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# Maintaining high- $Q$ in an optical microresonator coated with high-aspect-ratio gold nanorods

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## Abstract

We report methods to coat fused-silica microresonators with solution-grown high-aspect-ratio (AR) gold nanorods (NRs). Microresonators coated using our method maintain an optical quality factor ( $Q$ ) greater than  $10^7$  after coating. The more successful method involves silanization of the surface of the microresonator with 3-mercaptopropylmethyltrimethoxysilane (MPMDMS), to enable the adhesion of gold NRs. The high-AR NR-coated microresonator combines the field enhancement of localized surface plasmon resonances with the cavity-enhanced evanescent components of high- $Q$  whispering-gallery modes, making it useful for plasmonic sensing applications in the infrared. By coating with NRs having a different aspect ratio, the enhancement regime can be selected within a wide range of wavelengths.

**Keywords:** gold nanorods, microresonator, nano-optics, localized surface plasmons

(Some figures may appear in colour only in the online journal)

## 1. Introduction

In order to take advantage of tunable localized surface plasmon resonances to enhance the evanescent fields of the optical whispering-gallery modes of fused-silica microresonators, it is necessary to coat the microresonator's surface with high-aspect-ratio gold nanorods (NRs) that have been synthesized in aqueous solution. The growth of gold NRs using wet chemical synthesis has been studied in detail [1–3], and numerous coating methods exist. Adhesion of various nanomaterials such as single-walled carbon nanotubes and silver nanowires (NWs) on several different substrates has been reported [4, 5]. Gold NWs can be grown directly on a Si surface by surfactant-assisted galvanic reduction [6]. Self-assembly of ligand-covered gold nanoparticles from water colloid solution on a silica substrate that was modified by a low energy electron beam has been observed [7]. Attachment of gold nanoparticles to silica and oxidized Si surfaces of various geometries has also been studied [8–10]. To be useful in applications employing

optical microresonators, the gold NRs must be adhered to the surface of a microresonator without seriously degrading its optical quality. The high-quality-factor ( $Q$ ) fused-silica microresonator is fabricated by melting the end of an optical fiber using a hydrogen–oxygen torch. It has a long photon storage time, on the order of hundreds of nanoseconds, enabling various applications, including nonlinear optics, cavity quantum electrodynamics, low threshold lasers, environmental probes, nanoparticle detection, biosensing, and chemical sensing [11–19]. Numerical modeling predicts that localized surface plasmon resonances in a microtoroid biosensor coated with gold NRs give rise to strong enhancements in the electric field, thereby improving the sensitivity [20]; this is consistent with our earlier observations of enhancement of input coupling from a tapered fiber into a NR- or NW-coated microsphere [17, 21]. Because the plasmon resonance frequency depends on the aspect ratio (AR, ratio of length to width) of a NR, one can choose the wavelength region where enhancement occurs, in contrast to gold nanoparticle coated microcavities, in which the

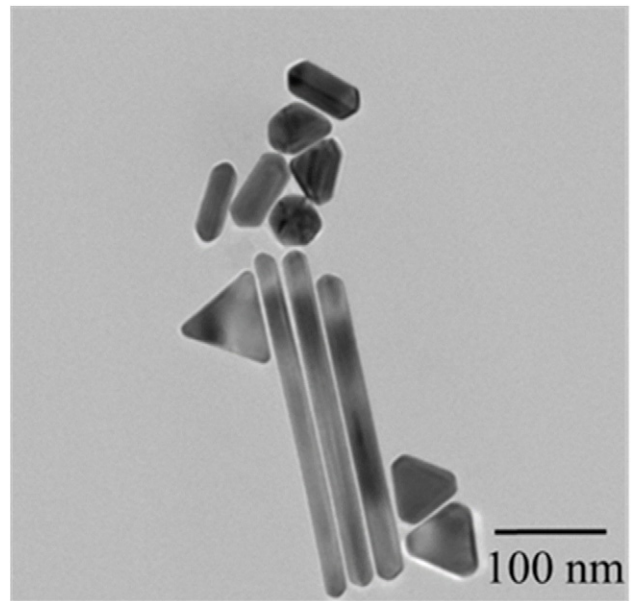
enhancement is not tunable and does not extend into the infrared [22]. Maintaining the high- $Q$  of a microresonator after coating with high-AR gold NRs is challenging [22], and little experimental work has been done to address this problem, motivating us to investigate and find a suitable method for coating fused-silica microresonators with gold NRs.

