Fabrication of gold nanoantennas on SiO₂/TiO₂ core/shell beads to study photon-driven surface reactions

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ABSTRACT

Plasmonic nanoantennas offer exciting perspectives for promoting and investigating light-driven chemical reactions. In particular, core/shell semiconductor beads coupled to gold nanoantennas represent an ideal platform for a systematic evaluation of multiple processes stimulated by light at different frequencies. Here we report the detailed fabrication of gold bowties on $\text{SiO}_2/\text{TiO}_2$ core/shell micro- and nano-beads, which is based on the combination of colloidal synthesis, atomic layer deposition and a modified version of induced deposition mask lithography. The critical steps of fabrication, including choice of mask material, etching rate and experimental setup are analyzed and strategies to pursue a successful fabrication of different nanoantennas are discussed.

1. Introduction.

Plasmon-enhanced chemical reactions are intensively investigated for production of solar fuels and degradation of environmental pollutants.¹⁻⁵ Using plasmonic nanoparticles in combination with semiconductor photocatalysts may allow for a full exploitation of hot-electrons to induce photodissociation of adsorbates,⁶⁻⁸ whereas localized heating can be harnessed to drive photothermal transformations⁹⁻¹² or steam generation.¹³ In this context, plasmonic nanoantennas represent a powerful tool to trigger and control kinetics, selectivity and spatial localization of surface reactions.^{14,15} Coupling optical nanoantennas to core/shell oxide microbeads is a very promising strategy for studying these processes *in situ*, under real working conditions. We have recently demonstrated that Au bowties deposited on the surface of SiO₂/TiO₂ core/shell microbeads result in a remarkable enhancement of photodegradation rates of different organic pollutants.¹⁵ These catalysts can also take advantage of enhanced surface light trapping due to the synergistic combination of plasmonic nanonantennas and morphology dependent resonances originating from the high-refractive index contrast between core and shell to monitor the progress of reactions by microRaman spectroscopy.¹⁶⁻¹⁸ Fabrication of plasmonic nanoantennas on spherical photocatalysts is not trivial. Conventional electron beam lithography (EBL) and shadow evaporation techniques are usually limited to planar substrates and self-assembly of nanoantennas obtained from chemical routes involves ligands that can alter the functional properties of the products. In general, nanoantennas can be transferred onto non-planar substrates using two main approaches: the first option relies on stripping nanonantenna arrays, previously deposited by electron beam lithography onto planar substrates, by means of a sacrificial thiol-ene films.¹⁹ The second method is based on induced deposition mask lithography (IDML). In IDML the antennas are fabricated by electron beam deposition of sacrificial hard masks on the material

that must be patterned. Subsequent Ar^+ ion milling etches both hard mask and unmasked material, giving rise to well-defined, highly reproducible antennas, which are not affected by chemical impurities. This approach has been successfully tested in fabrication of bowtie-type nanoantennas on silicon atomic force microscopy tips.²⁰

Here we report the detailed fabrication of gold nanoantennas on $\text{SiO}_2/\text{TiO}_2$ core/shell microbeads, which is based on a modification of IDML. The critical steps of fabrication will be analyzed, taking the specific requirements of the final application into account. Different types of nanoantenna-on-beads (NOBs) samples will be presented and discussed.

2. Materials and methods

2.1. Synthesis of SiO_2 spheres (cores)

The SiO_2 spheres were prepared through the Stöber method,²¹ starting from tetraethoxysilan (TEOS) ($\text{Si}(\text{C}_2\text{H}_5\text{O})_4$ 98%, Acrosorganics), milliQ-grade water, ammonium hydroxide (NH_4OH A.C.S. reagent, Sigma-Aldrich) and a mixture of alcohols (methanol-HPLC grade, 99.9%, Sigma-Aldrich; 1-propanol 99.5%, Sigma-Aldrich, n-butanol, 99.5%, Sigma-Aldrich), in different proportions that are related to the final size of the particles, according to the corrected Bogush equation.²² The colloidal spheres were separated from the reaction solution by centrifugation (4000 r.p.m. for 15 minutes), re-dispersed by sonication in ethanol. This procedure was repeated for three cycles, after that the resulting suspension was diluted 1:200 in ethanol. In the present work we will limit the description of bowtie-on bead samples obtained using SiO_2 spheres with diameters of 0.4 and 2 μm .

