



## Article

# Fabrication of Large-Area Ordered Au Nano-Ring Arrays for the Electrochemical Removal and Sensing of Rhodamine 6G Molecules

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**Abstract:** To understand the formation process of ordered Au nano-ring arrays (NRA), a series of factors—including etchant gas and flow rate, chamber pressure and RF power—were systematically studied and a set of optimum parameters were deduced to fabricate this interesting structure. With plenty of active sites previously reported, a new role of ordered Au NRA is unlocked in this work. The ordered Au NRA could perform the electrochemical removal of rhodamine 6G (R-6G) at a high concentration in seawater within 12 min and complete discoloration within 9 min, which demonstrates ~7 times efficiency improvement from previous studies. The nanostructured surface also makes the ordered Au NRA a good substrate material in R-6G sensing using surface-enhanced Raman spectroscopy, which performs with better accuracy than the ultraviolet–visible light technique.

**Keywords:** Au nano-ring arrays; formation process; rhodamine 6G removal; rhodamine 6G sensing; surface-enhanced Raman spectroscopy



**Citation:** Cao, X. Fabrication of Large-Area Ordered Au Nano-Ring Arrays for the Electrochemical Removal and Sensing of Rhodamine 6G Molecules. *Chemosensors* **2023**, *11*, 539. <https://doi.org/10.3390/chemosensors11100539>

Academic Editors: Núria Serrano and Manel del Valle

Received: 17 July 2023

Revised: 7 September 2023

Accepted: 11 October 2023

Published: 13 October 2023



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## 1. Introduction

As a derivative compound of the xanthene family, rhodamine 6G (R-6G) is a common synthetic dye that has long been used as a colorant in textiles, plastics, food, and cosmetic products [1–3]. It can also be used as a fluorescent dye that can be applied in chemical sensing [4–6], bio-imaging [7,8], forensic technology [1,2], water tracing [1], and used for single molecule detection based on surface-enhanced Raman spectroscopy (SERS) applications [9]. Because of their high solubility in water and many organic solvents, xanthene dyes could pose great harm to the eco-system via environmental pollution; they may also enter the bodies of mammals together with food, which causes acute poisoning in the short term and cancers in the long term [10,11]. It was reported that R-6G may cause irritation to the eyes, skin, and respiratory system of human beings [1]; exposure to excess amounts may even lead to reproductive, developmental, and chronic toxicities [1] due to its carcinogenicity [2,3]. Therefore, extensive research has been carried out on wastewater treatment and the removal of R-6G.

Currently, the removal of R-6G is mainly divided into physical, chemical, and biological methods [12,13]. Physical adsorption and chemical degradation remain the most effective and economical ways to remove persistent organic pollutants (POPs) like R-6G because biological degradation obviously does not work [12,13]. For efficient adsorption, the adsorbent material should possess a large specific surface area and adsorption capacity, as well as show excellent affinity to the adsorbate and good recyclability [14–16]. Furthermore, the generation of secondary waste is still an underlying issue to be solved after physical adsorption, thus chemical removal is believed to be a more eco-friendly method [12]. The reported R-6G degradation methods are focused on photocatalysis and the Fenton reaction [13] as advanced oxidation processes, which either require the utilization of hazardous ultraviolet radiation or complex chemical reactions that are usually time-consuming. In recent years, some researchers have reported their works on electrochemical removal of

R-6G [17,18], which has several advantages including a simple setup and high efficiency; however, the concentration of R-6G was low and the reported methods may not represent their actual application in wastewater treatment.

The electrochemical degradation of R-6G relies on the mass and charge transfer; therefore, the surface area-to-volume (SA/V) ratio of the electrode material and the presence of active sites play a crucial role in the entire process. It is reported that array structures could provide a significant enhancement in many fields of study, such as catalysis [19–23], anti-reflection coatings [24,25], solar cells [26,27], optoelectronics [28], surface property modifications [29], and biomedical applications [30]. Recent research works demonstrated that improvement could originate from an increased SA/V ratio and surface energy content of the samples, the presence of active sites and defects, as well as the charge transfer rate [31,32]. These are exceptionally obvious in noble metals, which have hybridized bands in the d-orbital electrons.

In the previous research, Au nanostructure arrays were fabricated on Si wafers using nanosphere lithography (NSL) followed by reactive ion etching (RIE) [22]. NSL created an ordered hexagonal arrangement of the structures over the entire Si substrate, which increased the SA/V ratio to facilitate the more efficient adsorption of the reactant; the RIE process led to the formation of nanoscale to atomic-scale active sites across each individual structure and increased the surface energy content, which could easily overcome the activation barrier and reduce the possible hindering of the charge transfer. These findings have demonstrated a remarkable improvement in the electrocatalysis of the ethanol oxidation reaction in an alkaline medium [22,23]. However, the formation process of ordered Au nano-ring arrays (NRA) is still mysterious and other potential applications of the Au NRA have not been explored. Besides the great enhancement in electrocatalysis, the literature has reported that Au may also have excellent properties in molecular sensing through SERS [33–35]. This is mainly due to the localized surface plasmon resonance effect of the extremely small nanoparticles or features [36,37], and this could have a significant impact on the SERS detection of R-6G molecules [33,35]. In this work, the factors affecting the formation of ordered Au NRA are systematically determined for their large-area fabrication with ~100% substrate coverage. The ordered Au NRA are also successfully applied in R-6G removal and sensing, which showed a fast and effective electrochemical removal of R-6G at high concentrations and excellent sensing performance towards R-6G at low concentrations.

## 2. Materials and Methods

The chemicals used in this study include hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30 wt%, VWR, Radnor, PA, USA), sulphuric acid ( $\text{H}_2\text{SO}_4$ , 98%, Merck, Rahway, NJ, USA), absolute ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ , 99.9%, Aik Moh, Tuas St, Singapore), polystyrene (PS) latex beads (500 nm diameter, Thermo Fisher Scientific, Waltham, MA, USA), and sodium dodecyl sulphate (SDS, 99%, Sigma-Aldrich, St. Louis, MO, USA). All of the above-mentioned chemicals were used as received without any further purification or modification. The deionized water was made by the Millipore™ system, which has the resistivity of  $18.2 \text{ M}\Omega\cdot\text{cm}$ . Commercial R-6G powder (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) was dissolved in absolute ethanol to form a 100 mM solution for later use.

### 2.1. Fabrication Process

The Si wafers were treated in piranha solution ( $\text{H}_2\text{O}_2:\text{H}_2\text{SO}_4 = 1:3$  by volume), rinsed with absolute ethanol in an ultrasonic bath, and dried in an oven. Magnetron sputtering was carried out at the direct current (DC) power of 200 W and Ar flow rate of 20 sccm; the target used was 99.99% Au and the chamber pressure was maintained at no more than  $5.0 \times 10^{-6}$  Torr. The deposition was held at room temperature for 2 min to obtain 100 nm Au thin film on Si. Following this, with the aid of SDS, monodispersed commercial PS colloidal nanospheres were self-assembled onto Au thin film to form a close-packed monolayer. Finally, the samples were individually loaded into the chamber of an RIE system and were

etched for 5 min with the variation of different parameters (etchant gas, chamber pressure, RF power, and flow rate).

