



Journal of Nanoscience and Nanotechnology Vol. 15, 1171–1179, 2015 www.aspbs.com/jnn

# Selective Two-Photon-Absorption-Induced Reactions of Anthracene-2-Carboxylic Acid on Tunable Plasmonic Substrate with Incoherent Light Source

Francesca Pincella<sup>1, 2</sup>, Katsuhiro Isozaki<sup>1, \*, †</sup>, Tomoya Taguchi<sup>1, 2</sup>, Yeji Song<sup>1, 2</sup>, and Kazushi Miki<sup>1, 2, \*</sup>

<sup>1</sup> Functional Heterointerface Group, Polymer Materials Unit, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan <sup>2</sup> Department of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8571, Japan

In this research, we report the development, characterization and application of various plasmonic substrates (with localized surface plasmon resonance wavelength tunable by gold nanoparticle size) for two-photon absorption (TPA)-induced photodimerization of an anthracene derivative, anthracene carboxylic acid, in both surface and solution phase under incoherent visible light irradiation. Despite the efficient photoreaction property of anthracene derivatives and the huge number of publications about them, there has never been a report of a multiphoton photoreaction involving an anthracene derivative with the exception of a reverse photoconversion of anthracene photodimer to monomer with three-photon absorption. We examined the progress of the TPA-induced photoreaction by means of surface-enhanced Raman scattering, taking advantage of the ability of our plasmonic substrate to enhance and localize both incident light for photoreaction and Raman scattering signal for analysis of photoreaction products. The TPA-induced photoreaction in the case of anthracene carboxylic acid coated 2D array of gold nanoparticles gave different results according to the properties of the plasmonic substrate, such as the size of the gold nanoparticle and also its resultant optical properties. In particular, a stringent requirement to achieve TPA-induced photodimerization was found to be the matching between irradiation wavelength, localized surface plasmon resonance of the 2D array, and twice the wavelength of the molecular excitation of the target material (in this case, anthracene carboxylic acid). These results will be useful for the future development of efficient plasmonic substrates for TPA-induced photoreactions with various materials.

Keywords: Gold Nanoparticle, Plasmonics, Two-Photon Absorption, Photoreaction.

# **1. INTRODUCTION**

Multiphoton processes are attracting a great deal of attention due to their interesting properties such as 3D spatial resolution, and shifting of excitation wavelengths from UV to Vis or NIR; nevertheless, such photoreactions can only be achieved with high-power pulsed lasers and molecules with huge two-photon absorption cross sections (e.g., porphyrin derivatives), limiting their actual application.<sup>1</sup> 2D or 3D metallic nanostructures are expected to break this limitation and expand the applications for a wide range of materials and weaker irradiation sources, because metallic nanoparticles (MNPs), especially gold and silver nanoparticles, possess intriguing plasmonic properties that allow them to harvest and concentrate light at their surface.<sup>2, 3</sup> Multiphoton-induced photoreaction in the presence of a plasmonic substrate (near-field enhanced photoreaction) was recently reported for a limited class of materials, such as diarylethenes,<sup>4–6</sup> photoresist polymers,<sup>7, 8</sup> and more recently, semiconductor photocatalysts.<sup>6, 9</sup> The plasmonic substrate serves to make up for the low quantum efficiency of the two-photon process (third-order quantum process) by increasing the electric field in the proximity of the metallic nanostructures.<sup>10–12</sup> Up to now, the use of such

J. Nanosci. Nanotechnol. 2015, Vol. 15, No. 2

<sup>\*</sup>Authors to whom correspondence should be addressed.

<sup>&</sup>lt;sup>†</sup>Present address: International Research Center for Elements Science, Institute for Chemical Research, Kyoto University, Gokasyo, Uji, Kyoto 611-0011, Japan.

Selective TPA-Induced Reactions of Anthracene-2-Carboxylic Acid on Tunable Plasmonic Substrate

metallic nanostructured substrates for TPA reactions suffered from some major limitations linked to the fabrication method, mainly lithography or wet chemistry process (colloidal MNPs). These limitations originate in the poor control of optical properties of the metallic nanostructures or small total area of the plasmonic substrates (typically in the range of a few  $\mu m^2$  for lithography). In the case of colloidal MNPs attached to the target material for the multiphoton process, the MNP loading is usually low<sup>6</sup> and thus it is not possible to take advantage of the "hot spots" (regions in the gap between particles) where MNPs exhibit strong near-field enhancement. In the case of plasmonic substrates prepared by top-down techniques, in addition to size and cost issues, the range of applications is limited to solid-state reactions. In order to apply plasmonic TPA reactions to a wide range of photochemical processes, scalability and generality need to be achieved by bottom-up technique.13-16 Regarding scalability, we have already succeeded in solution-phase TPA reaction with an incoherent light source<sup>11</sup> with the advantage of large-area plasmonic substrate prepared by a hybrid method developed by our group.<sup>12</sup> For generality, a different type of photoreaction needs to be proven to verify the wide-range applicability of our plasmonic TPA excitation system. Thus, we plan to use plasmonic substrate with a localized surface plasmon resonance (LSPR) wavelength that matches the optimal condition for TPA in the anthracene derivative to induce photodimerization in the molecule with visible light irradiation. Here, we demonstrate the successful fabrication of different plasmonic substrates with high gap ("hot spots") density and LSPR in a wide range of wavelengths depending on the AuNP size.