2.2. Atomic Layer Deposition of TiO_2 shell layers.

About 3 μL of the previously prepared suspensions of SiO_2 spheres was dropped onto the surface of a boron-doped (100) Si wafer, which had been cleaned with acetone, dried in nitrogen flow and UV-cleaned (PSD-UVT Novascan Technologies Inc., USA) for 5 min at 50 °C. The TiO_2 shell layer was deposited by atomic layer deposition (ALD) in a Savannah 200 reactor (Cambridge Nanotech, MA, USA), using tetrakisdimethylamido titanium (IV) (TDMAT, 99.9999%, Sigma-Aldrich) and milliQ water as titanium and oxygen sources, respectively and Nitrogen (purity 99.9999%) as a carrier gas for both the precursors and for purging the reaction chamber. The basal pressure in the chamber was set to be around 0.1 torr and deposition temperature was 90°C. Each cycle consisted of 0.1s pulse of TDMAT, 7s of chamber purging, 0.15 s pulse of water and again 7s of chamber purge. Under these conditions the growth-per-cycle was 0.068 nm. Ex-situ post-deposition annealing in air at 700°C for 4 h converted the amorphous titania into fully crystalline anatase. The thickness of the titania shell layers considered in this case was 100 nm. Titania is uniformly coated all over the SiO_2 spheres.¹⁶

2.3. Fabrication of gold bowties by Induced Deposition Mask Lithography

Induced Deposition Mask Lithography was carried out into a modified ZEISS CrossBeam 1540 EsB system (FESEM-FIB). This instrument was equipped with a commercial Zeiss gas injection system, a Xenos pattern generator that steered either the electron beam or the ion beam, and a NTI argon ion (Ar^+) gun for in situ Ar^+ milling. A thin layer of Au was deposited onto the $\text{SiO}_2/\text{TiO}_2$ beads by means of a Semicore SC600 e-beam and thermal evaporator System. The thickness variation of the coated layer across the sphere was less than 1%.

The carbon masks were produced through a XENOS pattern writer XeDraw 2. During exposure the pressure in the chamber was 8×10^{-6} mbar (basic vacuum chamber 2×10^{-6} mbar) and the accelerating voltage was set at 20 kV. The electron beam is focused on the region of interest

where the gaseous precursor decomposes into carbon, forming masks of increasing thickness linearly with exposition time and volatile component. The optimal exposure time was 250 ns/nm² (see supporting information SI 1). These masks were removed by Ar⁺ ion etching operating at 0.7 KeV and 10 μ A. The spot size of the sputtered area was around 1 mm². The etching rate of Au coatings was about 3 nm/min. Any residual carbon which is left upon ion etching was removed by ozone UV-cleaning.

3. Results and Discussion

Bowtie optical antennas consist of two opposing gold triangular nanoprisms separated by a certain gap. In the present work gold was chosen as a metal to fabricate the bowtie nanoantennas, because of its chemical stability and tunable surface plasmon resonance, which can span from visible to NIR in the electromagnetic spectrum.²³

The general route of fabrication of bowtie-on-bead nanoantennas (BOBs) is schematically shown in Figure 1a. Our procedure combines three different techniques: Stöber synthesis of colloidal spheres, ALD and IDML. Each technique offers peculiar advantages. Stöber's method allows for producing monodisperse SiO₂ spheres over a large scale. ALD provides a fully conformal deposition of TiO₂ shells with accurate control of their thickness. IDML, which will be the main focus of this report, is a very useful tool for transferring nanoantennas on colloidal beads. This stage consists of the following steps:

1) Deposition of a 30 nm-thick Au layer onto SiO₂/TiO₂ beads by thermal evaporation. The thickness of the Au layer corresponds to the final height of the bowties. An interesting point to highlight in this regard is the absence of any conventional adhesion layers (chromium or titanium thin films), which are usually introduced to improve the adhesion of gold to the substrate. Here

the mechanical stability provided by the TiO_2 shell layer is sufficient to use BOBs for promoting and monitoring chemical reactions in aqueous environment at near-neutral pH. This stability was tested by repeatedly dipping the BOB samples in water. No evidence of mechanical damages resulted from SEM analysis. Adhesion layers are known for damping the plasmonic properties of the antennas.²⁴ The absence of any further adhesion layers ensures the direct contact between the antennas and TiO_2 surface, which is essential to investigate electron-transfer phenomena at the metal/semiconductor interface without introducing any extra-junctions. This is a key factor for using BOBs as model-systems to investigate plasmon-enhanced chemical reactions.

2) *Deposition of bowtie-shaped carbon masks.* The size and shape of the final bowties are directly defined by the masks, which are patterned on the Au-coated beads with the system described in *Materials and Methods*. In general, thickness and alignment of the mask are critical parameters for controlling size and spacing of the antennas. Compared to conventional IDML,²⁰ the use of carbon instead of SiO_x or W for masking represents a key specific change. Compared to SiO_x masks, carbon allows for a better definition of the bowtie shape. Moreover, upon Ar^+ ion milling (*see below*), W flakes can peel off and surround the mask. These residues could affect the photodegradation experiments and should be avoided.

