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Regular Article Synthesis of various 3D porous gold-based alloy nanostructures with branched shapes

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 Selective laser heating was shown as synthesis platform for porous nanostructures.

- 3D porous gold-based nanostructures with different morphologies were obtained.
- Various nanoarchitectures were obtained by varying the experimental conditions.

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3D porous gold-iron nanostructures with various nanoarchitectures (brain-like, flower-like, cage-like, or raspberry-like structures) were synthesis by selective laser heating of colloidal nanoparticles and selective acid treatment.

This paper presents a facile and flexible synthesis platform for various 3D porous gold-iron nanostructures based on selective laser heating of colloidal nanoparticles and selective acid treatment. The presented approach allows to create porous gold-based nanostructures with different morphologies. In addition, for the first time, our studies indicate that various nanoarchitectures (brain-like, flower-like, cage-like, or raspberry-like structures) can be obtained by varying the experimental conditions such as size of Au and $Fe₃O₄$ nanoparticles, solvent, laser fluence, and irradiation time. We believe that these porous structures will find immediate applications in catalysis and separations, where high surface area and magnetic properties are often simultaneously required.

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1. Introduction

In the wide panorama of nanomaterials, gold is known to have a unique electronic, and amazing catalytic performance [\[1,2\],](#page--1-0) as well as excellent and tunable plasmonic properties [\[3,4\].](#page--1-0) Especially gold

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nanostructures with porous structures have attracted great attention in several fields, such as catalysis $[4-8]$, sensing $[9,10]$, drug delivery [\[11,12\],](#page--1-0) medical diagnostics and biomedical imaging [\[13,14\],](#page--1-0) because of their spatial configuration that displays low density, effective contact area and good fluid transmittance. For these applications, the separation of the porous material from the fluid is a crucial step. The use of porous magnetic particles allows separation by simply applying a magnetic field.

Porous gold nanostructures are usually fabricated, through galvanic replacement reactions with active metals as sacrificial templates and etching bimetallic nanostructures [\[6,15,16\].](#page--1-0) However, traditional etching route through a bimetallic precursor, such as Au/Ag, can only fabricate small-sized porous nanostructures. A protocol to fabricate large-sized (>100 nm) porous noble metal nanostructures would not be possible due to collapse or deformation in the process of growth. Unfortunately, small-sized porous nanostructures always suffer from the congregation during their application. Porous micrometer-sized particles are commonly prepared by several swelling methods of template micrometer-sized particles, e.g., polystyrene (PS) template particles obtained by dispersion polymerization, with appropriate monomers and initiators, e.g., multi-step swelling [\[17–23\]](#page--1-0), dynamic swelling [\[24,25\]](#page--1-0) and a single-step swelling. The monomer(s) swollen within the template microspheres are then polymerized, which is followed by a dissolution of the template part of the formed composite particles [\[26\].](#page--1-0)

Thus, fabrication of large-sized porous magnetic noble metal nanostructures is potentially very significant but still remains a challenge.

Among the developed synthetic protocols, the pulsed laser irradiation method is regarded as one of the most effective approaches to obtain highly uniform submicrometer-or micrometer-sized particles [\[27–34\]](#page--1-0). In fact, our group recently reported a unique synthetic pathway to prepare Au-based particles with well-defined spherical morphology, uniform submicrometer-size and integrated porosity-magnetic properties (by combining selective laser heating of nanoparticles dispersed in liquid and acid treatment processes) [\[31\]](#page--1-0).

Inspired by these results, we continued our quest toward the deliberate formation of porous gold-iron nanostructures with magnetic properties, because this novel 3D integration would represent

Fig. 1. SEM and TEM results of Au porous nanostructures prepared from Au and Fe₃O₄ nanoparticles solutions with different size of raw nanoparticles. (a) SEM image of Au (brain-like) nanostructures obtained from raw Au and Fe3O4 nanoparticles with diameters 20 nm and 6 nm, respectively. (b) SEM image of Au with flower-like structure (raw Au nanoparticles = 5 nm, raw Fe₃O₄ = 6 nm). (c), (d) SEM and TEM images of cage-like Au particles (raw Au = 20 nm, raw Fe₃O₄ = 40 nm). Laser irradiation conditions: laser fluence 100 mJ/pulse cm², irradiation time 1 h, solvent ethanol. (e) EDS spectrum obtained at the center of the particle, (f) SAED pattern of Au nanostructures obtained from raw Au and $Fe₃O₄$ nanoparticles with diameters 20 nm and 40 nm, respectively.

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