In this report, we demonstrate how plasmon-induced two-photon reaction can be successfully applied to the photodimerization of an anthracene derivative, i.e., anthracene carboxylic acid. The photoreaction of anthracene derivatives, which has been well investigated, gives anthraquinone in the presence of O2, 17, 18 photodimer in the absence of O2,19 and radical-mediated dihydroxybianthryl in the absence of O2 under a diluted aqueous condition,<sup>20</sup> respectively, by UV irradiation for wavelengths longer than 300 nm. Among these photoreactions, the photodimerization of anthracene<sup>18</sup> is a well-known reversible photoreaction that proceeds under UV irradiation for wavelengths longer than 300 nm and can be reversed thermally or under UV irradiation for wavelengths shorter than 300 nm, and thus is frequently used as a probing reaction for asymmetric photoreactions in the field of supramolecular photochemistry.<sup>21-23</sup> Despite the efficient photoreaction property of anthracene derivatives, to our knowledge, there have been no reports about TPAinduced photoreaction of anthracene, with the exception of a reverse photoconversion of anthracene photodimer to monomer with three-photon absorption.24 Here, we demonstrate the first plasmonic TPA-induced photoreaction of anthracene-2-carboxylic acid (ACA), which gave



**Scheme 1.** Selective TPA-induced reactions of anthracene-2-carboxylic acid both on dried surface and in solution phase with AuNP array.

different photoproducts according to the reaction media (Scheme 1).

# 2. RESULTS AND DISCUSSION

In order to obtain a large-scale and efficient plasmonic substrate for TPA-induced photoreaction, a series of gold nanoparticle (AuNP) arrays, dodecanethiol-capped 10-nm AuNP array (10Dod array) and mixed hexanethioldodecanethiol-capped 23- and 39-nm arrays (23HexDod, 39HexDod arrays), was prepared by a hybrid deposition method developed by our group (Fig. 1(a)).<sup>12</sup> The high density and close-packed morphology of these arrays were characterized by SEM observation (Figs. 1(b), 2). Optical properties of the AuNP arrays were analyzed by UV-Vis-NIR extinction spectroscopy (Figs. 1(c), 3), where the LSPR lies in different regions, from 605 nm of the 10Dod array, to 722 nm of the 23HexDod array, and 966 nm of the 39HexDod array, making them good candidates for visible and NIR light irradiation. These AuNP arrays were immersed in 5 mM ACA solution in H<sub>2</sub>O-DMSO containing 5.4 M NaOH to adsorb ACA molecules at the AuNP surface by hydrophobic interaction with alkanethiols.<sup>25</sup> Irradiation of samples proceeded under continuous Ar flow in a 5-mL glass (cutoff wavelength 300 nm) vessel sealed with a natural rubber septum (Aldrich). ACA-coated AuNP array samples were irradiated from the top with UV light  $(285-400 \text{ nm}, 300-400 \text{ nm} \text{ at the sample}, 59 \text{ mW/cm}^2)$ for 24 h, Vis light (422–750 nm, 220 mW/cm<sup>2</sup>) for 60 h, and NIR light (750-1050 nm, 294 mW/cm<sup>2</sup>) for 48 h, respectively.

First, we show the plasmonic TPA-induced photoreaction ACA on a dried surface (Scheme 1). Due to low ACA concentration on the surface, common spectroscopic techniques (e.g., UV-Vis) could not be used to study the photoreaction at the surface of the 2D array; therefore, taking advantage of the intrinsic ability of our array to enhance both incident (laser excitation) and scattered electromagnetic fields, we used surface-enhanced Raman scattering (SERS)<sup>26–29</sup> to determine the progress of the two-photoninduced photodimerization of dried ACA by comparing the SERS spectra with that of the starting ACA, possible photoreaction products such as anthraquinone-2-carboxylic acid (AQCA), and photodimer of ACA (ACAD). The most



Figure 1. (a) Schematic illustration of sample structure, (b) SEM image; inset shows higher magnification, and (c) extinction spectrum of 25HexDod array; UV spectrum of ACA is overlaid.