3) *Transferring bowtie nanoantennas onto $\text{SiO}_2/\text{TiO}_2$ beads by Ar^+ ion milling.* This step takes advantage of the different etching rates between the mask and the Au film to transfer the mask-defined pattern into the corresponding gold structure.^{25,26} In the time required for mask removal the surrounding gold layer was completely sputtered away, allowing the mask shape to be translated with high accuracy into the underlying gold film. Thus, Ar^+ ion milling leads to the final bowtie-shaped nanoantennas deposited on the core/shell beads (BOB samples). The spherical shape of the substrates prevents the use of a static sample holder, which is commonly

employed in IDML. Ar^+ ion milling under static conditions results in a non-optimal removal of unmasked gold layer in the proximity of the masks (see SI 2). This drawback was circumvented by tilting the Ar^+ beam at 30° relative to the sample surface normal and carrying out the etching process by means of a rotating sample holder. This setup results in bowties with relatively sharpened sidewalls. Figure 1b and c shows some examples of BOB samples fabricated onto either $2\text{ }\mu\text{m}$ or 400 nm -sized beads.

Different types of BOB arrays were fabricated through this procedure by changing the following parameters:

- size of bowtie intra-gap (*i.e.* the gap between two triangles)
- size of bowtie inter-gap (*i.e.* the array pitch)
- number of bowties-per-bead (the array density)
- size of the supporting $\text{SiO}_2/\text{TiO}_2$ bead

As we have demonstrated in our previous paper,¹⁵ intra-gap size is an important parameter to control the intensity of light that is concentrated in the hot-spot resulting from the junction between two facing Au triangles. Under resonant excitation, narrower gaps yield stronger electromagnetic fields. The minimum intra-gap size achieved in our samples was about 10 nm , even though 20 nm -gap bowties offer better control of gap size and reproducibility. The array pitch and density are two closely related parameters. A detailed evaluation on the accuracy of mask transfer process is reported in supporting information (SI 3).

Figure 1. a) Scheme of the fabrication steps for the production of BOB samples. Examples of bowtie-like nanoantennas fabricated onto either 2 μm - or 400 nm-sized SiO₂/TiO₂ colloids are given in Figure b) and c), respectively. Scale bars: 200 nm.

Figure 2 shows an example of BOB samples with different inter-gap distances, which are progressively reduced on passing from Figure 2a, characterized by an antenna-to-antenna lateral distance of about 240 nm, to Figure 2c that shows a high-density array of nanoantennas where the pitch is comparable to the size of each triangle (65 ± 5 nm). Although each 2 μm -sized bead might host up to 35-40 nanoantenna-arrays, for practical applications this number should be

limited and inter-gap distance between nanoantennas should exceed at least 100 nm, in order to reduce unwanted elastic scattering of light. In this regard, we note that the controlled activation of individual hot-spots requires an efficient collection of the incoming radiation. Due to the large size of each nanoantenna, light is strongly backscattered when their density is too high. This reduces the efficiency of coupling between light, metallic antenna and substrate, thus inhibiting

Figure 2. Examples of nanoantenna arrays with different inter-gap spacing and density before and after mask removal. Scale bars: 200 nm.

any plasmon-enhanced chemical reactions occurring at the BOB surface. Smaller beads bring major challenges in terms of mask alignment and fabrication. Nevertheless, single nanoantennas were successfully fabricated on 400 nm-sized beads. This IDML-based approach is quite general and can also be extended to the fabrication of other kinds of optical nanoantennas.

Figure 3. Example of a 3x3 array of trefoil-like nanoantennas. Scale bar: 200 nm.

Figure 3 shows an example of “trefoil”-shaped nanoantenna arrays deposited onto 2 μm -sized beads. This particular geometry was achieved by a simple modification of the mask drawing process and it is currently under investigation as a multifunctional tool for triggering and monitoring surface reactions with high spatial selectivity. Further extensions will allow for a more systematic comparison among different types of nanoconcentrators, setting the basis for a deep understanding of surface processes driven by either visible or NIR light.

4. Conclusions

Au nanoantennas can be precisely fabricated on photocatalytic SiO₂/TiO₂ core/shell colloidal beads with sizes ranging from 0.4 to 2 μm . The key step in nanoantenna fabrication onto non-planar substrates takes full advantage of IDML. We observed that the most critical parameters are related to the choice of mask material and control of Ar⁺ ion etching process. Carbon masks gave the best results in terms of shape and spatial resolution. The Ar⁺ ion etching process should be carried out by combining tilted ion beam and sample rotation. Different arrays of bowties and related configurations of other nanoantennas can be achieved with an excellent control of inter- and intra-gap sizes. This procedure opens exciting perspectives to the controlled fabrication of nanostructured devices for investigating and exploiting plasmon-enhanced reactions and related phenomena.

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Graphical Abstract