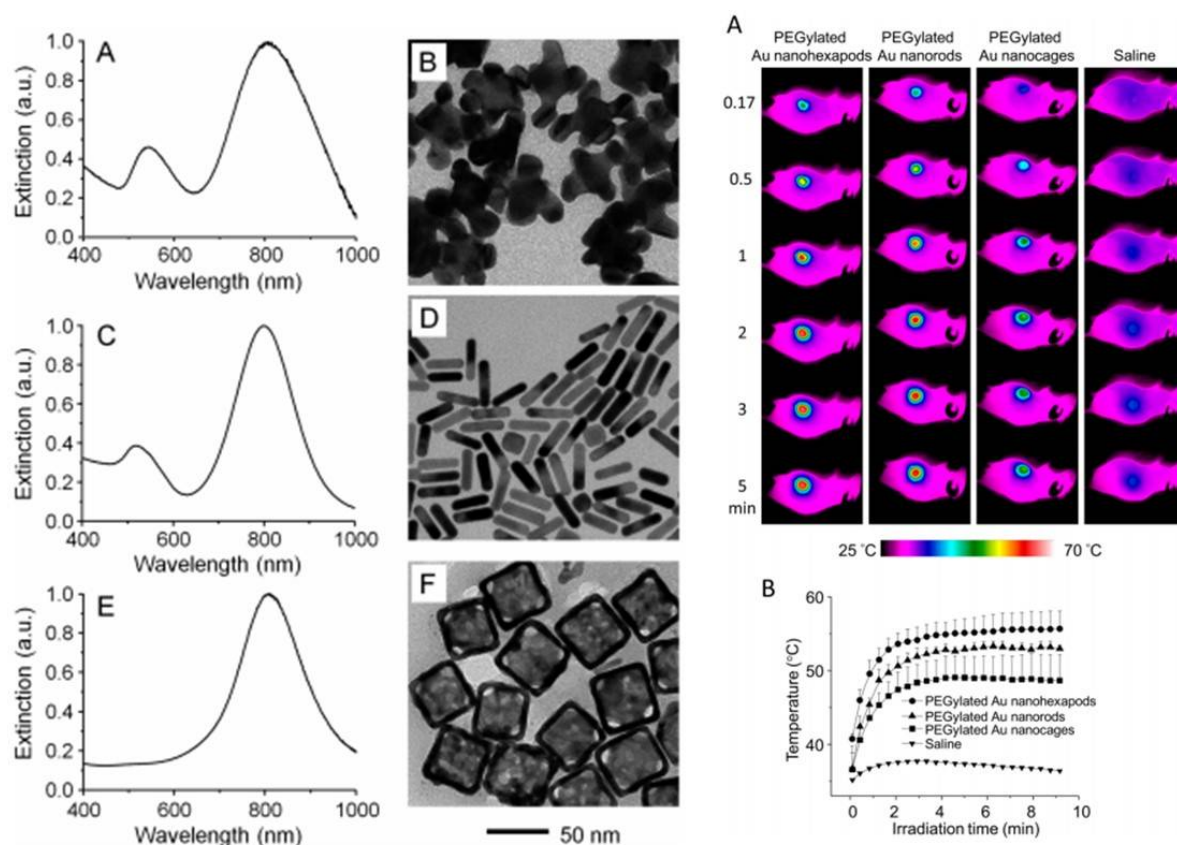


Figure 4. UV-Vis spectra taken from aqueous suspensions of (A) Au nanoheptapods, (C) Au nanorods, and (E) Au nanocages with their TEM images (B,D,F), respectively. Thermographs of tumor-bearing mice receiving photothermal treatment for different periods of time with each nanostructures (A, right) and measured temperature elevation (B, right). Reprinted with permission from ref.138. Copyright © 2013, American Chemical Society.

