Template-Directed Synthesis of Multibranched Gold with Surface Plasmon Resonance

This report features the work of Rong-Ming Ho and his co-workers published in Adv. Mater. ***25****, 1780 (2013).*

With extraordinary optical characteristics unobserved in bulk materials, metallic nanostructures show an intense absorption band due to surface plasmons and enhanced local electromagnetic fields because of a localized surface plasmon resonance (LSPR), which arises from oscillations of charge density confined among the nanostructures. Significant attention has been given to the investigation of surface plasmonic properties of metallic nanoparticles because of their prospective applications as components in diverse technologies such as electronics, plasmonic waveguides, biomedicine and chemical or biological sensors. Exhibiting LSPR characteristics in the visible range of the spectrum, silver (Ag) and gold (Au) are noble metals commonly used for nanoparticle production. Although Ag displays the sharpest and strongest bands among all metals, Au is preferable for biological applications because of its inert nature, biocompatibility and chemically stable properties.

The characteristic wavelength and intensity of the LSPR absorption bands are highly sensitive to the shape, size, interparticle distance and dielectric environment of the nanostructures; the fabrication of nanostructures with controllable size and shape have hence become a critical aim of extensive research over the past few years. An increase of edges or of the sharpness of nanostructures produces a red shift of the absorption spectra due to an increased charge separation; increasing the size of nanostructures enhances the cross section of scatter, but the spectral shifts of the LSPR maximum are influenced more by the geometric shape of nanostructures than by their increased size. To exploit LSPR properties and the corresponding applications, varied shapes such as sphere, cube, prism, rod, triangle and branched texture, as well as ordered nanostructured arrays, have been synthesized with wet chemical reduction methods or fabricated with lithographic methods. Although producing excellent nanostructures of large area with high reproducibility, the lithographic fabrication becomes costly of time and money for structures smaller than 20 nm with well defined edges.

Template synthesis has attracted significant interest as a highly versatile approach to prepare nanostructured materials with large area, predefined size and shape. This powerful approach provides a pre-existing template with desired nanoscale features, such as anodized aluminium-oxide films, colloidal templates and mesoporous silica, to direct nanomaterials into unique forms that are difficult to obtain with other methods. Templates based on block copolymers (BCP) have been extensively investigated because of their ability to self-assemble into nanostructures periodic in one, two and three dimensions, including lamellae, cylinder, sphere and gyroid phases, through tuning of the molecular mass and chemical compos-

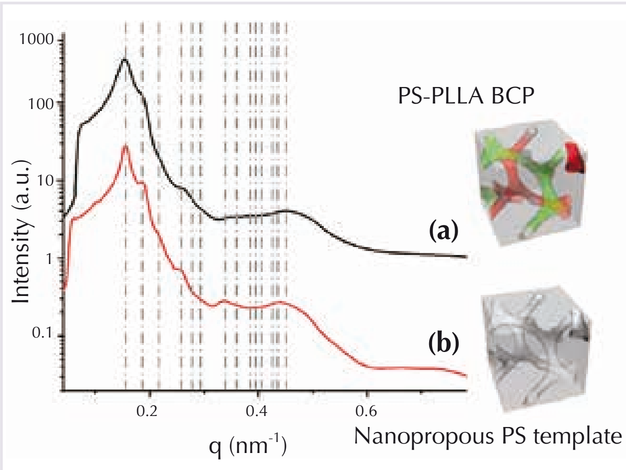

Fig. 1: One-dimensional SAXS profiles of (a) gyroid-forming PS-PLLA after thermal treatment; (b) nanoporous PS template forms the gyroid-forming PSPLLA after removal of minor PLLA networks. On the basis of the form and structure factors for the double gyroid, characteristic reflections with q ratios $\sqrt{6}:\sqrt{8}:\sqrt{14}:\sqrt{16}:\sqrt{20}:\sqrt{22}:\sqrt{24}:\sqrt{26}:\sqrt{30}:\sqrt{32}:\sqrt{38}:\sqrt{40}:\sqrt{42}:\sqrt{46}:\sqrt{48}:\sqrt{50}$ are discernible and indicated with vertical lines. (Reproduced from Ref. 1)

