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Island Growth in the Seed-Mediated Overgrowth of Monometallic Colloidal Nanostructures



Gold islands, gold colonies: by controlling reaction kinetics and surface chemistry, Yin and colleagues have discovered an unconventional growth mode of Au nanocrystals whereby Au islands are formed. The resulting Au islands showed excellent properties in surface-enhanced Raman scattering. This finding opens great opportunities for building sophisticated structural features of noble metals with intriguing properties and applications. Guoqing Wang, Yiding Liu, Chuanbo Gao, ..., Kuniharu Ijiro, Mizuo Maeda, Yadong Yin

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HIGHLIGHTS

Island growth has been achieved in a monometallic Au system without lattice mismatch

Island growth is enabled by controlled crystal-growth kinetics and surface properties

Island growth opens a way to novel monometallic nanocrystals with intriguing properties

Wang et al., Chem 3, 678–690 October 12, 2017 © 2017 Elsevier Inc. http://dx.doi.org/10.1016/j.chempr.2017.08.004





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Island Growth in the Seed-Mediated Overgrowth of Monometallic Colloidal Nanostructures

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SUMMARY

Manipulating the growth mode of colloidal nanocrystals is of both fundamental interest and technological importance because it is often connected to the control of their shape, morphology, and physicochemical properties. In conventional wisdom, island growth during thin-film deposition is restricted to lattice-mismatched materials. Here, we show that deposition of Au on Au nanostructures (e.g., nanoplates, nanorods, and nanospheres) can produce separate Au islands on the seed surface with tunable size and density while preserving the original crystal structure. The island growth in the system is ascribed to the synergistic effect of fast redox kinetics and surface capping of large polymeric ligands. Decreasing the reaction rate or changing the capping ligands could readily transform the deposition of Au on Au nanostructures from island growth to layer-by-layer mode. We further take advantage of the dense hotspots of the islands-on-plate nanostructures and demonstrate their excellence in surface enhanced Raman scattering detection.

INTRODUCTION

Recently, a seeded growth strategy in which nanoscale seeds are used for guiding their growth into well-defined nanostructures has been widely adopted for the synthesis of colloidal nanomaterials.^{1,2} Compared with direct chemical synthesis, seeded growth represents a simple yet effective route to controllable nanostructures with desired physicochemical properties, which have shown promise for applications in chemical and biological detection, biotherapy, and catalysis.³⁻⁵ Over the last decade, this well-established growth approach has undergone a quiet revolution. It has been expanded from controlling the size and/or shape of monometallic nanostructures to the creation of many bimetallic systems that involve relatively small lattice mismatches.^{1,2,6-11} Although layer-by-layer growth is often the preferred objective in seed-mediated processes, island growth on the seed surface could produce complex secondary features that promise superior performance to those with smooth surfaces. An appropriate example is surface-enhanced Raman scattering (SERS),¹²⁻¹⁴ where nanoscale roughness of plasmonic surfaces has been found to be highly beneficial to the performance.¹⁵⁻²² However, island growth has been mostly limited to a few binary metal and semiconductor systems that involve materials with large lattice mismatches, such as the growth of Pt islands on Au nanospheres and nanorods (lattice mismatch \sim 4.08%).²³⁻²⁶ It is unfortunate that such surface decoration with the Pt islands, which are plasmonically inactive in the visible spectrum, is detrimental to the performance of the Au nanostructures in applications such as chemical detection by SERS. In this paper, we reveal that island growth can

The Bigger Picture

Noble-metal nanocrystals find broad application in sensing, imaging, and catalysis, and their performance is heavily dependent on the nanostructures. Until now, general rules of crystal growth have been established and constitute the current wisdom in the structural design of noblemetal nanocrystals. For example, island growth of a metal on nanocrystals of another metal is usually induced by lattice mismatch between the two metals. However, in many cases, great possibilities lie beyond these rules for discovering new nanostructures with intriguing properties and applications. Here, we demonstrate this possibility by establishing a mechanism that allows an unusual island-growth mode of monometallic Au without involving any lattice mismatch. It enables production of a family of Au island structures, which showed superior performance in surface-enhanced Raman scattering. Our findings could inspire further efforts in building sophisticated metal nanostructures.

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