Figure 2. SEM image of (a) 10Dod 2D array, and (b) 50HexDod 2D array; insets shows higher magnification.



**Figure 3.** Extinction spectra of 10Dod (blue line), 23HexDod (red line), 39HexDod (black line) 2D array on Au substrate.

J. Nanosci. Nanotechnol. 15, 1171–1179, 2015

intense peaks for these compounds were observed at 756, 1409 cm<sup>-1</sup> for ACA; 710, 1035, 1179 and 1608 cm<sup>-1</sup> for ACAD; 1034, 1179, 1598 and 1667 cm<sup>-1</sup> for AQCA (Figs. 4(a)-(c)), respectively. When Vis light was irradiated, the SERS spectra of both the 10Dod and 39HexDod arrays still presented the typical features of ACA along with a clear contribution from AQCA (Figs. 5, 6). Contrastingly, the Vis-irradiated 23HexDod array showed a dramatic change in the SERS spectrum (Fig. 4(e)), which has some features common to both ACAD and AQCA at 1040, 1179, 1608 cm<sup>-1</sup>, and almost no contribution from ACA. This result suggests that ACA is completely converted to photoproducts by TPA-induced photoreaction at the surface of the 23HexDod array. As can be seen from Figure 3, Vis light is capable of exciting LSPR in the case of the 10Dod and 23HexDod arrays, while for the 39HexDod arrays Vis light can only excite the quadrupole peak (500 nm) and the shoulder of the main LSPR peak, thus explaining the photoreaction results of 23HexDod.



**Figure 4.** Raman spectra of (a) ACA on 23HexDod 2D array, (b) ACAD on Au substrate, (c) AQCA on 23HexDod 2D array, (d) UV-(e) Vis- (f) NIR-irradiated ACA-coated 23HexDod arrays, and (g) bare 23HexDod 2D array.

In order to explain the results for the 10Dod array, we have to consider that small AuNPs show low plasmonic enhancement<sup>30</sup> and limited "hot spot" volume compared to larger particle arrays. From these considerations we can understand the role of AuNP size in the development of efficient plasmonic reactors.

Once the role of metallic nanoparticle size had been ascertained, we attempted to verify the importance of matching the excitation wavelengths with the 2D arrays' LSPR or  $\lambda_{TPA}$ . In detail, the 23HexDod array (2D array with the best match between LSPR and  $\lambda_{TPA}$ ) was irradiated with UV and NIR light (Figs. 4(d), (f)). It can be clearly seen that the ACA contribution (red dotted line in Fig. 4) is still dominant after NIR irradiation, which suggests that no reaction occurred, as expected. In the case of UV irradiation (wavelength range for one-photon reaction), no clear peaks were observed, which was confirmed by SEM measurement to have arisen from the sintering of AuNPs caused by the cleavage of surface alkanethiols.<sup>31</sup> Next, in the case of the 39HexDod array, irradiation was also performed with light in a suitable range to excite



**Figure 5.** Raman spectra of (a) bare 10Dod array on Au substrate, (b) ACA/10Dod array, and (c) visible light irradiated ACA/10Dod array (green line).



**Figure 6.** Raman spectra of (a) bare 39HexDod array on Au substrate, (b) ACA/39HexDod array, (c) visible light irradiated ACA/39HexDod array, and (d) NIR light irradiated ACA/39HexDod array.

the LSPR in the array (NIR light). NIR irradiation on the ACA-coated 39HexDod array resulted in no detectable change from the original ACA spectrum, suggesting that excitation of the 2D array under resonant conditions alone  $(\lambda_{ex} \equiv \lambda_{LSPR})$  is not sufficient to trigger photoreaction, and that suitable irradiation wavelengths are needed to induce any photoreaction in the dried ACA (overlapping between  $\lambda_{ex}$  and  $\lambda_{TPA}$  is small in the case of 39HexDod 2D array).

After comparing the photoreaction progress for various plasmonic substrates, we sought to identify the photoproduct of the Vis-light-irradiated ACA-coated 23HexDod 2D array to gain further insight into the photoreaction mechanism. Thus, we performed DFT calculation of Raman spectra of all candidate products, such as ACAD, AQCA, and 10,10'-dihydroxy-9,9',10,10'-tetrahydro-bianthryl-dicarboxylic acid (HBAC), see Figure 7 and Table I. Although DFT-calculated Raman spectra and experimental data do not match completely for all compounds under investigation (Table I), the formation of HBAC could explain the appearance of several peaks around 870-890 cm<sup>-1</sup> (877-895 in DFT), 1140 cm<sup>-1</sup> (1156 in DFT), 1179 cm<sup>-1</sup> (1156 in DFT), 1250 and 1320 cm<sup>-1</sup> (1237 and 1345 in DFT) without any increase in intensity of the C=O peak at 1660 cm<sup>-1</sup> (strong peak of AQCA).



