2-D Study of Near-field Generated by Surface Plasmon Resonance of Short Axis of Gold Nano-rods on SiO₂ and CeO₂/SiO₂ Substrates for Optimisation of Water Splitting Reaction

M N S M Idris¹, H P Chiang²,³, Y F Chou Chau1, A H Mahadi,¹*, C M Lim¹

¹Centre for Advanced Material and Energy Sciences, Universiti Brunei Darussalam, Jalan Tungku Link, Gadong, BE 1410, Brunei Darussalam,

²Institute of Optoelectronic Sciences, National Taiwan Ocean University, No. 2 Pei-Ning Rd., 202, Keelung, Taiwan,

³Institute of Physics, Academia Silica, Taipei 11529, Taiwan

E-mail: hanif.mahadi@ubd.edu.bn

Abstract. Distinguishing near-field intensity distribution and plasmon resonance peak wavelength of surface plasmon resonance of gold nano-rods (AuNRs) can provide information for the optimisation of localised surface plasmon and gap plasmon resonances of gold nano-rods. This work, shows the influence of how refractive indexes of the surrounding medium and adjacent surface, as well as, AuNRs pair inter-particle gap contributes to the generation of surface plasmon resonances. The simulation model presented consists of AuNRs pair situated on silicon dioxide (SiO₂) and cerium dioxide/silicon dioxide (CeO₂/SiO₂) substrates with air and water as the surrounding media. The results show high near-field intensities at AuNRs/CeO₂ interfaces with CeO₂ refractive index (n = 2.38), and the near-field intensities contributed by the gap resonance is minimal between the AuNRs of inter-particle gap of 10 nm, however, the near-field intensities become significant near to the AuNRs/CeO₂ interfaces because of reduced near-field interference. The simulation set-up provides the conditions for water splitting in thermochemical redox reaction of CeO₂/CeO₂ₓ resulting in the production of hydrogen. AuNRs pair with inter-particle gap of 5 nm situated on 10 nm thick CeO₂ of CeO₂/SiO₂ substrate shows the most favorable conditions for water splitting.

1. Introduction

Plasmonic gold nano-particles (AuNPs) have been widely studied in the field of catalysis [1, 2], electronics [3, 4], sensors [5, 6], optics [7] and biomedicine [8]. These wide research fields of AuNPs are by virtue of its extensive optical properties related to surface plasmons (SP) [9], permissive of surface functionalisation for organic and biological molecules [10], and high physical and chemical stability [11, 12]. Amongst these aspects of AuNPs, the surface plasmons are the major attractions. Besides surface plasmon polariton (SPP), the optical properties of AuNPs are linked to non-propagating surface plasmons called localised surface plasmon resonance (LSPR) for AuNPs, where the AuNPs size is considerably smaller than the wavelength of the incident electromagnetic
(EM) wave [13]. LSPR can be tuned by changing the size [13], shape [14, 15], arrangement [16] of the AuNPs, and the dielectric constant (refractive index) [13, 17] of the surrounding medium.

One of the most interesting AuNPs is gold nano-rods (AuNRs) because of their structure which constitutes of short and long axes. This structure allows two excitations of SP modes which are (i) between 520 nm and 540 nm for the short axis excitation; and (ii) in the range of 600 – 1600 nm for the long axis excitation, in which both depend on the AuNRs aspect ratio [18]. The SP excitation via incident electrical field (E-field) of electromagnetic (EM) wave along the short axis and long axis of AuNRs generate transverse LSPR and longitudinal LSPR, respectively [19]. Furthermore, when a metallic nano-rod (MNR) is brought closer to another MNR (MNR pair) with a few nano-meters separation (plasmonic cavity) [20], SP excitation along the short axis of the MNR pair can induce another SP resonance phenomenon which is known as gap plasmon resonance (GPR). It arises from electrical field (E-field) localisation within the gap of the MNRs pair associated with the polarisation of SP oscillations on the short axis of MNRs pair [21-24]. The GPR disappears when the polarisation of SP oscillations are along the long axis of the MNRs pair. Thus, it is beneficial to incorporate both LSPR and GPR of short axis of AuNRs pair in developing its plasmonic behavior for specific applications, example for water splitting.

