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Photocatalysis Reaction on Ordered Arrays of Au Nanorods with Controlled Orientations[#]

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Surface photocatalysis reactions of aromatic compounds self-assembled on metal surfaces have been extensively explored for the past decades. For example, the C─S bonds of aromatic sulfide species, such as benzyl phenyl sulfide and dibenzyl sulfide, can be readily dissociated on Ag upon the irradiation of 514.5 nm radiation.[1] Aromatic nitro compounds, e.g., 4-nitrobenzoic acid and 4-nitrobenzenethiol, on Ag also undergo photocatalysis reaction by 514.5 nm light irradiation.[2–4] Recently, the generation of 4,4′-dimercaptoazobenzene (DMAB) from the photo-oxidative coupling of two 4-aminobenzenethiols (4-ABTs) during the surface-enhanced Raman scattering (SERS) measurements on the 4-ABT molecules self-assembled on Ag has been reported.[5,6] However, there are still debates in the SERS community on the reality of this photocatalysis reaction.[6,7] These surface photocatalysis reactions were attributed to the result of certain charge transfer from Ag to the adsorbates upon the light irradiation.[3,4]

Despite the numerous studies on the surface photocatalysis reactions of aromatic compounds, that on Au surface has rarely been reported due to the inefficiency of Au toward these reactions compared to Ag. However, considering the recent advances on the development of efficient photocatalytic systems based on plasmonic Au nanostructures, where photogenerated hot electrons in Au nanostructures originating from their localized surface plasmon resonance (LSPR) were utilized,[8,9] we can expect that the surface photocatalysis reactions on Au can also be possible by controlling the LSPR characteristics of Au nanostructures. In this regard, here we examine the surface photocatalysis reaction of 4-ABT on Au nanorod (AuNR) arrays with controlled orientations. In a number of previous works on the manipulation of the plasmonic characteristics of metal nanostructures, the controlled assembly of nanostructures has proved to be an effective strategy to tune their plasmonic properties.[10,11] The experimental results demonstrated that the photocatalysis of 4-ABT indeed occurred on the AuNR surfaces and the extent of photocatalysis reaction distinctly depended on the orientation of AuNRs in the arrays. This can be ascribed to the strong electromagnetic field enhancement at the ordered AuNR arrays.

AuNRs with a controlled aspect ratio (2.5) were prepared by following the reported seed-mediated growth approach.[12] By using cetyltrimethylammonium bromide-capped 2- to 3-nm Au nanoparticles as seeds, homogeneous AuNRs with average length and diameter of 58 and 23 nm, respectively, were successfully synthesized in water. To fabricate AuNR arrays, 10 mL of the prepared aqueous solution of AuNRs was centrifuged at 6000 rpm for 8 min, and then 10 μL of concentrated AuNR solution was dropped on a Si wafer, which was precleaned with acetone and isopropyl alcohol. The AuNRs suspended initially in an aqueous solution were aligned parallel or perpendicular to the supporting substrate after the evaporation of solvent by making the large domains of assembled NRs (Figure 1). Interestingly, the orientation of AuNRs depended on the evaporation conditions. When the droplet evaporation was proceeded under ambient conditions (fast evaporation condition), a parallel AuNR array was generated after 2 h (Figure 1(a) and (c)). In contrast, a perpendicular AuNR array was yielded when the droplet evaporation was progressed in a sealed container at room temperature for about 48 h (slow evaporation condition, see Figure 1(b) and (d)). The humidity of the sealed container was about 80%. The formation of AuNR arrays with different orientations to the support along with the different evaporation conditions can be due to different solvent fluidics associated with the different speed of droplet evaporation. Under the fast evaporation condition, outward flowing of solvent molecules from the interior to the edge of droplet, which resulted from the relatively fast solvent evaporation at the droplet edge under this condition, could carry the AuNRs to the pinned droplet edge, thus yielding the parallel AuNR array.[13,14] In fact, we found that most of the AuNRs accumulated at the droplet periphery with a characteristic so-called "coffee ring" pattern (Figure 1(a)).[13,14] On the contrary, the speed of solvent evaporation might be homogeneous throughout the entire surface of droplet under the slow evaporation condition. Thereby, the resultant perpendicular flow of solvent molecules from the interior to the surface of droplet formed the perpendicular AuNR array.

To examine the surface photocatalysis reaction of 4-ABT on the AuNR arrays, we measured the SERS spectra of 4-ABT self-assembled on the arrays by adding a few drops of ethanol solution of 4-ABT (20 μL, 0.1 mM) onto the

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[#] This paper is dedicated to Professor Kwan Kim on the occasion of his honorable retirement.