**Figure 7.** DFT-calculated Raman activity of (a) ACA, (b) AQCA, (c) ACAD obtained by averaging the 4 stereomers of ACAD, and (d) 10,10'-dihydroxy-9,9',10,10'-tetrahydro-bianthryl-dicarboxylic acid (HBAC).

J. Nanosci. Nanotechnol. 15, 1171-1179, 2015

Pincella et al.

Table I. Comparison of experimental (normal Raman NR and surface-enhanced Raman SERS) and DFT (B3LYP/6-31G(d)/B3LYP/6-31G(d)/calculated intense Raman lines of ACA, AQCA, ACAD and HBAC. All experimental data except NR AQCA peaks (obtained from Ref. [38]) was collected during this study.

ACA (NR-SERS on 2D array)	ACA (DFT)	AQCA (NR <sup>38</sup> -SERS on 2D array)	AQCA (DFT)	ACAD (NR-SERS on Au)	ACAD (DFT)	HBAC (DFT)
	· · · ·	57		· /	· · · ·	
-	-	687–696	712	718–710	712	679
754–756	776	-	-	-	-	733
-	-	839-852	856	-	-	877
-	_	-	_	-	944	958
-	1040	1037-1034	-	1032-1035	1040	1075
-	1168	1173-1179	1072	1177-1179	1192	1156
1248(?)-1250	1248	-	1272	-	1264	1237
-	-	-	1352	-	1320	1345
1406-1409	1456	-	-	-	-	_
1556-1560	1536	1605-1598	1608	1610-1608	_	_
1631–1631	1600	1668–1667	1656 (1672)	-	1648	1660 (1696)

The formation mechanism of HBAC was previously suggested to have originated from photo-induced one-electron oxidation of anthracene backbone, following a reaction with water and dimerization.<sup>20</sup> As we recently reported,<sup>25</sup> the alkanethiol-capped AuNP surface can trap molecules inside the hydrophobic molecular interface where ACA and water can be concentrated. Thus, once ACA is excited by TPA, such sequential reaction is supposed to occur at the AuNP surface. Also, placing ACA near the AuNP surface is considered to accelerate the one-electron oxidation of ACA by AuNP's electron relay property.<sup>32</sup> Incenta to: Nanya mass spectrum with no remaining ACA, which strongly

In order to confirm the SERS results, all photoreaction products were analyzed by mass spectra. NIR-irradiated ACA on the 23HexDod array was confirmed to have no changes from the starting ACA (m/z 495.1 [Na-ACA +  $ACA - CO_2 + CH_3OH + H_2O + Na]^+$  similar to the SERS result (Figs. 8(a), (f)). Mass analysis revealed that some ACA content on the 23HexDod array was converted to AQCA (m/z 491.3 [AQCA-H + AQCA-CO<sub>2</sub> + CH<sub>3</sub>OH]<sup>-</sup>)by UV irradiation (Figs. 8(c), (d)). Surprisingly, Visirradiated ACA on the 23HexDod array gave a clear





Figure 8. ESI mass spectra of (a) ACA, (b) ACAD, (c) AQCA, reaction products of (d) UV-, (e) Vis-, and (f) NIR-irradiated ACA-coated 23HexDod arrays.

J. Nanosci. Nanotechnol. 15, 1171-1179, 2015



Figure 9. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) spectra of Vis-irradiated ACA solution with (a) 25HexDod-array, (b) Au thin film, (c) ACA, and (d) ACAD.

suggests the formation of HBAC (m/z 803.5 [2BHAC-2CO<sub>2</sub>+Na]<sup>+</sup>) (Fig. 8(e)) as suggested by DFT calculation. From these results, the 23HexDod array was found to act as plasmonic substrate for TPA-induced photoconversion of ACA.