The LSPR of AuNPs relax into radiative and non-radiative decays [25]. The non-radiative decay is related to thermal generation of AuNPs [9]. This also applies to AuNRs as the size of AuNRs falls within the size of AuNPs. The heat transfer follows the Joule heating mechanisms [26], whereby the square of the electric field (E-field) is directly proportional to the Joule heating. Therefore, E-field enhancement (near-field) caused by LSPR of AuNRs results in the increase in the thermal generation and heat transfer. In addition, the heat is distributed from AuNRs to the surrounding and adjacent surface. This heat can be utilised to drive two-step thermochemical redox reaction of metal oxides for the hydrogen generation by water splitting [27]. Moreover, the LSPR can facilitate charge injection which further assists the redox reaction process [28].

This work, therefore, focuses on the study of near-field intensities and distributions, plasmon resonance peak wavelengths, and thermal generation corresponding to LSPR and GPR of the short axis of AuNRs pair. This investigation looks into the different models of AuNRs pairs that are supported by silicon dioxide (SiO$_2$) and cerium dioxide/silicon dioxide (CeO$_2$/SiO$_2$) substrates in search of optimum conditions for water spitting and other promising applications. The inter-particle gap between AuNRs, surrounding medium, and the thickness of CeO$_2$ are varied in order to study the effect of GPR and refractive index of adjacent surface to the LSPR of AuNRs pairs.

2. Simulation section

2.1. Simulation method

Two-dimensional finite-element method (2D-FEM) is used to perform numerical simulation of near-field intensities and distributions, and plasmon resonance peaks of the short axis of AuNRs pairs on different substrates as shown in Figure 1. The short axis of AuNR is clarified in Figure 2(D). The input power of light source used is 1 mW. To study the response of the GPR between AuNRs pair, and the refractive index of the adjacent surface to the LSPR of AuNRs pairs, the AuNRs pairs are excited by E-field oscillating in the x-direction (i.e. short axis). The induced LSPR and GPR are in the x-direction of the AuNRs pairs as illustrated in Figure 1. The permittivity data of gold is acquired from the literature [29] and amended with size effect using the Drude model [30]. Triangular high order edge element formulation is used in the simulation with direct implementation of anisotropic perfectly matched layers (PMLs) [31] at the outer boundaries (in Figure 2) to compromise with anisotropic material in terms of magnetic permeability and dielectric permittivity, respectively. The scattering boundary condition (SBC) and matched boundary (MB) are the simulation boundaries as shown in Figure 1.

In order to investigate the near-field intensities and distributions, and plasmon resonance peaks of the short axis AuNRs pair on different adjacent surface, SiO$_2$ and CeO$_2$/SiO$_2$ are used as substrates as shown in Figure 2. The refractive index of CeO$_2$ films at different thickness is obtained from the literature [32]. Approximately, at incident wavelength of 530 nm, the refractive index, n, of CeO$_2$ films
of 10 nm and 20 nm thick are 2.38 and 1.68, respectively. At 530 nm wavelength, the imaginary part, \(k\) of the refractive index is zero for both CeO\(_2\) films thickness. The dispersion equation for the refractive index of SiO\(_2\) is retrieved from Refs [33]. The wavelength range of the applied incident photon is between 300 nm to 1200 nm. Moreover, the nearfield intensities and plasmon resonance peaks are measured at the gap (point A), 0.5 nm from one of the AuNR (point B), and near Au/CeO\(_2\) interfaces (points C & D) as depicted in Figure 1. The two AuNRs are identical and symmetrical pair, therefore, these four points represent similar near-field intensities and plasmon resonance peaks for both the AuNRs.

In the case of thermal simulation on heat generation and transfer of AuNRs pairs, 2D-FEM is employed by using the Joule heating with general heat transfer module. The simulation used the heat balance equation [26].