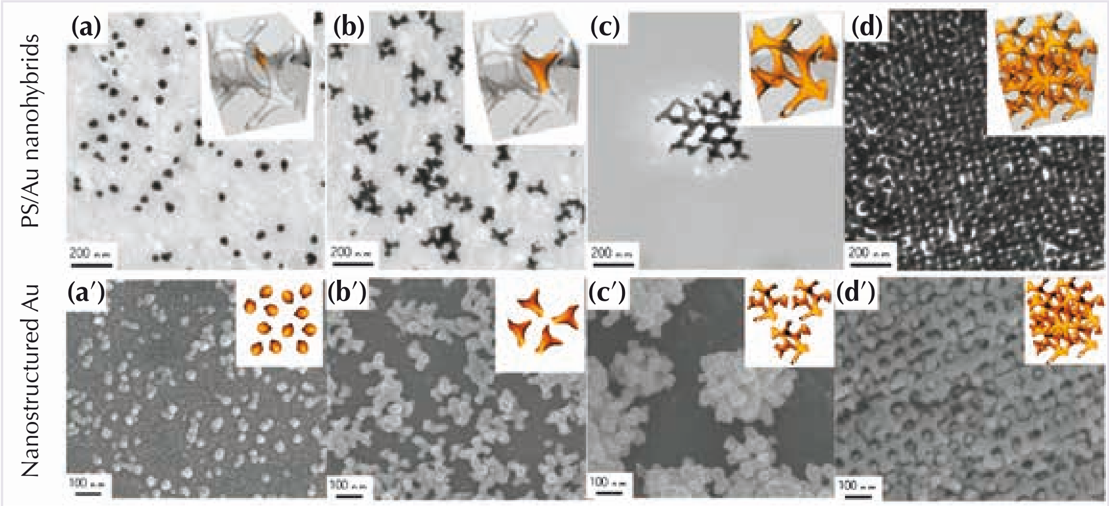

Fig. 2: Nanostructured Au from controlled seeding growth of Au at various stages: (a and a′) Au NP; (b and b′) branched Au; (c and c′) 3DON Au particles; (d and d′) Gyroid Au. Up: TEM images of Au within PS templates via template seeding growth. Down: FESEM image of nanostructured Au after removal of PS templates. (Reproduced from Ref. 1)

ition of copolymer blocks. By taking advantage of degradable BCP, one can prepare nanoporous BCP materials with well ordered textures on preferential removal of constituent components in BCP through ozonolysis, UV degradation or reactive ion etching. Most interestingly, BCP-based nanoporous templates can be utilized to manufacture metallic nanomaterials with templating processes, such as electrochemical deposition, electrolytic plating and sol-gel reactions.

A laboratory for frontier polymer research led by Rong-Ming Ho from National Tsing Hua University, Taiwan, is devoted to the investigation of self-assembly BCP, nanopatterning techniques via integration of top-down and bottom-up methods, and hybridization via block-copolymer templating. Ho and his co-workers have exploited a new approach to fabricate multibanched Au nanostructures as bulk or continuous thin films using gyroid-forming nanoporous BCP as a template for seed growth, followed by removal of the template.[1] The relation between the multibranched Au formed with gyroid-forming BCP templates and LSPR was investigated in their work. The basic double-gyroid (DG) shape is a three-fold junction of three arms, in which each arm connects to another set of three arms that are each themselves rotated to form a 3D network. The fabrication of highly branched DG Au nanostructures has great potential for the development of plasmonic materials. These researchers utilized synchrotron-based small-angle X-ray scattering (SAXS) at **BL23A1** of the TLS and a transmission electron microscope (TEM) to identify the formation of a gyroid phase on poly(styrene)-*block*-poly(L-lactide) PS-*b*-PLLA (Fig. 1). PS-*b*-PLLA is highly suitable for fabrication of a nanoporous polymer because of hydrolytically degenerated blocks in PLLA. Templated seeding growth was conducted to create precisely controlled Au nanostructures formed within the PS matrix, as shown in Figs. 2(a)-(d). After removal of the PS matrix, versatile Au nanostructures, such as Au nanoparticles, branched Au, three-dimensionally ordered nanoporous (3DON) Au particles, and gyroid Au, were fabricated as shown in Figs. 2(a′)-(d′). These resulting Au nanostructures displayed remarkable surface plasmon resonance in the near-infrared (NIR) region. In particular, the optical properties for branched Au and 3DON Au particles exhibited strong and stable NIR resonances that are promising for biological applications. This new approach for gyroid-forming BCP templating should provide a precisely controllable method to fabricate nanohybrids and nanostructured metals for various photonic and optoelectronic devices.

Reference

1. H. Y. Hsueh, H. Y. Chen, Y. C. Hung, Y. C. Ling, S. Gwo, and R. M. Ho, Adv. Meter. **25**, 1780 (2013).