Second, we show plasmonic TPA-induced photoreaction ACA in the solution phase (Scheme 1). The best substrate, the 23HexDod array, was applied to solution-phase TPA-induced reaction of ACA (Fig. 9), which is of greater interest for future applications. The substrate of the 23HexDod array was immersed in 10 mM ACA solution containing 10.8 mM NaOH in H<sub>2</sub>O–DMSO, where Vis light was irradiated for 33 h. The resultant solution was neutralized and extracted for <sup>1</sup>H NMR analysis. The <sup>1</sup>H NMR spectrum revealed the formation of trace amounts of ACAD (1.1% yield) and AQCA (84.1% yield) as a major product. A similar experiment was carried out to check the contribution of Au thin film used for the substrate of AuNP arrays, where complete conversion of ACA to AQCA was confirmed, which would have originated from recently



Figure 10. Extinction spectra of colloidal solution of 10 (blue line), 23 (red line) and 39 nm (black line) AuNP.

reported photocatalytic oxidation with Au.<sup>33</sup> Of course, without Au substrates, the ACA solution alone did not show any spectral change by Vis irradiation because of the absence of absorption bands at this wavelength range (Fig. 1(c)). Considering these results, although the background single-photon-based photocatalytic oxidation reaction by Au film is dominant, conversion of ACA to ACAD was successfully achieved by TPA-induced reaction by AuNP array. Our discovery of solution-phase as well as surface-phase TPA reactions paves the way for the selection of TPA reaction depending on the reaction media.

# 3. CONCLUSIONS

We succeeded in expanding the applicability of plasmonic metallic nanostructures to induce TPA reaction. We fabricated a series of AuNP arrays bearing LSPR ranging from UV, Vis, to NIR region depending on the AuNP size. Incoherent light in various wavelength ranges was irradiated to ACA-coated AuNP arrays and the photoreaction products were analyzed by SERS measurement and mass spectroscopy. The results confirmed that TPA-induced reaction requires matching between irradiation wavelength, LSPR, and twice the wavelength (half photon energy) of molecular excitation ( $\lambda_{irr} \equiv \lambda_{LSPR} \equiv 2\lambda_{ex}$ ). In addition, we found that even when matched conditions are met, the size of the AuNPs strongly affects the progress of the TPA-induced reaction. It was suggested by both DFT-calculated Raman analysis and mass spectra that the formation of HBAC had occurred through TPA-induced reaction at the surface of the 23HexDod array by Vis irradiation, while it was demonstrated by <sup>1</sup>H NMR that solution-phase TPAinduced reaction of ACA gave ACAD. Although higher reaction efficiency is necessary to apply TPA-induced reaction for chemical synthesis, we consider that this limitation can be overcome by combining AuNP array substrates with microchannel reaction systems, making this system

J. Nanosci. Nanotechnol. 15, 1171-1179, 2015

a promising candidate for the development of an efficient and cost-effective "lab-on-a-chip" for photoreactions.

# 4. EXPERIMENTAL DETAILS

# 4.1. General

Extinction spectra were recorded with a Jasco V-670 double-beam spectrophotometer equipped with a liquid cell holder module and a specular reflectance module, and SEM images were acquired with a Hitachi S-4800 FE-SEM. Raman measurements were performed with a Horiba Jobin Yvon T-64000 micro-Raman spectrometer equipped with He/Ne laser (632.8 nm excitation line was used), single monochromator with notch filter for laser line rejection, 1800 gr/mm grating, and liquid nitrogen cooled CCD detector. <sup>1</sup>H and <sup>13</sup>C spectra were recorded on JEOL JNM-AL300 and JNM-ECS400 spectrometers. Mass spectra were measured by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) coupled with electron spray ionization (ESI) technique using a SolariX FT-ICR-MS spectrometer (Bruker Daltonics GmbH). An Asahi-Spectra 300 W Xe lamp (Max-302) equipped with UV (250-385 nm), Vis (385-740 nm) and IR (750–1050 nm) mirror modules and a visible bandpass filter (422-750 nm) was used for the photodimerization experiments. Laser power and Xe lamp power (low incident) were measured on an Si photodiode (Thorlabs Inc. S120VC, wavelength range 200-1100 nm) power meter. Xe lamp power (high incident) was measured with a thermal power sensor (Thorlabs Inc. S302C). DFT calculation was carried out using the Gaussian 03 program.<sup>34</sup>

## 4.2. Materials

Plastic-formed carbon counter electrodes were purchased from Tsukuba Materials Information Laboratory Ltd. (TMIL) and used after cutting and cleaning by sonication in DI water and hexane. 2-Anthracene carboxylic acid (ACA), 9,10-anthraquinone 2-carboxylic acid (AQCA), hexadecyltrimethylammonium bromide (CTAB), and 1-hexanethiol were purchased from TCI. 1,6-Hexanedithiol (Hexdt), and chloroauric acid trihydrate were purchased from Sigma–Aldrich. All other chemicals were purchased from Nacalai-Tesque. All chemicals were guaranteed reagent grade and were used as received. Ultrapure water (Milli-Q by Millipore Co., 18.2 M $\Omega$  cm) was used throughout the experiments.