The input power of the light source is reduced from 1.0 mW to 0.017 \(\mu\)W and 8.0 \(\mu\)W for AuNRs pairs in air and water, respectively. In order to incorporate the contribution of LSPR of AuNRs pair to the heat generation, the average near-field intensity of AuNRs pair is taken as electric field strength which is then used to calculate the heat source of the AuNRs pair. The simulation temperature boundary conditions are held at 25 °C. The parameters such as thermal conductivity, density, heat capacity, relative permittivity of AuNRs, air and water that are used for the simulation, are retrieved from Refs [26, 29, 34] and tabulated in table 1.

### Table 1. The thermal conductivity, density, specific heat, relative permittivity of AuNRs, air and water.

| Material    | Thermal Conductivity (W/mK) | Density (kg/m\(^3\)) | Heat Capacity (J/kgK) | Relative Permittivity |
|-------------|----------------------------|-----------------------|-----------------------|-----------------------|
| AuNRs       | 317                        | 19300                 | 129.0                 | (-4.5461) + i2.4577  |
| Air         | 0.0262                     | 2.7900                | 1000                  | 1.00                  |
| Water       | 0.600                      | 998.30                | 4182                  | 1.78                  |

### 2.2. Simulation model

The simulation model composed of AuNRs on SiO\(_2\) substrate (AuNRs/SiO\(_2\)), AuNRs on CeO\(_2\)/SiO\(_2\) substrate with ceria thickness of 10 nm (AuNRs/CeO\(_2\)-T10/SiO\(_2\)), and AuNRs on CeO\(_2\)/SiO\(_2\) substrate with ceria thickness of 20 nm (AuNRs/CeO\(_2\)-T20/SiO\(_2\)) are shown in Figure 2(A), 2(B) and 2(C), respectively. The thickness of SiO\(_2\) for all model is equivalent to 1 \(\mu\)m. The diameter and length of AuNRs pairs are kept constant at 10 nm and 100 nm. In this study, air and water are used as the surrounding media with refractive index of 1.00 and 1.33, respectively. The gap between AuNRs pairs is set to 5 nm and 10 nm. In the case of thermal simulation on heat generation and transfer, AuNRs pairs are simulated without the substrates in order to avoid complexity.

### 3. Results and discussion

#### 3.1. Near-field intensities and distribution of AuNRs pair

The simulation results showed a variation of the near-field intensities and distributions, and the plasmon resonance peak wavelength in the vicinity of the AuNRs pairs with inter-particle gap of 5 nm and 10 nm in air and water media; adjacent to SiO\(_2\) substrates; and CeO\(_2\)/SiO\(_2\) substrates with ceria thickness of 10 nm and 20 nm, are presented in Figure 3 to 6. The plasmon resonance wavelength of AuNRs pairs is discussed in the latter section.

In the case of the AuNRs pair with inter-particle gap of 5 nm (Figure 3), the near-field intensities at the gap (point A) and surface (point B) of AuNRs pair for AuNRs/SiO\(_2\) model in water (Figure 3(D)) are higher than AuNRs/SiO\(_2\) model in air (Figure 3(A)). These effects are also observed for AuNRs/CeO\(_2\)-T10/SiO\(_2\) model (Figure 3(D)) and AuNRs/CeO\(_2\)-T20/SiO\(_2\) model (Figure 3(F)) in water medium. The refractive index of the surrounding medium affects the LSPR and GPR of AuNRs pair.
showing distinct near-field intensities. On the other hand, in Figure 3, the nearfield intensities that are close to the AuNRs pair interfaces (point C and D) of AuNRs/SiO$_2$ model (Figure 3(A)&(D)) and AuNRs/CeO$_2$-T20/SiO$_2$ model (Figure 3(C)&(F)) are lower than the AuNRs/CeO$_2$-T10/SiO$_2$ model (Figure 3(B)&(E)) for both in air and water media. Moreover, the nearfield intensity at point D is higher than at point C for the AuNRs/CeO$_2$-T10/SiO$_2$ model. This is because of destructive interference of the near-field produced by both AuNRs at point C [35]. It is demonstrated that the high near-field intensities occur at AuNRs/CeO$_2$ interfaces as a consequence of high CeO$_2$ refractive index ($n = 2.38$). In addition, the nearfield intensities distributions of AuNRs pair with interparticle gap of 5 nm on SiO$_2$ and CeO$_2$/SiO$_2$ substrates are presented in Figure 4.