Gold NRs can be grown directly on silica by modifying the surface, either from HgTe nanoparticle seeds deposited on a polyelectrolyte layer, or from gold nanoparticle seeds deposited on a silanized surface [23, 24]. However, these direct-growth methods generally produce only low-AR ( $<6$ ) gold NRs that are nonuniformly distributed, limiting the enhancement to wavelengths shorter than about 1000 nm. For enhancement at longer wavelengths (1000–2000 nm), high-AR (7–20) NRs must be attached to the fused-silica microresonator's surface. The surface can be modified to improve the adhesion of wet-chemically grown high-AR gold NRs; we compare two methods here. One is functionalization of the surface with 3-mercaptopropylmethyldimethoxysilane (MPMDMS), before coating it with NRs as grown in solution [9]. The other method involves coating the silica surface with a layer of the polyelectrolyte poly(diallyldimethylammonium chloride) (PDDA) and then attaching solution-grown NRs functionalized with poly(acrylic acid) (PAA) [25]. We use scanning electron microscopy (SEM) for characterizing the coated surfaces.

## 2. Adhesion methods

The adhesion study requires us to know the surface charges and chemical reactions between various combinations of NRs, polymer coating layers, and substrates (whose surfaces may be functionalized). A fused-silica microresonator's surface has a weak positive charge (zeta potential of  $<+2$  mV), and the gold NRs capped with cetyltrimethylammonium bromide (CTAB) are positively charged (zeta potential of  $+30$  mV) [25]. Having like charges, the surface and NRs repel each other, as verified by dipping the microresonator in a gold NR solution for 2 min, after which SEM imaging showed no presence of gold NRs on the surface. The chemicals required for the experiments using the two adhesion methods studied here are MPMDMS ( $>99\%$ ), PDDA ( $M_w = 500\,000$ ), and PAA ( $M_w = 450\,000$ ), purchased from Sigma Aldrich; and ethyl alcohol (200 proof), purchased from the Chemistry Store at Oklahoma State University.

The high-AR ( $12 \pm 2$ ) gold NRs grown in-house are imaged to determine their size distribution using transmission electron microscopy (TEM) as shown in figure 1. The steps involved in the first method are illustrated in figure 2. First, the fused-silica microsphere is cleaned with ethanol as soon as it is fabricated. After cleaning, it is dipped in a 1:20 solution of MPMDMS in ethanol for  $>10$  h forming a thiol-terminated (SH) layer on the surface. Then the microsphere is removed from the solution, rinsed in ethanol, and dried in nitrogen for 1–3 min. Finally, the microresonator is dipped in a gold NR solution for 5 s–50 min, depending on the concentration