## 4.3. Substrate Preparation

Quartz substrates  $(1 \times 1 \text{ cm}^2)$  were cleaned by immersion for 15 min at RT in fresh piranha solution  $(H_2SO_4 30\%: H_2O_2 = 2:1 \text{ v/v};$  handle with care: piranha solution is highly corrosive and reacts violently with organic matter) and rinsed three times with milli-Q water. Quartz substrates were then coated with Cr (10 nm) (adhesion layer) and Au (40 nm) by electron beam deposition. Afterwards, samples were UV-ozone cleaned for 3 h and later

J. Nanosci. Nanotechnol. 15, 1171-1179, 2015

immersed in a 1% v/v solution of Hexdt in ethanol for 12 h, rinsed with 2-propanol (IPA) three times and dried under a nitrogen stream.

# 4.4. Gold Nanoparticle Synthesis 4.4.1. 10-nm Gold Nanoparticles

Small gold nanoparticles were synthesized by a seedmediated method<sup>35</sup> starting from a  $(3.5 \pm 0.7)$ -nm seed. 0.12 mL of ice-cold 0.1 M aqueous NaBH<sub>4</sub> solution was added to 4 mL aqueous solution containing  $2.5 \times 10^{-4}$  M HAuCl<sub>4</sub> · 3H<sub>2</sub>O and  $2.5 \times 10^{-4}$  M trisodium citrate while continuously stirring.

The growth solution was prepared by adding 0.2 mL of a 50 mM solution of  $HAuCl_4 \cdot 3H_2O$  to 39.8 mL of milli-Q water. Then, 1.2 g of solid CTAB was added to the solution to reach a final concentration of 0.08 M. The solution was stored in an incubator at 40 °C until it turned to an orange color and then finally cooled to RT before use. To obtain a final size of 10 nm, 2.07 mL of seed solution was added to a pre-prepared solution of 99.5  $\mu$ L of freshly prepared 0.1 M ascorbic acid solution and 17.83 mL of growth solution. The extinction spectrum of the solution is shown in Figure 10.

# 4.4.2. 23 nm and 39 nm Gold Nanoparticles

Large gold nanoparticles (AuNPs) were synthesized by another seed-mediated method<sup>36</sup> from a 13-nm seed. First, a gold seed solution was prepared by the citrate reduction method<sup>37</sup> (average size  $13 \pm 1.5$  nm): a 50 mL solution of 0.5 mM HAuCl<sub>4</sub>·3H<sub>2</sub>O was brought to boiling in a roundbottom flask while continuously stirring, then 2.5 mL of a 38.8 mM aqueous sodium citrate solution was added at once. The solution was refluxed for 20 min to allow complete reduction (solution turned wine red). The colloidal solution was left to cool slowly and then was used as the seed solution to obtain larger (23 or 39 nm) gold nanoparticles.

To prepare the growth solution, 0.8 mL of 20 mM aqueous  $HAuCl_4 \cdot 3H_2O$  solution and 80  $\mu$ L of 10 mM aqueous AgNO<sub>3</sub> solution were added to 34 mL of milli-Q water.

To obtain the desired final size, 6.12 mL (23-nm AuNPs) or 0.6 mL (39-nm AuNPs) of seed solution was added to the growth solution while stirring vigorously, and 6 mL of aqueous ascorbic acid solution (5.3 mM) was added dropwise (feeding rate 0.6 mL/min) to the solution by means of a mechanical syringe pump (KD Scientific). The extinction spectra of the colloidal solutions are shown in Figure 10.

# 4.4.3. Alkanethiol-Capped AuNPs

AuNPs of 10, 23 and 39 nm were then capped with alkanethiols:<sup>11</sup> The colloidal solution of 10-nm AuNPs was mixed with a 0.55% v/v dodecanethiol solution (10 mL) in acetone. The colloidal solution of 23- and 39-nm AuNPs was mixed with a 0.55% v/v solution of

hexanethiol:dodecanethiol = 3:1 (10 mL) in acetone. Stirring was performed for 12 h at RT, and then alkanethiolcapped AuNPs were extracted with methanol and hexane and purified by sequential centrifuge and redispersion into hexane three times.

## 4.5. 2D Array Deposition

The 2D array of AuNPs was deposited on the gold substrates by means of a hybrid method developed by our laboratory.<sup>12</sup> Briefly, a dithiol-functionalized gold substrate was used as a cathode, while a plastic carbon electrode was used as an anode. The distance between the electrodes was kept at 1.2 mm, while the voltage applied was 1.1 V. Alkanethiol-capped AuNPs were redispersed in a 2-mL hexane:acetone (10:1 v/v) solution. The electrodes were immersed in the colloidal solution (in a 3-mL plastic vessel) and left in a nitrogen-purged environment until complete evaporation of the colloidal solution took place. Afterwards, samples were put on a hot plate at 50 °C for 24 h to induce chemisorption of the AuNPs on the substrate and finally they were sonicated for 20 s to remove multilayers. The extinction spectra of the 10-, 23- and 39-nm AuNP 2D arrays are shown in Figure 3.