The GPR effects are minor for the AuNRs pairs with interparticle gap of 10 nm (Figure 5) and for all the models, where the simulation results show poor near-field intensities at the gap (point A) of the AuNRs pair. In contrast, the near-field intensities that are close to AuNRs pair interfaces (at point C and D) show significant results in particular for the AuNRs/CeO$_2$-T10/SiO$_2$ model (Figure 5(B) & (E)). It exhibits high near-field intensities at the interfaces when compared to the AuNR/SiO$_2$ model (Figure 5(A) & (D)), and the AuNRs/CeO$_2$-T20/SiO$_2$ model (Figure 5(C) & (F)) for both air and water. Furthermore, the near-field intensities at the interfaces of AuNRs/CeO$_2$-T10/SiO$_2$ model are almost equivalent and this is due to LSPR of the AuNRs pair, and showing less near-field interference. In addition, the influence of GPR of AuNRs pair becomes less as the inter-particle gap is increased to 10 nm. Therefore, only LSPR of AuNRs pair contributes to the generation of the near-field. Moreover, the refractive index, $n$, of CeO$_2$ affects the occurrence of high near-field intensities of the AuNRs pair at the AuNRs/CeO$_2$ interfaces for both the AuNRs pair inter-particle gap of 5 nm and 10 nm, where CeO$_2$ with $n = 2.38$ (10 nm thick) has been demonstrated to have high near-field intensities when compared to CeO$_2$ with $n = 1.68$ (20 nm thick). The near-field intensities distributions of AuNRs pair with interparticle gap of 10 nm on SiO$_2$ and CeO$_2$/SiO$_2$ substrates are displayed in Figure 6.

**Figure 1.** Schematic diagram of AuNRs pair on a substrate with the parameters for the simulation method. The incident TM mode plane wave has its magnetic field ($H$) in the $z$-direction, and electric field ($E$) in the $x$-direction propagating in the direction of wave vector ($k$) in $y$-direction. The length between PMLs is 2600 nm.
Figure 2. Schematic diagram of simulation models of AuNRs pairs on SiO\textsubscript{2} (A); and CeO\textsubscript{2}/SiO\textsubscript{2} substrates with CeO\textsubscript{2} film thickness of 10 nm (B); and 20 nm (C), respectively. (D) showing the short axis and long axis of an AuNR.

Figure 3. Simulation results of near-field intensities versus wavelength of AuNRs pair with inter-particle gap of 5 nm in air for AuNRs/SiO\textsubscript{2} (A), AuNRs/CeO\textsubscript{2}-T10/SiO\textsubscript{2} (B), and AuNRs/CeO\textsubscript{2}-T20/SiO\textsubscript{2} (C); and in water for AuNRs/SiO\textsubscript{2} (D), AuNRs/CeO\textsubscript{2}-T10/SiO\textsubscript{2} (E), and AuNRs/CeO\textsubscript{2}-
T20/SiO$_2$ (F). The measurement points for near-intensities are A (at the gap: black); B (0.5 nm from Au surface: blue); and, C and D (near AuNRs/CeO$_2$ interfaces: green and red, respectively).

3.2. Plasmon resonance peaks of AuNRs pair

The plasmon resonance peak of spherical gold nano-particles (AuNPs) has been reported in the visible range of the electromagnetic spectrum, typically at 532 nm [9]. The crosssection of the short axis of AuNRs is analogous to AuNPs. Hence, the plasmon resonance peak of AuNRs is close to that of AuNPs. The plasmon resonance peak wavelength of AuNPs is indicated as dashed arrows, and labelled as 530 nm instead of 532 nm, as shown in Figure 3 and Figure 5. This is because the smallest resolution used for the wavelength in the simulation is 10 nm.