## 2.2. Characterization and Testing Techniques

The surface morphologies of the nanostructures were examined using a dual-beam scanning electron microscope/focused ion beam (SEM/FIB) system (Nova NanoLab 600i, FEI, Hillsboro, OR, USA), which was operated at electron accelerating voltage of 5 kV and probe current of 0.40 nA under field emission mode for secondary electron imaging. The physical stability of the Au NRA was tested by  $\text{Ga}^+$  ion beam illumination in the FIB system, which was operated at ion accelerating voltage of 30 kV and probe current of 0.46 nA. The subsequent elemental compositions of the surface microstructures were analyzed by energy-dispersive X-ray (EDX) spectroscopy, which was performed using a laser-cooled EDX detector (Octane Elite Plus, EDAX, Mahwah, NJ, USA) attached to the FIB system.

Following the procedure of previous studies [17,18], electrochemical removal of R-6G was carried out in a two-electrode system powered by a DC power supply. The sensing of remaining R-6G in solution was performed by both ultraviolet–visible light (UV–Vis) spectroscopy and SERS. The absorption spectra of R-6G solution were collected using a UV–Vis spectrophotometer (UV-2700, Shimadzu, Kyoto, Japan), and SERS detection was conducted on a backscattering confocal Raman system (CRM200, Witec, Ulm, Germany) equipped with 457 nm laser source.

## 3. Results

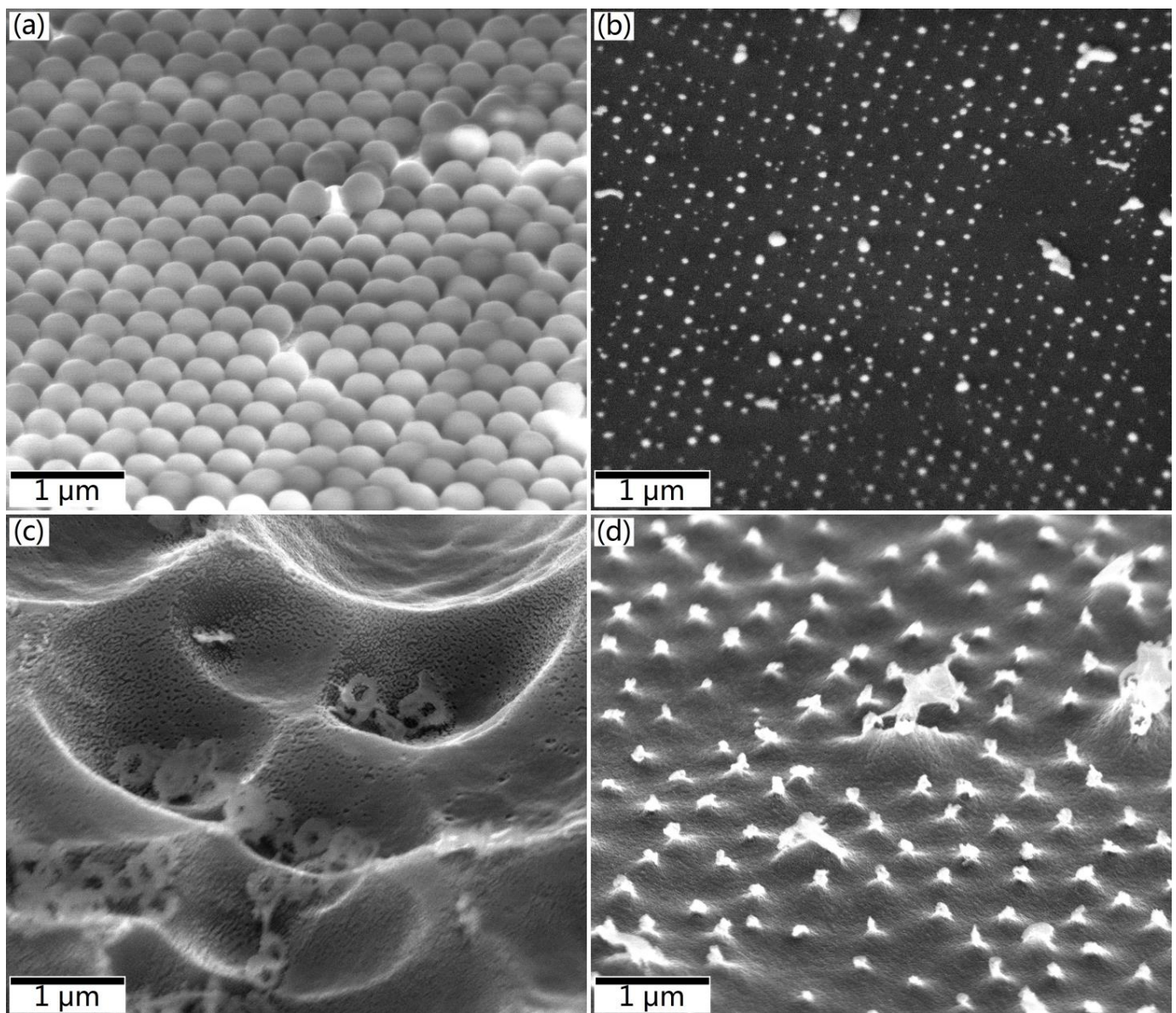
### 3.1. Etchant Gas

The etching profiles in the RIE system strongly depend on the process parameters, such as the etchant gas, flow rate, chamber pressure, RF power, and etching duration. In the first set of experiments, the etchant gas was varied while all other parameters were strictly controlled to be the same (chamber pressure: 300 mTorr; etchant gas flow rate: 20 sccm; RF power: 100 W). Figure 1 shows the FEG-SEM images of the samples before and after the RIE process.

Figure 1a displays a single-layer densely packed self-assembly of PS colloidal spheres on the surface of the Au-coated Si substrate, which has highly ordered arrangement with few defects identified. After RIE with Ar, most of Au was removed; the remaining Au can be observed as the bright spots in image Figure 1b, in which the Au nano-dots render a high level of orderliness but are not uniform in size and have quite a significant quantity of defects. The heterogeneous sizes of the Au structures would severely affect the SPR effect of the sample, which is unfavorable in the SERS detection tests. RIE with tetrafluoromethane ( $\text{CF}_4$ ) produces regular nanoporous trough morphology, as shown in Figure 1c. The Si substrate was etched to form large and deep valleys while many PS nanospheres were retained within these valleys; this is because the fluorine-rich etchant  $\text{CF}_4$  is highly selective and it chemically reacts with the Si substrate.

However, a fatal problem is that the remaining PS hinders the proper functioning of the samples; when the sample was immersed in toluene to remove the remaining PS, the Au coating becomes easily detached from the substrate, which is probably due to the high porosity of the structure. A PS nipple array was formed after RIE with  $\text{O}_2$ , as shown in Figure 1d, which has a similar orderliness as compared to Figure 1b, but much more Au was kept on the substrate; this is because the  $\text{O}_2$  plasma preferentially etches PS over Au and Si, which could be determined using EDX analysis.

