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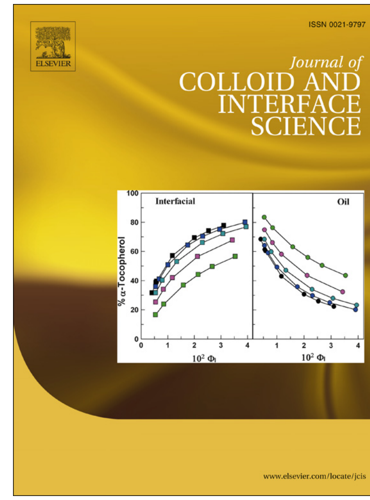

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Radial Growth of Plasmon Coupled Gold Nanowires on Colloidal Templates

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ABSTRACT

The library of plasmonic nanosystems keeps expanding with novel structures with the potential to provide new solutions to old problems in science and technology. We report the synthesis of a novel plasmonic system based on the growth of gold nanowires radially branching from the surface of silica particles. The nanowires length could be controlled by tuning the molar ratio between metal salt and surface-grafted seeds. Electron microscopy characterization revealed that the obtained one-dimensional nanoparticles are polycrystalline but uniformly distributed on the spherical template. The length of the nanowires in turn determines the optical response of the metallodielectric particles, so that longer wires display red-shifted longitudinal plasmon bands. Accurate theoretical modeling of these complex objects revealed that the densely organized nanowires display intrinsically coupled plasmon modes that can be selectively decoupled upon detachment of the nanowires from the surface of the colloidal silica template.

1. Introduction

The research on the optical properties of plasmonic nanoparticles is progressively shifting from individual particles to ensembles [1,2]. The plasmon hybridization model to explain optical interactions between metallic nanoparticles [3], opened new possibilities not only at the level of theoretical understanding of complex optical phenomena, but also as a guide in the rapidly developing field of applied plasmonics [4]. Plasmon coupling is especially interesting in anisotropic nanoparticles. Gold nanorods, for example, support longitudinal and transverse plasmon resonances, which shift depending on mutual orientation of the nanoparticles [5]. Thus, tip-to-tip arrangements lead to red shifts of the longitudinal surface plasmon band whereas side-to-side assembly induces blue shifts. Geometry-dependent plasmon modulation is in fact an interesting property in the design of platforms for optical biosensing [6,7].

Large electromagnetic field localization is the main prerequisite for surface-enhanced Raman scattering (SERS) spectroscopy, and this is typically achievable on plasmonic supercrystals composed of anisotropic nanoparticles [8–10]. Although, extended supercrystals of anisotropic nanoparticles will find application in chip-based, point-of-care devices, they are not suitable for use in complex biological media in suspension (*e.g.* in vivo). Thus, a large scientific and technological effort goes into the production of 3D platforms based on standing nanorod arrays that are stable in colloidal phase [11]. Naturally, the most attractive strategy in achieving such a system is the use of pre-made colloidal particles as building blocks for bottom-up self-assembly into complex 3D clusters with controlled size, shape and even interparticle distance [12]. Although progress has been made toward this, the self-assembly approach for standing rods arrays on 3D clusters remains a challenging task.

To overcome the inherent difficulties in controlled self-assembly we present here an alternative strategy for the synthesis of anisotropic nanoparticles in the side-to-side mode, directly on colloidal templates. Recent work by Chen and co-workers make such strategy feasible [13]. These authors demonstrated a relatively simple protocol for the synthesis of forest-like assemblies of gold nanowires on glass substrates. We recently showed that such gold nanowire forests constitute a promising architecture as SERS substrate [14].

We thus propose a novel type of plasmonic architecture consisting of a dielectric core covered with radially distributed gold nanorods/nanowires branching out from the silica surface. The radial growth of nanoparticles is based on one-directional seeded growth from covalently attached gold seeds (Fig.1). The molar ratio between seeds and metal precursor determines the length of the nanoparticles, which in turn affects the plasmon response. Theoretical modeling of this multi-particle system points toward strong plasmon coupling between arrayed wires.