The simulation results showed that most of the plasmon resonance peaks wavelength of AuNRs pairs are shifted away from 530 nm wavelength. This is associated with the change in the refractive index of the medium and the adjacent surface (Figure 3). In the case of AuNRs/SiO$_2$, AuNRs/CeO$_2$-T10/SiO$_2$, and AuNRs/CeO$_2$-T20/SiO$_2$ models in air, the plasmon resonance peaks wavelength of AuNRs pairs at point A, B, C and D are consistent. However, in water medium, the plasmon resonance peaks wavelength varied except for AuNRs/CeO$_2$-T10/SiO$_2$. Moreover, the plasmon resonance peak wavelengths of AuNRs pair in AuNRs/CeO$_2$-T20/SiO$_2$ model remained at 530 nm at all measured points whereas AuNRs/SiO$_2$ and AuNRs/CeO$_2$-T20/SiO$_2$ models in water medium showed the 530 nm plasmon resonance peak wavelength to be located at point D.

The majority of the measured points of the plasmon resonance peak wavelengths of AuNRs pair in AuNRs/SiO$_2$, AuNRs/CeO$_2$-T10/SiO$_2$, and AuNRs/CeO$_2$-T20/SiO$_2$ models are deviated from the 530 nm peak wavelength. These are caused by the change in the refractive index of the surrounding medium and the adjacent surface (substrate), as mentioned previously. The plasmon resonance peak wavelength of AuNRs pair in AuNRs/SiO$_2$ model showed similar peaks at 520 nm for all measured points. In the case of AuNRs/CeO$_2$-T10/SiO$_2$, and AuNRs/CeO$_2$-T20/SiO$_2$ models, the plasmon resonance peak wavelengths are inconsistent.

**Figure 4.** The Near-field intensities and distributions of AuNRs pair with inter-particle gap of 5 nm for AuNRs/SiO$_2$ in air (A), and water (B); AuNRs/CeO$_2$-T10/SiO$_2$ in air (C), and water (D); and
AuNRs/CeO$_2$-T20/SiO$_2$ in air (E), and water (F). The schematic design of AuNRs/SiO$_2$ (i), AuNRs/CeO$_2$-T10/SiO$_2$ (ii), and AuNRs/CeO$_2$-T20/SiO$_2$ (iii).

![Diagram showing schematic designs of nanoparticles](image)

**Figure 5.** Simulation results of near-field intensities versus wavelength of AuNRs pair with inter-particle gap of 10 nm in air for AuNRs/SiO$_2$ (A), AuNRs/CeO$_2$-T10/SiO$_2$ (B), and AuNRs/CeO$_2$-T20/SiO$_2$ (C); and in water for AuNRs/SiO$_2$ (D), AuNRs/CeO$_2$-T10/SiO$_2$ (E), and AuNRs/CeO$_2$-T20/SiO$_2$ (F). The measurement points for near-intensities are A (at the gap:black); B (0.5 nm from Au surface:blue); and, C and D (near AuNRs/CeO$_2$ interfaces:green and red, respectively).

Furthermore, the 530 nm plasmon peak wavelength of AuNRs pairs are observed at point A and B of the AuNRs/SiO$_2$ model in water; and AuNRs/CeO$_2$-T10/SiO$_2$ model in air, as well as, at point C and D of AuNRs/CeO$_2$-T20/SiO$_2$ model in air and water media. It is also detected at point B of AuNRs/CeO$_2$-T20/SiO$_2$ model in water.

### 3.3. Local E-field enhancement of AuNRs pair

The local E-field enhancements of AuNRs pair are observed as near-field of high intensities and distributions whereby it is found within the gap of the AuNRs pair and the AuNRs/substrate interfaces correspond to the GPR and LSPR of the AuNRs pair, respectively. Based on the previous near-field intensities and distribution analyses, the local E-field enhancements are allocated within the gap of the AuNRs pair in AuNRs/SiO$_2$, AuNRs/CeO$_2$-T10/SiO$_2$, and AuNRs/CeO$_2$-T20/SiO$_2$ models having inter-particle gap of 5 nm in water media. These models can be used in visible light Raman spectroscopy to detect low concentration of foreign molecules in water solution by amplifying the Raman signals.