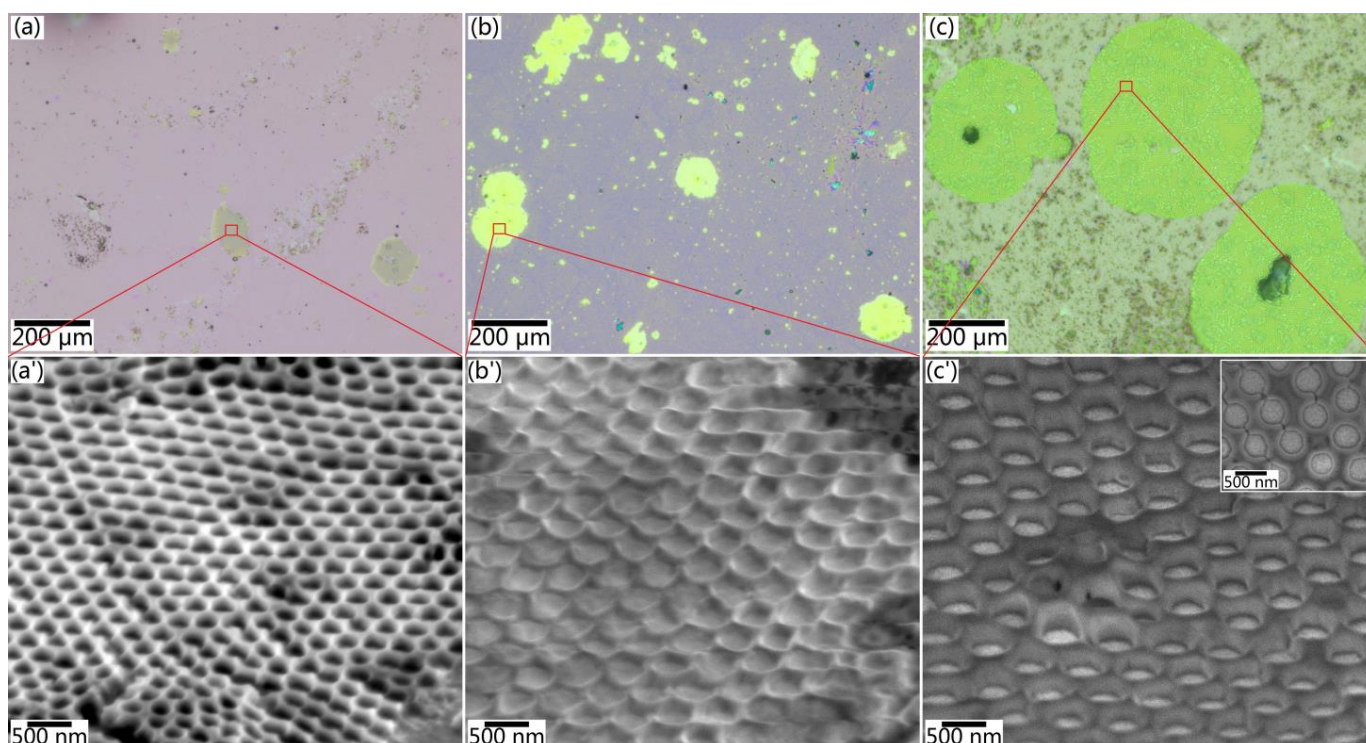
Being the core active material, Au is expected to be continuous for good performance; on the other hand, the plane and smooth surface of the Si substrate helps to support and maintain the Au thin film with patterns. As the targeted outcome is a patterned Au thin film without sacrificing the Si substrate, the etchant gas is chosen to be oxygen, which has the least attacking effect on both the Au and the Si substrates.



**Figure 1.** The 52° tilted FEG-SEM images of Si/Au/PS samples at 100 k×: (a) before and (b–d) after the RIE process. The etchant gas used was (b) Ar; (c) CF<sub>4</sub>; and (d) O<sub>2</sub>.

### 3.2. Chamber Pressure

Chamber pressure is another important factor that could affect the etching profiles, thus samples were individually loaded, and the system was maintained at different chamber pressures before RIE, while all other parameters were kept constant (etchant gas: O<sub>2</sub>; etchant gas flow rate: 20 sccm; RF power: 100 W). Figure 2 demonstrates the polarized optical microscope (POM) and FEG-SEM images of these samples. In the POM images (Figure 2a–c), the green spots are regions where ordered array structures could be found; it is obvious that as the chamber pressure is reduced, more spots start to form arrays and they tend to aggregate to form larger continuous areas. The regions boxed up in red are further enlarged for the FEG-SEM images.