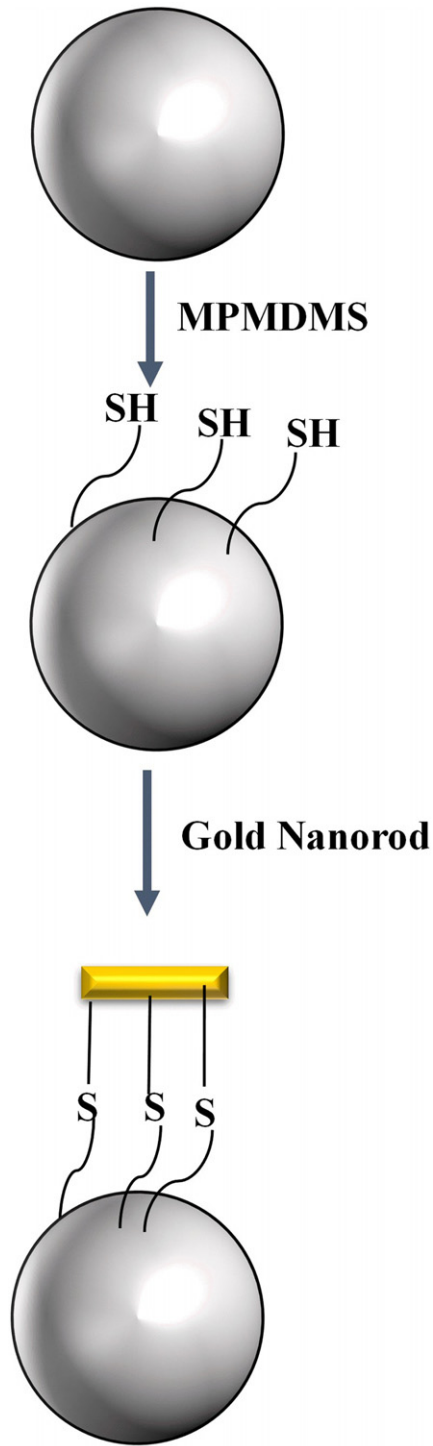
**Figure 1.** TEM image of gold NRs with an AR  $12 \pm 2$ . All images are taken at 40 000 magnification, scale bar is 100 nm.

of NRs required on the surface. Figures 3 and 4 show SEM images of high-AR ( $12 \pm 2$ ) gold NRs, solution-grown in-house and coated on a fused-silica microresonator, taken at different magnifications. The deposition is seen to be uniform and non-aggregated.

The second method of modifying the microresonator surface involves using PAA and PDDA. The PAA was used to make the gold NRs negatively charged by taking  $100\ \mu\text{l}$  of 1% PAA solution in water and adding it to 1 ml of the purified high-AR gold NR solution while stirring vigorously. The NRs end up with a net negative charge provided by excess COOH groups formed by electrostatic attraction between PAA and the gold NRs, as verified by zeta potential ( $-25$  mV) measurements [25]. The microresonator is first coated by dipping it for 30 min in a solution of PDDA in deionized (DI) water (1:20), followed by rinsing in DI water to remove any unbonded PDDA; this deposits a thin film of PDDA with a strong positive charge. Next, the PDDA-coated microresonator is dipped in the negatively charged gold NR solution for 10–15 min, followed by rinsing in DI water. Figure 5 shows an SEM image of the fused-silica microresonator coated with gold NRs using this second procedure. This method did not provide a uniform NR distribution over the surface of the microresonator, unlike the first method. Another drawback to this method is aggregation (as seen in figure 5). This suggests that we will not be able to use this method for any applications which require a high- $Q$  microresonator, because of the increased scattering losses; this is confirmed by the following results.

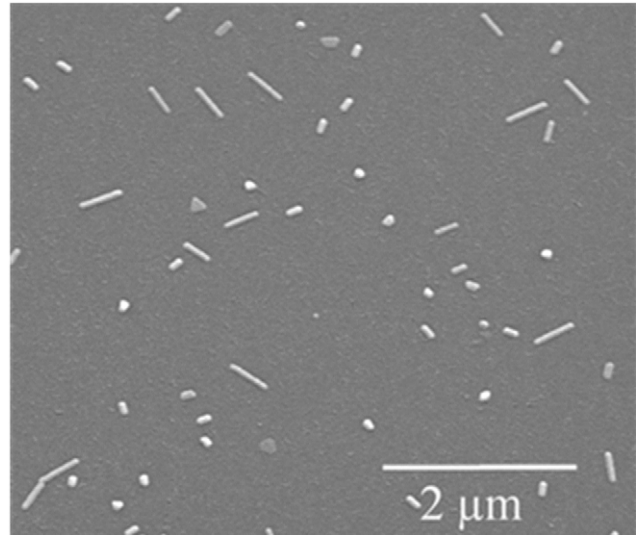
## 3. Experiment and analysis

A simplified schematic of the setup is shown in figure 6(a). Light from a cw tunable diode laser (New Focus 6328) with a wavelength of 1550 nm is launched through a