Furthermore, in the case of AuNRs/CeO$_2$-T10/SiO$_2$ model, the local E-field enhancement is also observed at the AuNRs/CeO$_2$ interfaces. A charge (electron) injection has been reported at metal/metal oxide interfaces under visible light excitation [28, 36]. Therefore, it is possible for the charge to be transferred from the AuNRs to the CeO$_2$ surface. In order to determine whether redox reaction at CeO$_2$ surface has taken place or not, visible light Raman spectroscopy can be performed in which the generation of molecules caused by the redox reaction at AuNRs/CeO$_2$ interfaces can be identified in this model.
3.4. Thermal generation and heat transfer of AuNRs pair

The heat source of AuNRs pair is directly proportional to the square of E-field strength [26]. The LSPR of AuNRs pair enhanced the local E-field strength in the form of near-field on the surface of AuNRs pair at plasmon resonance peak wavelength of 530 nm. The near-field is averaged and then used to determine the heat source of AuNRs pair for the thermal simulation. As a result, the AuNRs pairs produced heat with temperature higher than 500 °C as shown in Figure 7 and Figure 8. The E-field strength, and relative permittivity of surrounding media affect the heat source of AuNRs pair. An increase in the light input power resulted in an increase in the average near-field (i.e. local E-field strength). This caused a large increase in the heat source of AuNRs pair due to the proportionality which remarkably increases the temperature of AuNRs pair over its melting point. In addition, the variation in thermal conductivity of media allows different heat conduction which then influence the rate of heat transfer from the AuNRs pair to the surrounding. Therefore, in order for AuNRs pair to produce heat with temperature below its melting point, various simulations are performed in search of the right input power of light for AuNRs pair in different media. It is found that the suitable input power of light for AuNRs pair in air and water are 0.017 μW and 8.0 μW, respectively. Despite the scaled down of light input power from 1 mW to 0.017 μW and 8.0 μW, the near-field distributions and plasmon resonance peaks of the AuNRs pairs on SiO$_2$ and CeO$_2$/SiO$_2$ substrates in air and water are similar whereas only the near-field intensities (local E-field strength) are decremented. Thus, only the near-field intensities are taken into account (for the thermal simulation) without presenting the simulation results of near-field distributions and plasmon resonance peaks.

The temperature profile for AuNRs pairs with inter-particle gap of 5 nm is shown in Figure 7. The temperature of AuNRs pair (grey regions) in air and water medium reached 1056 °C and 976 °C, respectively. The temperature decreased to 57 °C as the distance from the AuNRs increased as shown in the green regions. The temperature at the inter-particle gap (white region) showed curves profile which centered at 978 °C and 904 °C for AuNRs pair in air and water, respectively. In the case of AuNRs pairs with inter-particle gap of 10 nm, the temperature profile is presented in Figure 8. The temperature of AuNRs pair (grey regions) reached 584 °C in air whereas 529 °C in water. The temperature decreased to 100 °C as the distance from the AuNRs increased as shown in the green regions. The temperature at the inter-particle gap (white region) showed curves profile which centered at 408 °C and 307 °C for AuNRs pair in air and water, respectively. The temperature curves are larger than AuNRs pair with inter-particle gap of 5 nm.

3.5. Water splitting in CeO$_2$ based thermochemical reaction

Water splitting in CeO$_2$ (ceria) based thermochemical reaction consists of two processes; (1) the reduction of CeO$_2$ to CeO$_{2-x}$, and (2) the oxidation of CeO$_{2-x}$ to CeO$_2$ [27]. In the first process, oxygen vacancies sites are formed, and this is followed by re-oxidation of CeO$_{2-x}$ which can be induced by exposing the reduced ceria to water, and resulting in hydrogen production [37, 38]. Heat is essential in these processes. The heat generated from AuNRs pair can be utilised to drive the redox reactions. Based on the simulation results on the nearfield intensities and distributions, as well as, the thermal modelling of AuNRs pair, the optimum combination for water splitting in CeO$_2$ based thermochemical reaction is by coupling the AuNRs pair with CeO$_2$/SiO$_2$ substrate and with AuNRs inter-particle gap of 5 nm, and CeO$_2$ thickness of 10 nm (i.e. AuNRs/CeO$_2$-T10/SiO$_2$ model). In addition, a charge injection at AuNRs/CeO$_2$ interfaces coalesced with heat generation by the AuNRs pair at high temperature enhances the redox reaction of CeO$_2$. The water splitting process in CeO$_2$ based thermochemical reaction can be described by the two reactions below:

Thermal reduction of CeO$_2$ in air,

\[
\frac{1}{x} \text{CeO}_2 \rightarrow \frac{1}{x} \text{CeO}_{2-x} + \frac{1}{2} \text{O}_2(g)
\]

(2) Thermal oxidation of reduced CeO$_{2-x}$ by water (vapor),

\[
\text{H}_2\text{O}(g) + \frac{1}{x} \text{CeO}_{2-x} \rightarrow \frac{1}{x} \text{CeO}_2 + \text{H}_2(g)
\]

8
According to temperature programmed reduction (TPR) of CeO$_2$, the thermal reduction of CeO$_2$ can occur at temperature of 497 °C (surface) and 827 °C (bulk) [39]. The AuNRs pair is capable of producing temperature of 1056 °C with light input power of 0.017 μW in air (Figure 7). Hence, surface and bulk reduction of CeO$_2$ to CeO$_{2-x}$ (reaction 1) can be induced. The thermal oxidation of CeO$_{2-x}$ by water (reaction 2) can occur at temperature of about 800 °C (bulk) [37, 40]. The heat produced by the AuNRs pair can reach a temperature of 976 °C in water with a given light input power of 8.0 μW (Figure 7). Therefore, the AuNRs pair in AuNRs/CeO$_2$-T10/SiO$_2$ model with AuNRs interparticle gap of 5 nm provides the most favorable conditions for splitting of water in CeO$_2$ based thermochemical reaction.

Figure 6. Near-field intensities and distributions of AuNRs pair with inter-particle gap of 10 nm for AuNRs/SiO$_2$ in air (A), and water (B); AuNRs/CeO$_2$-T10/SiO$_2$ in air (C), and water (D); and AuNRs/CeO$_2$-T20/SiO$_2$ in air (E), and water (F). The schematic design of AuNRs/SiO$_2$ (i), AuNRs/CeO$_2$-T10/SiO$_2$ (ii), and AuNRs/CeO$_2$-T20/SiO$_2$ (iii).

Figure 7. Temperature profiles for AuNRs pairs with inter-particle gap of 5 nm in air (0.017 μW) and water (8.0 μW) at light wavelength of 530 nm. The x-axis indicated the position and size of AuNRs pair by using coordinates (x, y) system.
Figure 8. Temperature profiles for AuNRs pairs with inter-particle gap of 10 nm in air (0.017 µW) and water (8.0 µW) at light wavelength of 530 nm. The x-axis indicated the position and size of AuNRs pair by using coordinates (x, y) system.

4. Conclusion
In conclusion, under incident EM wave excitation, the nearfield intensities distribution and plasmon resonance peak wavelength related to LSPR and GPR of the short axis of AuNRs pair changed with the refractive index of the surrounding medium and adjacent surface. A tunable wavelength light source is required to excite SP resonance at a precise wavelength for optimal occurrence of LSPR and GPR, as well as, the local E-field enhancement along the short axis of the AuNRs pair. In addition, the local E-field enhancements of the AuNRs pair in AuNRs/SiO2, AuNRs/CeO2-T10/SiO2, and AuNRs/CeO2-T20/SiO2 models with inter-particle gap of 5 nm in water media can be employed to visible Raman spectroscopy as molecules detector in water solution. In water splitting using CeO2 based thermochemical reaction, light input power control is crucial for AuNRs pair to produce heat for redox reaction in CeO2/CeO2 system without melting the AuNRs pair. The optimum conditions for the water splitting are achieved in AuNRs/CeO2-T10/SiO2 model with AuNRs pair inter-particle gap of 5 nm. Thoroughly, the AuNRs pair inter-particle gap, support, medium and light input power all play important roles in resolving specific applications for the local E-field enhancement and thermal generation from LSPR and GPR of AuNRs pair.