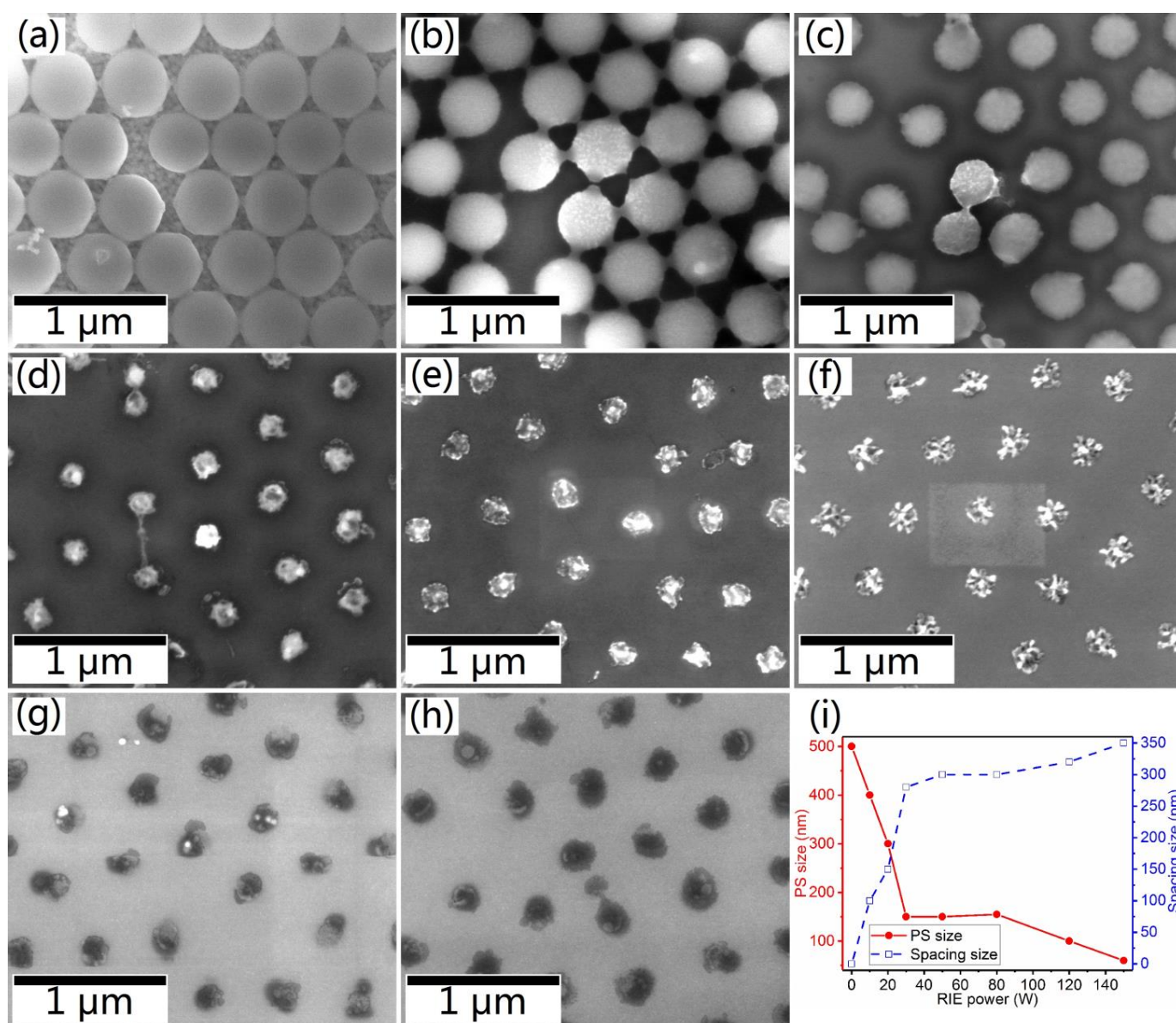


**Figure 2.** POM images taken at 1 k $\times$  (**top**) and 52° tilted FEG-SEM images taken at 50 k $\times$  (**bottom**) of Si/Au/PS sample after RIE. The chamber pressure was kept at (a,a') 300 mTorr; (b,b') 250 mTorr; and (c,c') 200 mTorr. The inset of (c') is a top view FEG-SEM image taken at a magnification of 50 k $\times$ .

From the FEG-SEM images (Figure 2a'–c'), it could be observed that within the green spots in the POM images, all PS was etched away and the Au array structures were nicely formed. When the chamber pressure was kept at 300 mTorr, a thick Au skeleton structure was obtained with a height almost equal to that of the deposited Au thin film (Figure 2a'); this might be because 300 mTorr is a relatively high chamber pressure and there is more scattering during the RIE process, thus leading to less effective etching and the production of smaller continuous areas. When the chamber pressure is lowered to 250 mTorr, the skeleton structure becomes thinner (Figure 2b') and a larger area could be observed (Figure 2b); this should be as a result of more effective etching due to less scattering by the residual air molecules. When the chamber pressure was further reduced to 200 mTorr (Figure 2c'), the extended etching brought about the formation of a shallow bowl-shaped structure. The inset of Figure 2c' shows the structure in its top view; the array forms a “ring” outside each individual feature which is in fact the oblique inner wall of the bowl structure. This has a different contrast compared to the regions between the features. Further reducing the chamber pressure to 100 mTorr leads to the large-area formation of the nanostructures in Figure 2c' with almost full coverage of the entire Si substrate.

### 3.3. RF Power

In order to investigate the effect of RF power on feature size, the power was varied from 10 W to 150 W with all other parameters kept constant (chamber pressure: 100 mTorr; etchant gas: O<sub>2</sub>; etchant gas flow rate: 20 sccm). Figure 3 is a collection of the top view FEG-SEM images of this set of samples. Figure 3a illustrates the state of the original sample before RIE, in which the PS spheres are in touch with each other and have a beautiful hexagonal arrangement. RIE using O<sub>2</sub> plasma etches the PS spheres and they become more separated. When the RF power was set from 10 W up to 30 W (Figure 3b–d), the size of the PS sharply dropped from 500 nm to ~150 nm, and the separation spacing increased quickly to ~280 nm (Figure 3i); spherical shapes and spatial orderliness were well maintained as well.



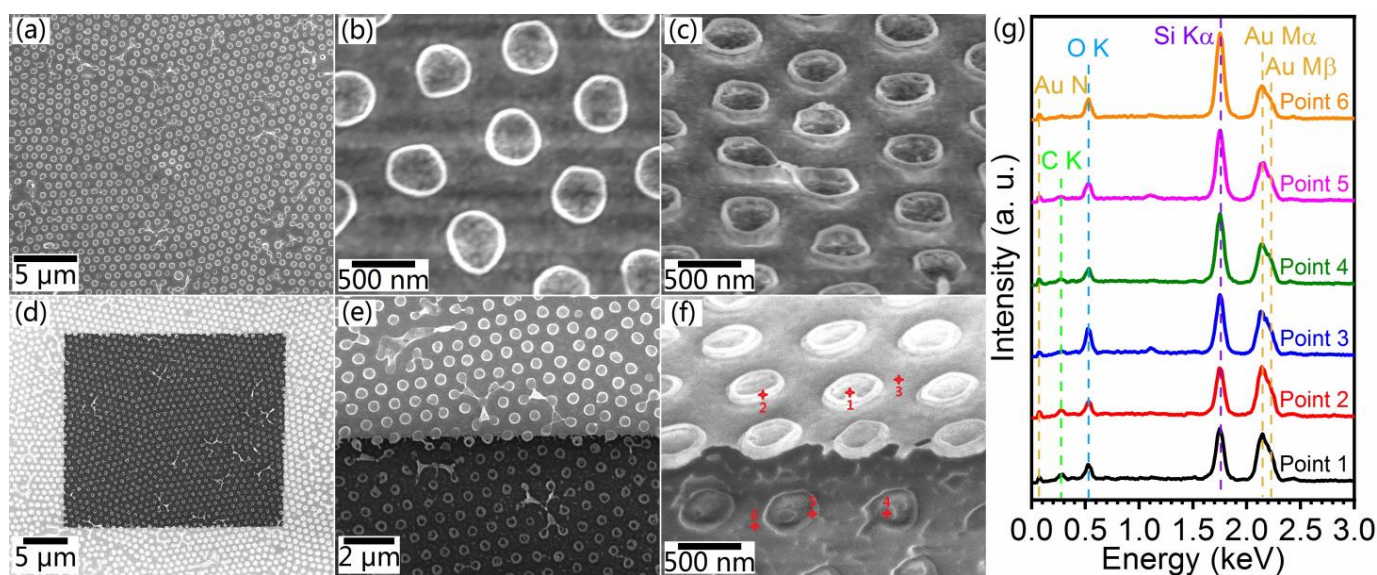
**Figure 3.** (a–h) Top view FEG-SEM images of Si/Au/PS sample taken at 100 k $\times$ : (a) before RIE; (b–h) after RIE at the power of (b) 10 W; (c) 20 W; (d) 30 W; (e) 50 W; (f) 80 W; (g) 120 W; and (h) 150 W. (i) Diagram showing the relationship of the remaining PS spheres and feature spacing sizes with RIE power.

As the power was increased from 30 W to 80 W (Figure 3d–f), the sizes of the remaining PS and the separation spacing stayed steady and little variation could be observed (Figure 3i); the only trend was that the shape of the remaining PS became less spherical, but the spatial orderliness remained good. Upon the continued ramping of RF power from 80 W to 150 W (Figure 3f–h), the size of the remaining PS was further reduced down to ~60 nm and the separation spacing was enlarged to ~350 nm (Figure 3i); this again led to the formation of the bowl structure shown previously (Figure 2c'), but a trace amount of PS remained, possibly because the chamber pressure might have small fluctuations during the RIE process.