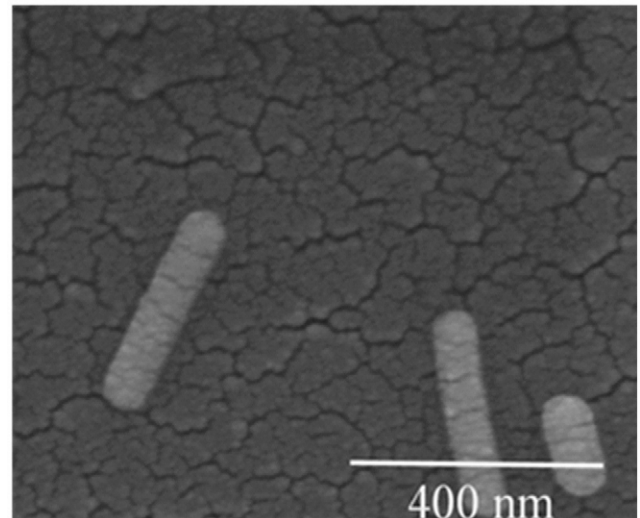


**Figure 2.** Simple schematic representation of the fused-silica microresonator silanization process using MPMDMS followed by coating with gold NRs. Top to bottom: bare sphere, silanized sphere, and NR (size greatly exaggerated relative to the size of the sphere) attachment.

fiber-coupler-assembly (FC) into a single-mode optical fiber that is tapered or reduced in diameter. The tapered fiber is used to tunnel the evanescent light into the microsphere to excite WGMs of the microresonator. Typical diameters of the tapered fiber and microsphere are 3–4  $\mu\text{m}$  and 600–700  $\mu\text{m}$

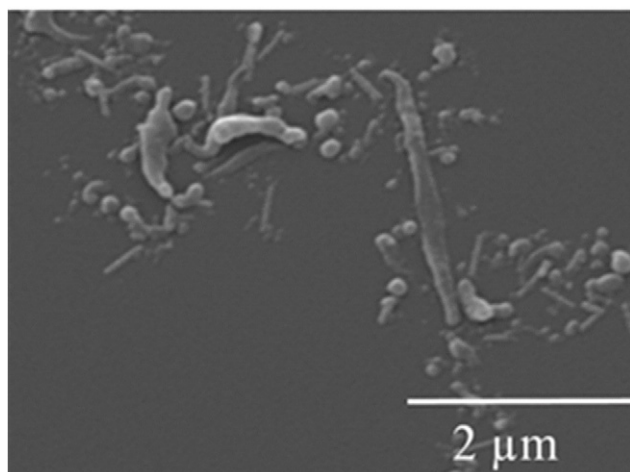


**Figure 3.** SEM image of high-AR gold NRs on a silanized fused-silica microresonator. Taken at 40 943 magnification, scale bar is 2  $\mu\text{m}$ .



**Figure 4.** SEM image of high-AR gold NRs on a silanized fused-silica microresonator. Taken at 282 694 magnification, scale bar is 400 nm.

respectively. The distance between the tapered fiber and the microresonator is varied using a micrometer-controlled  $xyz$  translation stage until fiber and microsphere are in contact. The polarization incident on the microresonator can be selected by a polarization controller (PC), and a polarization analyzer (PA) reads the polarization of the throughput light. From the tapered part of the fiber, frequency-scanned (30 MHz up to 30 GHz) light at 1550 nm is evanescently coupled into the whispering-gallery modes (WGMs) of the microresonator. As shown in figure 6(b), by recording the sharp throughput dips of WGM resonances, we can determine the  $Q$  of a microresonator by dividing the resonant frequency by the linewidth of the dip for a coated resonator using first method. The optical quality factor ( $Q$ ) of a microresonator is measured before and after NR coating. The results show