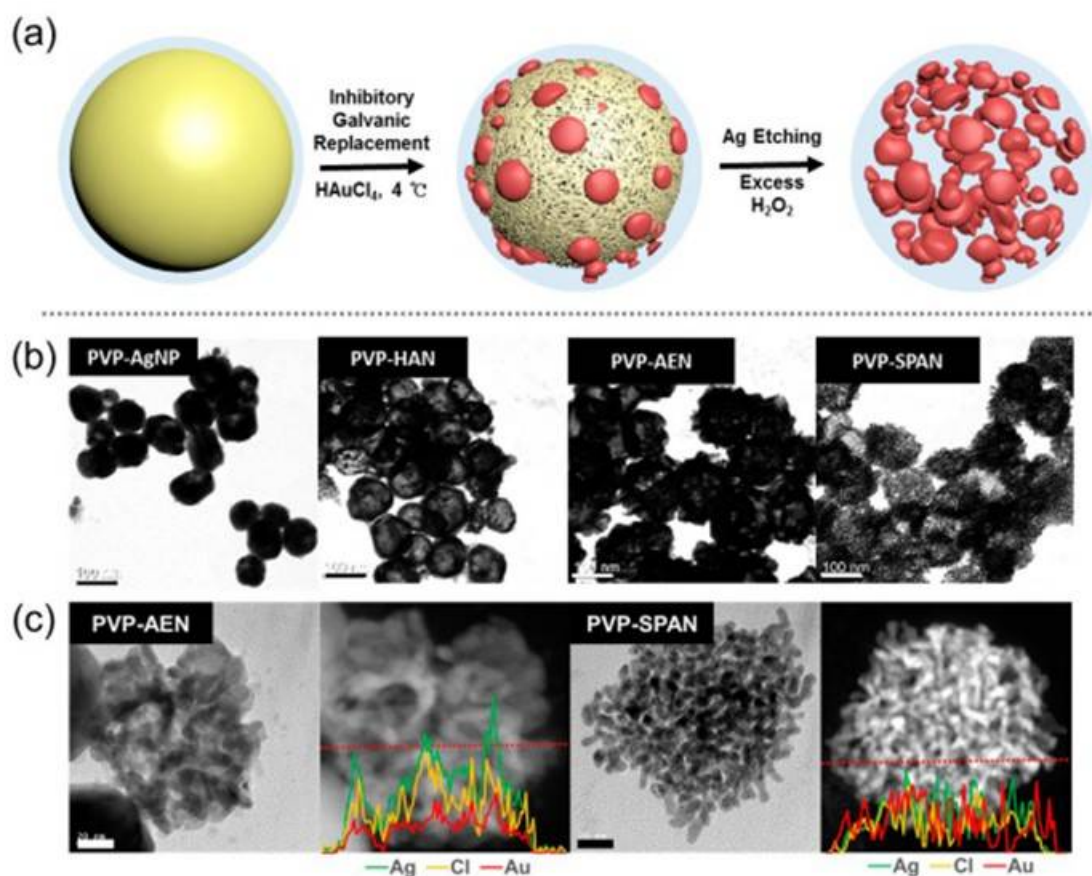


Figure 5. (a) Schematic illustration of porous Au nanoparticle synthesis by inhibitory galvanic replacement with subsequent etching process. (b,c) TEM and HR-TEM images with EDX line profiling. Reprinted with permission from ref.212. Copyright © 2015, American Chemical Society.

