FLUORESCENCE ENHANCEMENT USING SILVER NANO PARTICLES FABRICATED BY MODIFIED SILVER MIRROR REACTION

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ABSTRACT

We demonstrate enhancement of fluorescent signals in close proximity to silver nanoparticles manufactured by the modified silver mirror reaction. The manufacturing process is bottom-up, non-vacuum, and completed in only 15 minutes, and thus, is differentiated from other deposition processes of metal nanoparticles. We have extended the process to manufacture submicron silver nano-islands composed of nanoparticles using micro-contact-printing of SAM. The fluorescent signals of rhodamin-6G was enhanced by a factor of 5 on the silver nano-islands substrate.

KEYWORDS: Fluoresence Enhancement, Self Assembly, Nano Particle, Chemical Sensor

INTRODUCTION

The fluorescence enhancement analysis utilizing metal nano structures is considered one of the most effective techniques for ultra-sensitive chemical sensing. The enhancement strongly depends on the geometry of the silver nano-structures. Therefore, development of reliable as well as low-cost deposition processes of silver nanoparticles is the key point to achieve ultra-sensitive analyses. This report demonstrates fluorescence enhancement utilizing silver nano-islands fabricated by combinig the modified silver mirror reaction and micro contact-printing, which is a low-cost and highly reproducible process. The process was developed by our group and previously applied to manufacture SERS (Surface Enhanced Raman Scattering) substrates[1,2]. Silver nano-islands are composed several hundreds of silver nanoparticles deposited uniformly and densely.

THEORY

Many research groups recently reported the fluorescence enhancement when the fluorophores were located in close proximity to metal nano structures[3,4]. The signal enhancement originates from the interactions between the fluorophores and the silver surface plasmons. The radiative decay rate and quantum yield are increased by these interactions with fluorescence enhancement. The ratio of enhancement depends on the geometory of nano structures since non-uniform nano structures which are various sizes and shapes have different surface plasmonic modes. Flurescence signals are drastically enhanced at "hotspots." It is crucial to manufacture hotspots densely and uniformly to achieve high-performance microTAS.

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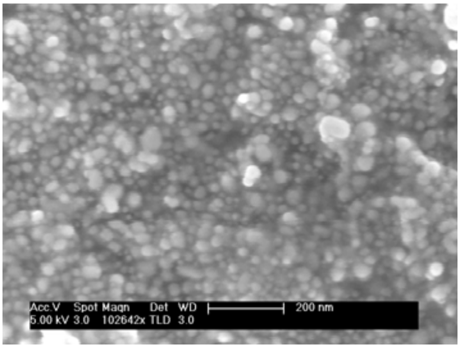
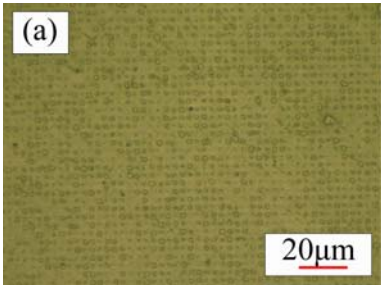


Fig.1 FESEM image of silver nanoparticles deposited by the modified silver mirror reaction. A monolayer of particles 10 to 50nm in diameter is deposited uniformly and densely.



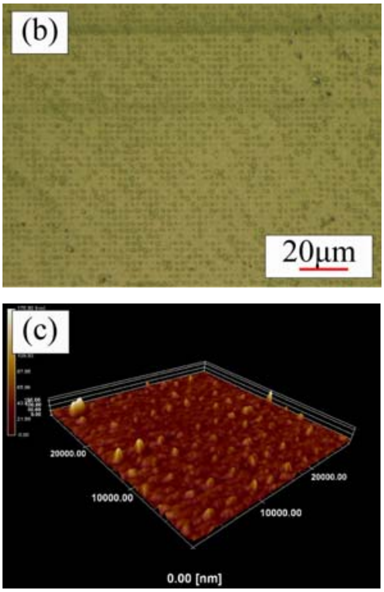


Fig.2 Silver nano islands manufactured by combining the modified silver mirror reaction and micro-contact-printing of SAM. Optical images of (a) 1μm-square and (b) 0.8μm-square silver nano islands. (c) An AFM image of 1μm-square-silver nano-islands.

EXPERIMENTAL

The modified silver mirror reaction, where dispersants are added to the conventional silver mirror solution (silver nitrate solution + ammonia water), deposits silver nanoparticles 10-50nm in diameter uniformly and densely on glass substrates as shown in Figure 1. This uniformity contributes the reliability and reproducibility of the silver-nanoparticles substrates. This process can be combined with micro-contact-printing of SAM (self-assembled monolayer), which is a non-photolithographic top-down process, to achieve site-selective deposition of silver nanoparticles. We have manufactured microTAS containing the detection sites with the nanopraticles as well as micro-fluidic components to handle analytes using this technology [2]. We have extended it to achieve submicronsquare silver islands, each of which consists of several hundreds of silver nanoparticles. We used a PDMS mold as a stamp whose patterns were transferred from a quartz mold for nanoimprinting. 800nm-square silver islands were successfully manufactured as shown in Figure 2. These island structures enable the effective utilization of evanescent waves originating from the total internal reflection of the excitation laser irradiated from the backside of the substrate. Without these island structures, the substrate with silver nanoparticles is not transmittive.

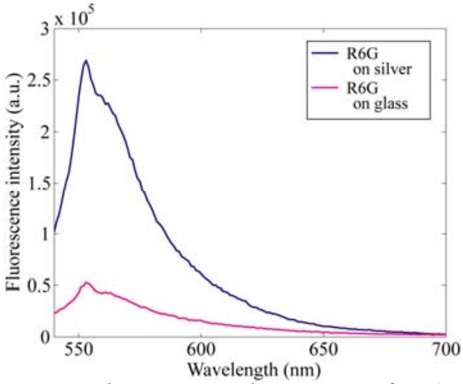


Fig.3 Fluorescent enhancement of R6G

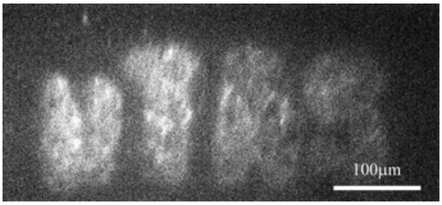


Fig.4 Fluorescent image of a glass substrate with a silver pattern of "μTAS" with 10nM R6G. The fluorescent enhancement illuminates the letters. Some "hot spots" are observed on the pattern.

RESULTS AND DISCUSSION

We evaluated the fluorescence enhancement of the developed substrate using 4nM rhodamine-6G dye. The excitation wavelength was 495nm. Fluorescence emission was measured on a bare glass slide and silver nanoislands deposited on a glass slide. As depicted in Figure 3, the fluorescence intensity was successfully enhanced by a factor of 5 on the silver nano-islands. Figure 4 shows the fluorescence image of 10nM rhodamine-6G dye on the silver patterns of "μTAS." The letters are illuminated due to the fluorescence enhancement. Some bright points, i.e. hotspots, are found on the silver structures, where the surface plasmons to contribute the enhancement are strongly enhanced by the nano-geometry. The "local" fluorescence enhancement at the hot spots is much greater than 5.

CONCLUSIONS

The silver nano-islands structures proposed herein are readily applicable to ultra-sensitive chemical sensing. The fabrication processes of silver nano structures have good compatibility with microfabrication of microfluidic components, which will enable conveyance of analytes to the hotspots to take advantage of the local fluorescence enhancement.

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