### 3.4. Etchant Gas Flow Rate

To further manifest the formed array structures, the etchant gas flow rate was doubled from 20 sccm to 40 sccm, with all other parameters being fixed (etchant gas: O<sub>2</sub>; chamber

pressure: 100 mTorr; RF power: 150 W). The FEG-SEM images taken using the FIB system (Figure 4) reveal that the fabricated array structures are large-area structures and are well-aligned in a hexagonal shape (Figure 4a). Under a much larger etchant gas flow rate, the formed arrays no longer have bowl-shaped structures; they turn to form rings instead, which protrude outwards from the surface of the Au thin film. The Au nano-rings are ~500 nm in their outer diameter with a wall thickness of ~25 nm (Figure 4b), and the height of the rings is ~83 nm (Figure 4c). This might be due to the upwards movement of the Au beneath the PS during RIE, or alternatively, the Au might be softened by the plasma during RIE and the PS nanospheres may partially sink into the Au film at their original positions.



**Figure 4.** FEG-SEM images of Si/Au/PS sample after RIE taken using the dual-beam FIB system: (a,b) 10 k $\times$  and 100 k $\times$  top view and (c) 100 k $\times$  at 52° tilt; (d,e) 7 k $\times$  and 20 k $\times$  top view and (f) 100 k $\times$  at 52° tilt, showing contrast before and after irradiation by Ga<sup>+</sup> ion source at 30 kV and 0.46 nA for 30 s; (g) EDX spectra of the spots marked in (f). The C K signal is contributed by PS residue after RIE.

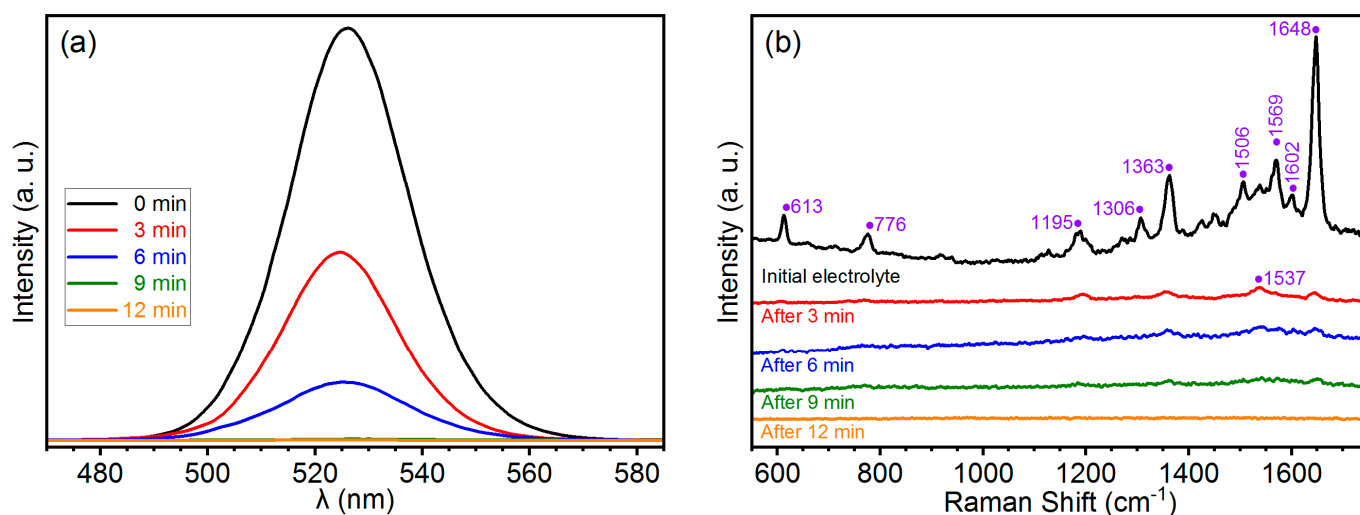
To investigate the physical stability of the Au NRA upon external attacking, the ion beam was unblanked and left unattended for 30 s of ion illumination. Under the irradiation of the Ga<sup>+</sup> ion beam, the illuminated area darkens out and the obvious contrast difference is contributed to by the height difference (Figure 4d). Further magnifying (Figure 4e,f) shows that the Au nano-rings kept well in their original shape and alignment, which means the sample has high chemical inertness and could withstand strong external attacks. From Figure 4f, six individual points were selected and the EDX analyses (Figure 4g) reveal that the nano-rings before and after the Ga<sup>+</sup> ion beam irradiation, including the wall and the regions inside and outside of the rings, are gold, which have a strong Au M $\alpha$  intensity at 2.14 keV and a weak but detectable Au N signal at 0.07 keV; the signals of Si K $\alpha$  and O K (contributed from substrate) appear to be stronger in the darkened area as the Au becomes thinner after the Ga<sup>+</sup> irradiation.

### 3.5. R-6G Removal and Sensing

In aqueous and ethanol solutions with a neutral pH value of 7, R-6G monomers start to aggregate and form ~2% dimers at a 1 μM concentration; as the concentration increases, the dimers may constitute up to 4% and 15.1% at 10 μM and 50 μM concentrations, respectively [38]. At even higher concentrations, trimers and oligomers start to form, which greatly increase the difficulty of R-6G removal due to the strong interactions with the solvent molecules via hydrogen bonding. The addition of specific organic compounds, such as certain carboxylic acids or surfactants, may help to decelerate the dimerization

process [39,40], but they cannot ease the situation and the requirement of the R-6G removal is still present. In the case of which R-6G molecules have already aggregated and dimerized to a substantial extent, making use of free radicals was reported to be an ideal choice to tackle the dyes with high efficiency [31,38,41], due to their oxidative nature and extraordinary reactivity.

Under extreme physical conditions, such as super high temperatures or electrical flux per unit time, free radicals can be easily produced. In aqueous environments, water molecules can be dissociated into other molecular species like  $H_2$  and  $H_2O_2$ , charge carriers like  $e^-_{aq}$  and  $H_3O^+$ , and free radicals like  $\cdot H$  and  $\cdot OH$  [31]. Other available free radicals may include  $\cdot Cl$  from the dissociation of  $Cl^-$  ions dissolved in salt solutions, which also possess a similar power in the chemical degradation of POPs. Therefore, seawater is the best choice of electrolyte, which is readily available in almost inexhaustible amounts, and would contain almost all desirable free radicals upon successful dissociation. As such, 2 mL of a 100 mM R-6G solution was added into 28 mL of synthetic seawater (3.5% NaCl, pH = 8) [42], and the resultant solution was homogeneously mixed while being used as the electrolyte. The resultant electrolyte had an R-6G concentration of  $\sim 6.67$  mM (equivalent to  $\sim 3.1935$  g/L), which is  $\sim 3$ – $15$  times higher than the values given in the previous studies (200–800 mg/L) [17,18]. The Au NRA samples imaged in Figure 4a–c (etchant gas:  $O_2$ ; chamber pressure: 100 mTorr; RF power: 150 W; flow rate: 40 sccm) were newly fabricated and used as both the anode and the cathode. Throughout the electrochemical removal cycle, a small volume of the electrolyte was retrieved every 3 min for analysis and the respective UV–Vis absorption spectra were shown in Figure 5a. The initial color of the electrolyte was orange-red. As the process proceeded, the concentration of R-6G gradually decreased and the electrolyte became completely decolorized in about 9 min. This is evident from the reduction of the intensities of the absorption peak at  $\sim 525$  nm [43–45], which diminished in the spectra collected after 9 and 12 min of electrochemical removal. The duration for complete discoloration is less than twice that for an electrolyte with much lower concentrations ( $\sim 5$  min for 200 mg/L R-6G) [17,18], indicating  $\sim 7$  times efficiency improvement.