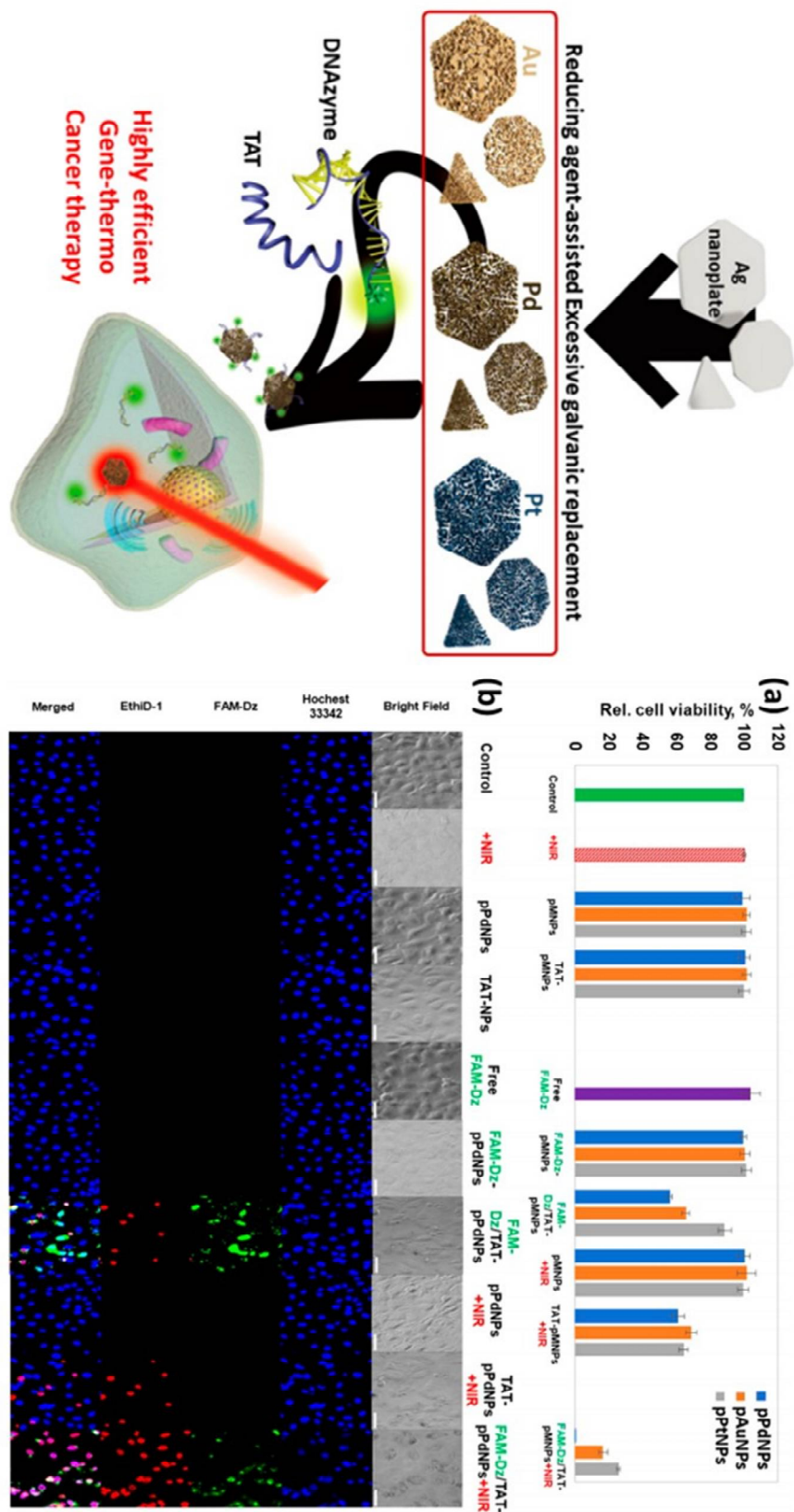


Figure 6. Schematic illustration of porous Au, Pd, and Pt nanoplate synthesis and their efficiency comparison in gene-thermo cancer treatment (top). (a) quantitative gene-thermo cancer treatment efficiency by cell viability

assay and (b) fluorescence microscope image of porous Pd nanoplate mediated cancer treatment. Reprinted with permission from ref.224. Copyright © 2018, American Chemical Society.