## 4.6. Deposition of Anthracene Derivative

ACA, AQCA, and ACA photodimer (ACAD) were deposited onto the AuNP 2D arrays by the immersion method. Deposition by immersion was performed by introducing a substrate in a sealed vessel containing a nitrogen gas-purged (15 min bubbling with  $N_2$  gas) 5 mM anthracene derivative solution prepared by adding 1 mL of 50 mM solution in DMSO to 9 mL of 6 mM aqueous NaOH solution. The samples were kept overnight in the anthracene derivative solution and then dried under a nitrogen stream. The anthracene derivative-coated samples were then characterized by Raman spectroscopy to verify the effective deposition of the anthracene derivative.

### 4.7. Synthesis of ACAD

ACAD was prepared by photodimerization under UV light irradiation (UV handheld lamp, HIROTA Co.). 15 mL of a 50.3 mM solution of ACA in DMF was irradiated with 365 nm excitation (power density 1407  $\mu$ W/cm<sup>2</sup> at 0.5 cm distance) for 12 h in a sealed glass vessel under N<sub>2</sub> atmosphere. After irradiation, ACA photodimer (white precipitate) was collected with a filter paper (Kiriyama Glass Works Co.). The product was confirmed by thin-layer chromatography (hexane/ethyl acetate 1/2 v/v as mobile phase) and by <sup>1</sup>H NMR spectrum.

### 4.8. Raman Measurements

Raman measurements were performed in order to verify all ACA, AQCA and ACAD coated samples. Raman spectra of anthracene compounds on 23- and 39-nm AuNPs 2D arrays were acquired with an incident power of 95  $\mu$ W

(with a 5% ND filter), 0.42 NA objective lens (45 × Super Long Working Distance Plan APO from Photon Design), integration time of 60 s and two acquisitions. For detection of ACA Raman peaks with the 10-nm AuNP 2D array as substrate, the power at the sample was set to 190  $\mu$ W (with a 10% ND filter), and acquisition time was set to 180 s (due to the low near-field enhancement of the substrate). The Raman peaks relative to ACA, ACAD and AQCA were identified by comparison of the SERS spectra with DFT-calculated spectra of the same compounds, as shown in Table I.

Acknowledgments: We thank the Japan Society for the Promotion of Science (JSPS) and the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT) for financial support; Grant-in-Aid for Challenging Exploratory Research (Kazushi Miki, 24656040); Grant-in-Aid for Scientific Research on Innovative Areas "Integrated Organic Synthesis" (Kazushi Miki, 22106545 and 24106746); and Grant-in-Aid for Young Scientists (Katsuhiro Isozaki, 30455274), Japan Science and Technology Agency (JST) for financial support of e-ASIA JRP. Also, a part of this research was supported both by the Research Foundation for Opto-Science and Technology and by Grant for Environmental Research Projects from The Sumitomo Foundation. We are grateful to Professor M. Nakamura and Professor H. Takaya (Kyoto University) for their assistance with the analysis and helpful discussions. This study was supported by NIMS Molecule and Material Synthesis Platform in "Nanotechnology Platform Project" operated by the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