**Figure 5.** Detection of R-6G using (a) UV–Vis spectroscopy and (b) SERS during its discoloration.

Apart from the UV–Vis spectroscopy, the electrolyte with R-6G solutions after various durations of electrochemical removal was also analyzed by SERS, as shown in Figure 5b. A fixed amount of electrolyte was coated onto a clean piece of Au NRA sample dropwise and dried before each individual analysis. The spectrum of the initial electrolyte renders multiple strong peaks, all of which could be indexed to R-6G referenced by the commercial powder. After electrochemical removal for 3 min, most of the peaks for R-6G become hardly detectable and only several peaks can be clearly identified. As the removal duration lengthens, the intensities of these peaks gradually become weakened and show four distinct

peaks after 6 min of removal. The SERS signals of the R-6G are left with two weakly identifiable peaks after 9 min of removal, implying that there is still a tiny amount of R-6G present in the electrolyte. Complete removal is determined by the featureless SERS spectrum after 12 min of electrochemical removal.

The fast removal is inseparable from the adsorption of R-6G on a Au NRA with a nanostructured surface and the presence of a sufficient amount of active sites [22]. Apart from the Au...H-X bonding reported in the previous work [22], the adsorption could also occur by building noncovalent Au-N interactions featuring an ultrafast charge transfer [46], in which the dative Au←:N bond can be electrochemically converted to an electronically transparent Au-N bond [47]. As supported in another study, the Au-N or Au-O anchor bonds can also be reinforced by N-H...Au bonds [48], thus with the NaCl-rich nature of the electrolyte [49] and rough surface of the Au NRA [50], R-6G could be easily adsorbed during the electrochemical removal process. The difference in the detection results might origin from the mechanisms of the respective techniques; SERS detects the analytes through their adsorption on and interactions with the substrates [51], while UV-Vis detection follows the Beer-Lambert law through optical absorption and subsequent calculated concentrations of the analytes [52]. The excellent adsorption afore mentioned would greatly enhance SERS detection. This further implies that Au NRA could serve both as a good SERS substrate in sensing R-6G molecules at low concentrations and an excellent material in R-6G removal at high concentrations, both of which have not been concurrently achieved by past research works.

#### 4. Conclusions

This research has systematically studied the factors in the formation of ordered Au NRA structures on Si wafers using an NSL-RIE approach, as reported in previous work. A set of optimum parameters were deduced for large-area fabrication with ~100% substrate coverage. Previous work showed that the nanostructured surface of Au NRA has plenty of active sites, which could play an important role in electrochemical processes, including but not limited to the material removal reported in this research. New pieces of Au NRA samples were used as both the electrode material in electrochemical removal of R-6G and the substrate material in its SERS detection. The performance was assessed by corresponding detections using UV-Vis and SERS techniques, both of which proved almost complete removal after 12 min. Apart from being an efficient electrocatalyst in the ethanol oxidation reaction, this work demonstrates that ordered Au NRA perform well in the electrochemical removal of R-6G using seawater with ~7 times efficiency improvement compared to previous studies, which unlocks another role of ordered Au NRA in their multi-functionality. The removal of R-6G at high concentrations and the sensing of R-6G at low concentrations can be concurrently achieved using ordered Au NRA, which has not been featured in any previous studies.

**Funding:** This research was supported by the MOE AcRF Tier 1 grant M4011528. The FEG-SEM/FIB and EDX characterizations were carried out at Microelectronics Reliability and Characterization (MRC) Lab.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data presented in this study are available on request from the corresponding author.

**Acknowledgments:** Not applicable.

**Conflicts of Interest:** The author declares no conflict of interest. The funder had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