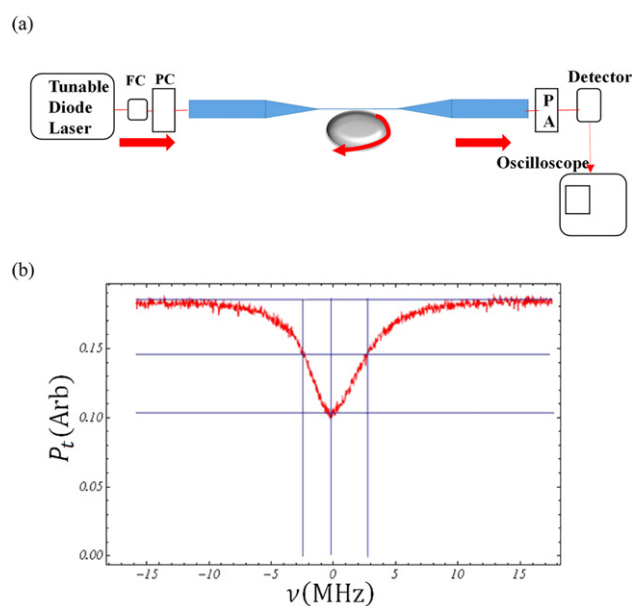


**Figure 5.** SEM image of (PAA-coated) high-AR gold NRs on a PDDA-coated fused-silica microresonator. Taken at 46 460 magnification, scale bar is 2  $\mu\text{m}$ .

that the first method (silanization with MPMDMS) maintains a higher  $Q$  than the second method (PAA-functionalized NRs on a PDDA-coated surface). Measured values of  $Q$ , averaged over multiple modes in several resonators, were as follows. First method: before coating,  $Q = 1 \times 10^8$ ; after coating,  $Q = 1.5 \times 10^7$ . Second method: before coating,  $Q = 1 \times 10^8$ ; after coating,  $Q = 7 \times 10^5$ . Only the first method retains the advantage of high- $Q$ . Because of the relatively large ratio of microsphere diameter to wavelength, the dependence of the evanescent component on radial order is weak, and so the effect of NRs deposited on the surface is about the same for all modes. In addition, the large sphere sizes mean that fiber coupling and surface scattering are by far the largest losses. The NRs reduce the  $Q$  because they increase the fiber–sphere coupling, as we demonstrated in [17, 21], and because they increase the absorption and scattering losses. For sensing applications, it is desirable to maintain the fiber and sphere in contact, so the loaded  $Q$  that is measured that way is what is relevant, and that is what is preserved at a high value.

#### 4. Conclusions

The ability to deposit high-AR gold NRs on curved surfaces is important in developing applications based on these nanostructures in the infrared. The more successful of the two methods compared here involves silanization of the surface of a fused-silica microsphere with MPMDMS and coating with gold NRs, which preserves a high optical quality factor and, as demonstrated through SEM characterization, provides a uniform distribution of NRs on the surface. These coating methods can make high- $Q$  microresonators useful for plasmonic sensing applications, surface-enhanced Raman scattering (SERS) studies, and perhaps also plasmonic switching applications (with the aid of an external laser beam), farther into the infrared as the AR of the NRs is increased. This technique would also enhance coupling of 1550-nm light into the coated microsphere from an adjacent



**Figure 6.** (a) Simplified experimental setup for quality factor measurement. Laser light (polarization controlled by PC and analyzed by PA) is evanescently coupled to excite the WGMs of a microresonator coated with gold NRs. (b) Typical throughput power dip, illustrating how the  $Q$  of a mode is determined by linewidth measurement ( $Q = 3.6 \times 10^7$  in this case).

tapered optical fiber, as previously seen by us using a microresonator coated with gold NWs [17].

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