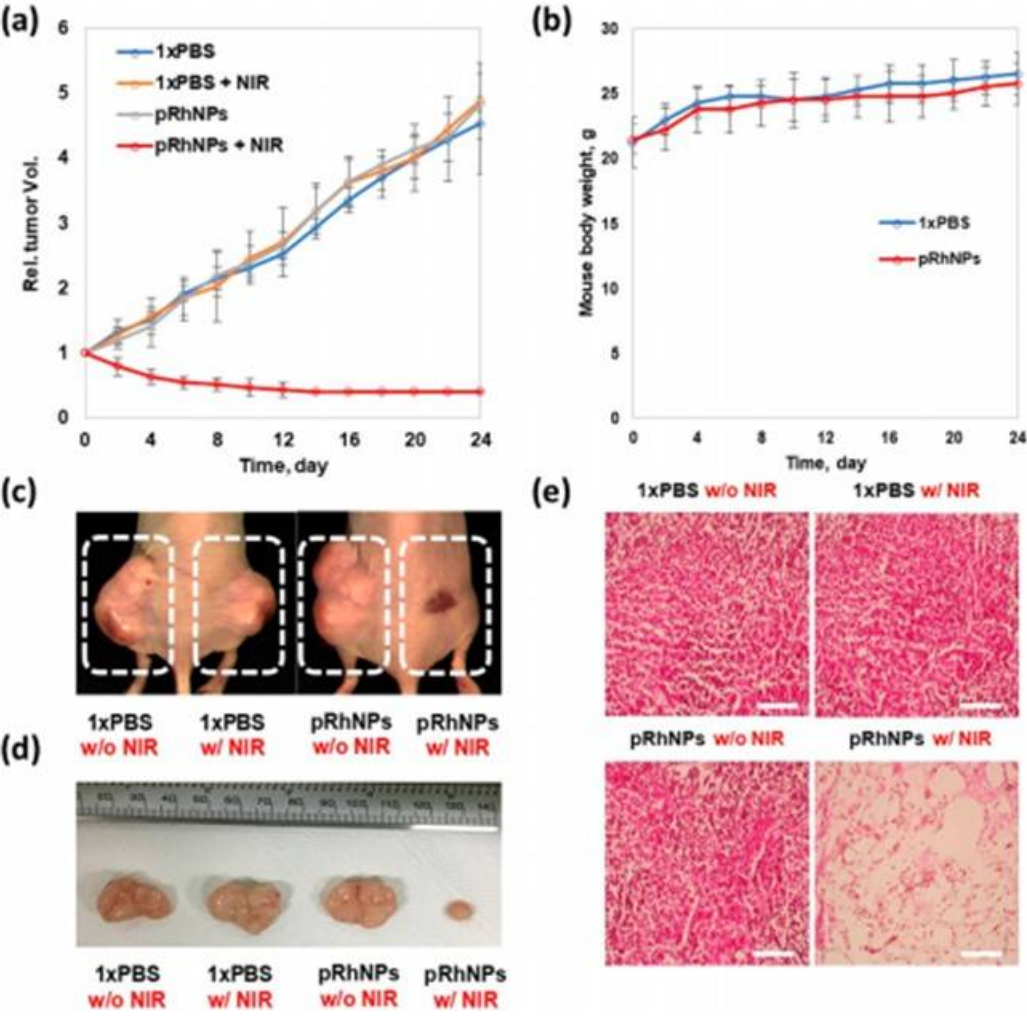
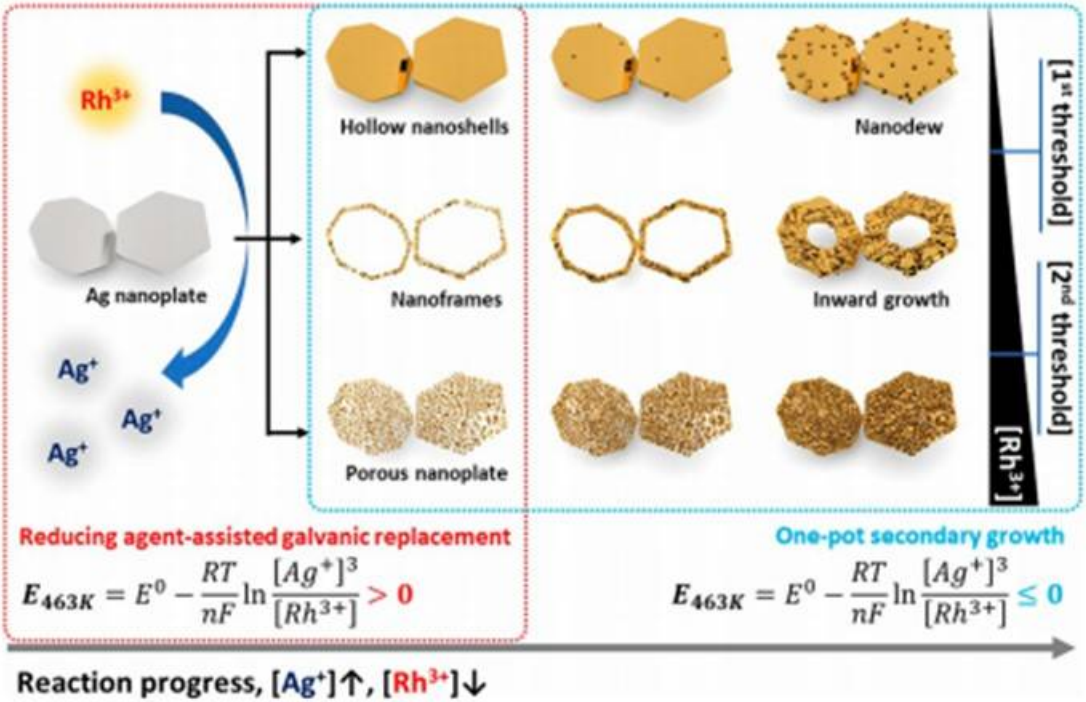


Figure 7. Schematic illustration of hollow Rh nanoshell, Rh nanoframe and porous Rh nanoplate synthesis through inverse directional galvanic replacement (top). (a) in vivo tumor ablation by porous Rh nanoplate with 808 nm NIR laser irradiation with (b) body weight tracking. (c,d) Digital images clearly exhibited the efficient cancer treatment. (e) H&E staining mediated tumor tissue observation. Reprinted with permission from ref.229. Copyright © 2018, American Chemical Society.