## References

1. Ranjbari, E.; Hadjmohammadi, M.R. Optimization of magnetic stirring assisted dispersive liquid–liquid microextraction of rhodamine B and rhodamine 6G by response surface methodology: Application in water samples, soft drink, and cosmetic products. *Talanta* **2015**, *139*, 216–225. [\[CrossRef\]](#) [\[PubMed\]](#)
2. Biparva, P.; Ranjbari, E.; Hadjmohammadi, M.R. Application of dispersive liquid–liquid microextraction and spectrophotometric detection to the rapid determination of rhodamine 6G in industrial effluents. *Anal. Chim. Acta* **2010**, *674*, 206–210. [\[CrossRef\]](#) [\[PubMed\]](#)
3. Xiao, N.; Deng, J.; Huang, K.; Ju, S.; Hu, C.; Liang, J. Application of derivative and derivative ratio spectrophotometry to simultaneous trace determination of rhodamine B and rhodamine 6G after dispersive liquid–liquid microextraction. *Spectrochim. Acta Part A* **2014**, *128*, 312–318. [\[CrossRef\]](#) [\[PubMed\]](#)
4. Beija, M.; Afonso, C.A.M.; Martinho, J.M.G. Synthesis and applications of Rhodamine derivatives as fluorescent probes. *Chem. Soc. Rev.* **2009**, *38*, 2410–2433. [\[CrossRef\]](#) [\[PubMed\]](#)
5. Das, D.; Alam, R.; Ali, M. Rhodamine 6G-based efficient chemosensor for trivalent metal ions ( $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$ ) upon single excitation with applications in combinational logic circuits and memory devices. *Analyst* **2022**, *147*, 471–479. [\[CrossRef\]](#)
6. Zhang, E.; Ju, P.; Li, Q.; Hou, X.; Yang, H.; Yang, X.; Zou, Y.; Zhang, Y. A novel rhodamine 6G-based fluorescent and colorimetric probe for  $\text{Bi}^{3+}$ : Synthesis, selectivity, sensitivity and potential applications. *Sens. Actuators B Chem.* **2018**, *260*, 204–212. [\[CrossRef\]](#)
7. Fu, Y.; Jiang, X.-J.; Zhu, Y.-Y.; Zhou, B.-J.; Zang, S.-Q.; Tang, M.-S.; Zhang, H.-Y.; Mak, T.C.W. A new fluorescent probe for  $\text{Al}^{3+}$  based on rhodamine 6G and its application to bioimaging. *Dalton Trans.* **2014**, *43*, 12624–12632. [\[CrossRef\]](#)
8. Alam, R.; Bhowmick, R.; Islam, A.S.M.; Katarkar, A.; Chaudhuri, K.; Ali, M. A rhodamine based fluorescent trivalent sensor ( $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ) with potential applications for live cell imaging and combinational logic circuits and memory devices. *New J. Chem.* **2017**, *41*, 8359–8369. [\[CrossRef\]](#)
9. Smith, W.E.; Rodger, C. Surface-Enhanced Raman Scattering (SERS), Applications. In *Encyclopedia of Spectroscopy and Spectrometry*, 2nd ed.; Academic Press: Cambridge, MA, USA, 1999; pp. 2822–2827.
10. Nestmann, E.R.; Douglas, G.R.; Matula, T.I.; Grant, C.E.; Kowbel, D.J. Mutagenic Activity of Rhodamine Dyes and Their Impurities as Detected by Mutation Induction in Salmonella and DNA Damage in Chinese Hamster Ovary Cells. *Cancer Res.* **1979**, *39*, 4412–4417.
11. Sulistina, D.R.; Martini, S. The Effect of Rhodamine B on the Cerebellum and Brainstem Tissue of Rattus Norvegicus. *J. Public Health Res.* **2020**, *9*, 101–104. [\[CrossRef\]](#)
12. Gusain, R.; Gupta, K.; Joshi, P.; Khatri, O.P. Adsorptive removal and photocatalytic degradation of organic pollutants using metal oxides and their composites: A comprehensive review. *Adv. Colloid Interface Sci.* **2019**, *272*, 102009. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Brillas, E.; Sirés, I.; Oturan, M.A. Electro-Fenton Process and Related Electrochemical Technologies Based on Fenton’s Reaction Chemistry. *Chem. Rev.* **2009**, *109*, 6570–6631. [\[CrossRef\]](#)
14. Uddin, M.J.; Ampia, R.E.; Lee, W. Adsorptive removal of dyes from wastewater using a metal-organic framework: A review. *Chemosphere* **2021**, *284*, 131314. [\[CrossRef\]](#) [\[PubMed\]](#)
15. Xiao, W.; Jiang, X.; Liu, X.; Zhou, W.; Garba, Z.N.; Lawan, I.; Wang, L.; Yuan, Z. Adsorption of organic dyes from wastewater by metal-doped porous carbon materials. *J. Clean. Prod.* **2021**, *284*, 124773. [\[CrossRef\]](#)
16. Wang, S.; Sun, H.; Ang, H.M.; Tadé, M.O. Adsorptive remediation of environmental pollutants using novel graphene-based nanomaterials. *Chem. Eng. J.* **2013**, *226*, 336–347. [\[CrossRef\]](#)
17. Yunus, R.F.; Zheng, Y.-M.; Nadeeshani Nanayakkara, K.G.; Chen, J.P. Electrochemical Removal of Rhodamine 6G by Using  $\text{RuO}_2$  Coated Ti DSA. *Ind. Eng. Chem. Res.* **2009**, *48*, 7466–7473.
18. Zheng, Y.-M.; Yunus, R.F.; Nadeeshani Nanayakkara, K.G.; Chen, J.P. Electrochemical Decoloration of Synthetic Wastewater Containing Rhodamine 6G: Behaviors and Mechanism. *Ind. Eng. Chem. Res.* **2012**, *51*, 5953–5960. [\[CrossRef\]](#)
19. Liu, H.; Khoo, C.Y.; Yadian, B.; Liu, Q.; Gan, C.L.; Tang, X.; Huang, Y. The role of metal layers in the formation of metal-silicon hybrid nanoneedle arrays. *Nanoscale* **2014**, *6*, 3078–3082. [\[CrossRef\]](#)
20. Liu, H.; Yadian, B.; Liu, Q.; Gan, C.L.; Huang, Y. A hybrid nanostructure array for gas sensing with ultralow field ionization voltage. *Nanotechnology* **2013**, *24*, 175301. [\[CrossRef\]](#)
21. Liu, H.; Wu, J.; Wang, Y.; Chow, C.L.; Liu, Q.; Gan, C.L.; Tang, X.; Rawat, R.S.; Tan, O.K.; Ma, J.; et al. Self-Organization of a Hybrid Nanostructure consisting of a Nanoneedle and Nanodot. *Small* **2012**, *8*, 2807–2811. [\[CrossRef\]](#)
22. Cao, X.; Li, C.; Lu, Y.; Zhang, B.; Wu, Y.; Liu, Q.; Wu, J.; Teng, J.; Yan, W.; Huang, Y. Catalysis of Au nano-pyramids formed across the surfaces of ordered Au nano-ring arrays. *J. Catal.* **2019**, *377*, 389–399. [\[CrossRef\]](#)
23. Cao, X.; Peng, D.; Wu, C.; He, Y.; Li, C.; Zhang, B.; Han, C.; Wu, J.; Liu, Z.; Huang, Y. Flexible Au micro-array electrode with atomic-scale Au thin film for enhanced ethanol oxidation reaction. *Nano Res.* **2021**, *14*, 311–319. [\[CrossRef\]](#)
24. Raut, H.K.; Ganesh, V.A.; Nair, A.S.; Ramakrishna, S. Anti-reflective coatings: A critical, in-depth review. *Energy Environ. Sci.* **2011**, *4*, 3779–3804. [\[CrossRef\]](#)
25. Sun, C.-H.; Jiang, P.; Jiang, B. Broadband moth-eye antireflection coatings on silicon. *Appl. Phys. Lett.* **2008**, *92*, 061112. [\[CrossRef\]](#)
26. Oh, J.; Yuan, H.-C.; Branz, H.M. An 18.2%-efficient black-silicon solar cell achieved through control of carrier recombination in nanostructures. *Nat. Nanotechnol.* **2012**, *7*, 743–748. [\[CrossRef\]](#)
27. Krunks, M.; Katerski, A.; Dedova, T.; Oja Acik, I.; Mere, A. Nanostructured solar cell based on spray pyrolysis deposited ZnO nanorod array. *Sol. Energy Mater. Sol. Cells* **2008**, *92*, 1016–1019. [\[CrossRef\]](#)