#### **References and Notes**

- 1. J. Bhawalkar, G. He, and P. Prasad, *Rep. Prog. Phys.* 59, 1041 (1996).
- M. Pelton, J. Aizpurua, and G. Bryant, *Laser Photon. Rev.* 2, 136 (2008).
- 3. S. Kawata, Y. Inouye, and P. Verma, Nat. Photon. 3, 388 (2009).
- 4. Y. Tsuboi, R. Shimizu, T. Shoji, and N. Kitamura, J. Am. Chem. Soc. 131, 12623 (2009).
- B. Wu, K. Ueno, Y. Yokota, K. Sun, H. Zeng, and H. Misawa, J. Phys. Chem. Lett. 3, 1443 (2012).
- A. Tanaka, K. Hashimoto, B. Ohtani, and H. Kominami, *Chem. Commun.* 49, 3419 (2013).
- A. Sundaramurthy, P. J. Schuck, N. R. Conley, D. P. Fromm, G. S. Kino, and W. E. Moerner, *Nano Lett.* 6, 355 (2006).
- K. Ueno, S. Juodkazis, T. Shibuya, Y. Yokota, V. Mizeikis, K. Sasaki, and H. Misawa, J. Am. Chem. Soc. 130, 6928 (2008).
- 9. F. Pincella, K. Isozaki, and K. Miki, Light Sci. Appl. 3, e133 (2014).
- **10.** K. Ueno, S. Juodkazis, V. Mizeikis, K. Sasaki, and H. Misawa, *Adv. Mater.* 20, 26 (**2008**).
- 11. T. Ochiai, K. Isozaki, F. Pincella, T. Taguchi, K. Nittoh, and K. Miki, *Appl. Phys. Express* 6, 102001 (2013).
- 12. K. Isozaki, T. Ochiai, T. Taguchi, K. Nittoh, and K. Miki, *Appl. Phys. Lett.* 97, 221101 (2010).
- K. Ariga, Y. Yamauchi, T. Mori, and J. P. Hill, *Adv. Mater.* 25, 6477 (2013).
- 14. J. W. Colson and W. R. Dichtel, Nature Chem. 5, 453 (2013).

J. Nanosci. Nanotechnol. 15, 1171–1179, 2015

- K. S. Mali, J. Adisoejoso, E. Ghijsens, I. de Cat, and S. de Feyter, Acc. Chem. Res. 45, 1309 (2013).
- 16. R. K. Joshi and J. J. Schneider, Chem. Soc. Rev. 41, 5285 (2012).
- 17. M. A. Fox and S. Olive, Science 205, 582 (1979).
- N. Sugiyama, M. Iwata, M. Yoshioka, K. Yamada, and H. Aoyama, Bull. Chem. Soc. Jpn. 42, 1377 (1969).
- 19. M. O'Donnell, Nature 218, 460 (1968).
- 20. M. E. Sigman, S. P. Zingg, R. M. Pagni, and J. H. Burns, *Tetrahedron Lett.* 32, 5737 (1991).
- Y. Kawanami, H. Umehara, J.-I. Mizoguchi, M. Nishijima, G. Fukuhara, C. Yang, T. Mori, and Y. Inoue, *J. Org. Chem.* 78, 3073 (2013).
- 22. A. Dawn, T. Shiraki, S. Haraguchi, H. Sato, K. Sada, and S. Shinkai, *Chem. Eur. J.* 16, 3676 (2010).
- 23. A. Nakamura, Y. Inoue, J. Am. Chem. Soc. 125, 966 (2003).
- 24. T. Yatsuhashi, Y. Nakahagi, H. Okamoto, and N. Nakashima, J. Phys. Chem. A 114, 10475 (2010).
- 25. T. Taguchi, K. Isozaki, and K. Miki, Adv. Mater. 24, 6462 (2012).
- 26. Y. Zheng, J. Payton, T. Song, B. Pathem, Y. Zhao, H. Ma, Y. Yang, L. Jensen, A. K.-Y. Jen, and P. S. Weiss, *Nano Lett.* 12, 5362 (2012).
- 27. B. Nikoobakht and M. A. El-Sayed, J. Phys. Chem. A 107, 3372 (2003).
- 28. L. Bao, P. Sheng, J. Li, S. Wu, Q. Cai, and S. Yao, *Analyst* 137, 4010 (2012).
- 29. B. Sharma, M. F. Cardinal, S. Kleinman, N. G. Greeneltch, R. R. Frontiera, M. G. Blaber, G. C. Schatz, and R. P. Van Duyne, *MRS Bull.* 38, 615 (2013).
- 30. C. Deeb, X. Zhou, J. Plain, G. P. Wiederrecht, and R. Bachelot, J. Phys. Chem. C 117, 10669 (2013).

- S. Pocoví-Martínez, M. Parre, S. Agouram, and P. Julia, *Langmuir* 27, 5234 (2011).
- 32. Y. Xiao, F. Patolsky, E. Katz, J. F. Hainfeld, and I. Willner, *Science* 299, 1877 (2003).
- 33. T.-L. Wee, L. C. Schmidt, and J. C. Scaiano, J. Phys. Chem. C 116, 24373 (2012).
- 34. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT (2004).
- 35. N. Jana, L. Gearheart, and C. Murphy, *Langmuir* 17, 6782 (2001).
- 36. Y.-K. Park and S. Park, Chemistry of Materials 20, 2388 (2008).
- 37. G. Frens, Nature 241, 20 (1973).
- 38. S. Han, S. Joo, and T. Ha, J. Phys. Chem. B 104, 11987 (2000).

Delivered by Ingenta to: Narvarged: 17 December 2013. Accepted: 25 December 2013.

Copyright: American Scientific Publishers