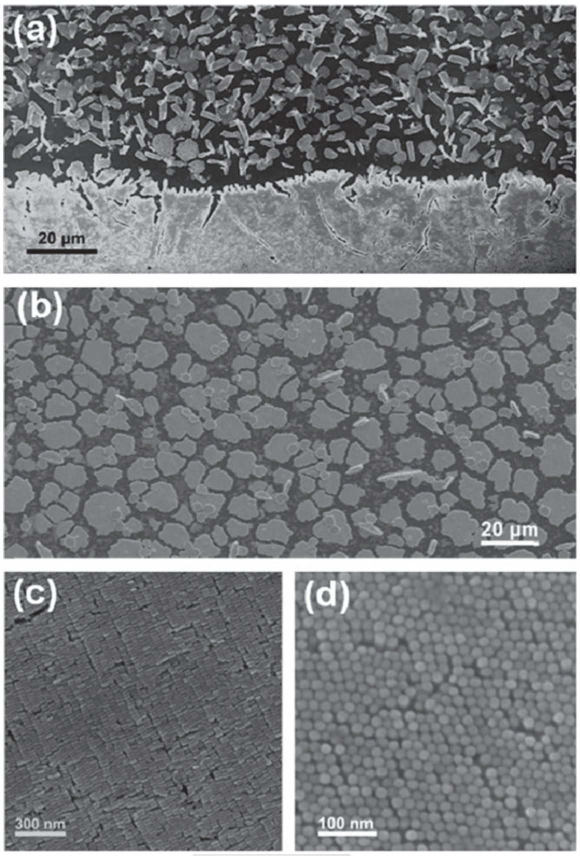

Figure 1. (a, b) Low- and (c, d) high-magnification scanning electron microscopy (SEM) images of the ordered arrays of AuNRs aligned (a, c) parallel or (b, d) perpendicular to the support.

arrays (Figure 2). SERS spectra were obtained using a Jobin Yvon/HORIBA LabRAM spectrometer (Kyoto, Japan) equipped with an integral microscope (Olympus BX 41, Tokyo, Japan). The 632.8 nm line of an air-cooled He/Ne laser was used as an excitation source. The laser beam (6 mW) was focused onto a spot (ca. 1 µm diameter) with an objective lens (×50, NA = 0.50). Data acquisition times were usually 90 s. Notably, as shown in Figure 2(b), the characteristic b_2 mode peaks of DMAB (denoted by arrows) were clearly identified at 1143, 1392, and 1435 cm^{-1} with considerable intensities, which can be assigned to 9b, 3, and 19b modes, respectively,[6] in the SERS spectrum of 4-ABT on the perpendicular AuNR array. However, the intensities of these b_2 mode peaks in the spectra obtained with the parallel AuNR array were drastically lower than those obtained with the perpendicular array (Figure 2(a)). Although we cannot completely rule out the possibility that the enhanced b_2 mode peaks are chemically enhanced SERS signals of 4-ABT, our findings indicate that the photocatalysis reaction of 4-ABT to DMAB can occur on the AuNR surfaces during the SERS measurements and the extent of photocatalysis highly depends on the orientation of AuNRs in the arrays. The higher photocatalytic efficacy of the perpendicular AuNR array compared to the parallel one might be due to the stronger electromagnetic field enhancement derived from their assembly structure.[11] The detailed experimental and theoretical studies on the mechanism of the enhanced photocatalytic function of the AuNR arrays are currently underway.

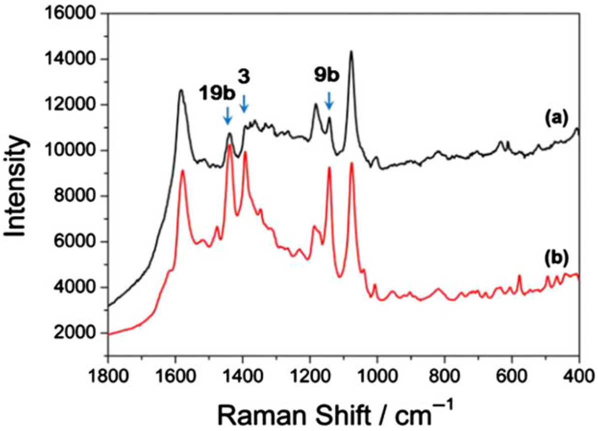

Figure 2. SERS spectra of 4-ABT on the (a) parallel and (b) perpendicular AuNR arrays.

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