28. Yadian, B.; Liu, H.; Wei, Y.; Wu, J.; Zhang, S.; Sun, L.; Zhao, C.; Liu, Q.; Ramanujan, R.V.; Zhou, K.; et al. Towards Perfectly Ordered Novel ZnO/Si Nano-Heterojunction Arrays. *Small* **2014**, *10*, 344–348. [\[CrossRef\]](#)
29. Li, L.; Li, Y.; Gao, S.; Koshizaki, N. Ordered Co<sub>3</sub>O<sub>4</sub> hierarchical nanorod arrays: Tunable superhydrophilicity without UV irradiation and transition to superhydrophobicity. *J. Mater. Chem.* **2009**, *19*, 8366–8371. [\[CrossRef\]](#)
30. Yue, K.; Trujillo-de Santiago, G.; Alvarez, M.M.; Tamayol, A.; Annabi, N.; Khademhosseini, A. Synthesis, properties, and biomedical applications of gelatin methacryloyl (GelMA) hydrogels. *Biomaterials* **2015**, *73*, 254–271. [\[CrossRef\]](#)
31. Li, C.; Rao, Y.; Zhang, B.; Huang, K.; Cao, X.; Peng, D.; Wu, J.; Xiao, L.; Huang, Y. Extraordinary catalysis induced by titanium foil cathode plasma for degradation of water pollutant. *Chemosphere* **2019**, *214*, 341–348. [\[CrossRef\]](#)
32. Rao, Y.; Cao, X.; Li, C.; Xiao, L. Bifunctional copper cathode induced oxidation of glycerol with liquid plasma discharge. *Sep. Purif. Technol.* **2019**, *220*, 328–333. [\[CrossRef\]](#)
33. Zheng, M.; Zhu, X.; Chen, Y.; Xiang, Q.; Duan, H. Three-dimensional donut-like gold nanorings with multiple hot spots for surface-enhanced raman spectroscopy. *Nanotechnology* **2017**, *28*, 045303. [\[CrossRef\]](#) [\[PubMed\]](#)
34. Qi, J.; Xiang, Y.; Yan, W.; Li, M.; Yang, L.; Chen, Z.; Cai, W.; Chen, J.; Li, Y.; Wu, Q.; et al. Excitation of the Tunable Longitudinal Higher-Order Multipole SPR Modes by Strong Coupling in Large-Area Metal Sub-10 nm-Gap Array Structures and Its Application. *J. Phys. Chem. C* **2016**, *120*, 24932–24940. [\[CrossRef\]](#)
35. Yang, Y. SERS enhancement dependence on the diameter of Au nanoparticles. *J. Phys. Conf. Ser.* **2017**, *844*, 012030. [\[CrossRef\]](#)
36. Chan, T.-Y.; Liu, T.-Y.; Wang, K.-S.; Tsai, K.-T.; Chen, Z.-X.; Chang, Y.-C.; Tseng, Y.-Q.; Wang, C.-H.; Wang, J.-K.; Wang, Y.-L. SERS Detection of Biomolecules by Highly Sensitive and Reproducible Raman-Enhancing Nanoparticle Array. *Nanoscale Res. Lett.* **2017**, *12*, 344. [\[CrossRef\]](#) [\[PubMed\]](#)
37. Aroca, R.F. Plasmon enhanced spectroscopy. *Phys. Chem. Chem. Phys.* **2013**, *15*, 5355–5363. [\[CrossRef\]](#) [\[PubMed\]](#)
38. Navaratnam, S.; Parsons, B.J. Kinetic and spectral properties of rhodamine 6G free radicals: A pulse radiolysis study. *J. Photochem. Photobiol. A* **2002**, *153*, 153–162. [\[CrossRef\]](#)
39. Kaoru, I.; Mitsuo, M.; Takayuki, T.; Yuji, O.; Hideaki, K. Dominant Factors of Preventing Rhodamine 6G from Dimer Formation in Aqueous Solutions. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1197–1202.
40. Vogel, R.; Harvey, M.; Edwards, G.; Meredith, P.; Heckenberg, N.; Trau, M.; Rubinsztein-Dunlop, H. Dimer-to-Monomer Transformation of Rhodamine 6G in Aqueous PEO–PPO–PEO Block Copolymer Solutions. *Macromolecules* **2002**, *35*, 2063–2070. [\[CrossRef\]](#)
41. Rajoriya, S.; Bargole, S.; Saharan, V.K. Degradation of a cationic dye (Rhodamine 6G) using hydrodynamic cavitation coupled with other oxidative agents: Reaction mechanism and pathway. *Ultrason. Sonochem.* **2017**, *34*, 183–194. [\[CrossRef\]](#)
42. Cao, X.; Zhang, L.; Huang, K.; Zhang, B.; Wu, J.; Huang, Y. Strained carbon steel as a highly efficient catalyst for seawater electrolysis. *Energy Mater.* **2022**, *2*, 200010. [\[CrossRef\]](#)
43. Kitching, H.; Kenyon, A.J.; Parkin, I.P. The interaction of gold and silver nanoparticles with a range of anionic and cationic dyes. *Phys. Chem. Chem. Phys.* **2014**, *16*, 6050–6059. [\[CrossRef\]](#) [\[PubMed\]](#)
44. Barzan, M.; Hajiesmaeilbaigi, F. Effect of gold nanoparticles on the optical properties of Rhodamine 6G. *Eur. Phys. J. D* **2016**, *70*, 121. [\[CrossRef\]](#)
45. Langer, J.; Jimenez de Aberasturi, D.; Aizpurua, J.; Alvarez-Puebla, R.A.; Auguie, B.; Baumberg, J.J.; Bazan, G.C.; Bell, S.E.J.; Boisen, A.; Brolo, A.G.; et al. Present and Future of Surface-Enhanced Raman Scattering. *ACS Nano* **2020**, *14*, 28–117. [\[CrossRef\]](#) [\[PubMed\]](#)
46. Kladnik, G.; Cvetko, D.; Batra, A.; Dell’Angela, M.; Cossaro, A.; Kamenetska, M.; Venkataraman, L.; Morgante, A. Ultrafast Charge Transfer through Noncovalent Au–N Interactions in Molecular Systems. *J. Phys. Chem. C* **2013**, *117*, 16477–16482. [\[CrossRef\]](#)
47. Zang, Y.; Pinkard, A.; Liu, Z.-F.; Neaton, J.B.; Steigerwald, M.L.; Roy, X.; Venkataraman, L. Electronically Transparent Au–N Bonds for Molecular Junctions. *J. Am. Chem. Soc.* **2017**, *139*, 14845–14848. [\[CrossRef\]](#)
48. Kryachko, E.S.; Remacle, F. Complexes of DNA Bases and Gold Clusters Au<sub>3</sub> and Au<sub>4</sub> Involving Nonconventional N–H···Au Hydrogen Bonding. *Nano Lett.* **2005**, *5*, 735–739. [\[CrossRef\]](#)
49. Wang, X.; Ham, S.; Zhou, W.; Qiao, R. Adsorption of rhodamine 6G and choline on gold electrodes: A molecular dynamics study. *Nanotechnology* **2023**, *34*, 025501. [\[CrossRef\]](#)
50. Wang, J.; Qiu, C.; Mu, X.; Pang, H.; Chen, X.; Liu, D. Ultrasensitive SERS detection of rhodamine 6G and p-nitrophenol based on electrochemically roughened nano-Au film. *Talanta* **2020**, *210*, 120631. [\[CrossRef\]](#)
51. Han, X.X.; Rodriguez, R.S.; Haynes, C.L.; Ozaki, Y.; Zhao, B. Surface-enhanced Raman spectroscopy. *Nat. Rev. Methods Primers* **2022**, *1*, 87. [\[CrossRef\]](#)
52. Mayerhöfer, T.G.; Pahlow, S.; Popp, J. The Bouguer-Beer-Lambert Law: Shining Light on the Obscure. *ChemPhysChem* **2020**, *21*, 2029–2046. [\[CrossRef\]](#) [\[PubMed\]](#)

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