Acknowledgement
This work was fully supported by Universiti Brunei Darussalam grants UBD/RSC/1.9/FICBF(b)/2018/005 and UBD/RSC/1.9/FICBF(b)/2018/002. The authors would also like to thank the support by AUN-SEED/Net Japan ASEAN Collaborative Education Programme (JACEP) under the CEP 2019.

References
[1] Albero J, García H. 2.05 - Catalysis by Supported Gold Nanoparticles. In: Andrews DL, Lipson RH, Nann T, editors. Comprehensive Nanoscience and Nanotechnology (Second Edition). Oxford: Academic Press; 2019. p. 91-108.
[2] Chen X, Zhu H, Groarke RJ. Catalysis by Supported Gold Nanoparticles. Reference Module in Materials Science and Materials Engineering: Elsevier; 2016.
[3] Wu W, Han S-T, Venkatesh S, Sun Q, Peng H, Zhou Y, et al. Biodegradable skin-inspired nonvolatile resistive switching memory based on gold nanoparticles embedded alkali lignin. Org Electron. 2018;59:382-8.
Cho ES, Kim J, Tejerina B, Hermans TM, Jiang H, Nakanishi H, et al. Ultrasensitive detection of toxic cations through changes in the tunnelling current across films of striped nanoparticles. *Nature Materials.* 2012;11(11):978-85.

Branagan D, Breslin CB. Electrochemical detection of glucose at physiological pH using gold nanoparticles deposited on carbon nanotubes. *Sensors Actuators B: Chem.* 2019;282:490-9.

Ly TN, Park S. Highly sensitive gas sensor using hierarchically self-assembled thin films of graphene oxide and gold nanoparticles. *Journal of Industrial and Engineering Chemistry.* 2018;67:417-28.

Churchyard S, Fang X, Vrcelj R. Laser ignitibility of energetic crystals doped with gold nanoparticles. *Optics & Laser Technology.* 2019;113:281-8.

Elahi N, Kamali M, Baghersad MH. Recent biomedical applications of gold nanoparticles: A review. *Talanta.* 2018;184:537-56.

Amendola V, Pilot R, Frasconi M, Maragò OM, Iati MA. Surface plasmon resonance in gold nanoparticles: a review. *J Phys: Condens Matter.* 2017;29(20):203002.

Dreaden EC, Alkilany AM, Huang X, Murphy CJ, El-Sayed MA. The golden age: gold nanoparticles for biomedicine. *Chem Soc Rev.* 2012;41(7):2740-79.

Daniel M-C, Astruc D. Gold nanoparticles: assembly, supramolecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology. *Chem Rev.* 2004;104(1):293-346.

Amendola V, Meneghetti M. Laser ablation synthesis in solution and size manipulation of noble metal nanoparticles. *PCCP.* 2009;11(20):3805-21.

Maier SA. Plasmonics: fundamentals and applications: Springer Science & Business Media; 2007.

Xia Y, Halas NJ. Shape-controlled synthesis and surface plasmonic properties of metallic nanostructures. *MRS Bull.* 2005;30(5):338-48.

Wi J-S, Park J, Kang H, Jung D, Lee S-W, Lee TG. Stacked gold nanodisks for bimodal photonic and optical coherence imaging. *ACS nano.* 2017;11(6):6225-32.

Zohar N, Chuntonov L, Haran G. The simplest plasmonic molecules: Metal nanoparticle dimers and trimers. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews.* 2014;21:26-39.

Mayer KM, Hafner JH. Localized surface plasmon resonance sensors. *Chem Rev.* 2011;111(6):3828-57.

Link S, Mohamed M, El-Sayed M. Simulation of the optical absorption spectra of gold nanorods as a function of their aspect ratio and the effect of the medium dielectric constant. *The Journal of Physical Chemistry B.* 1999;103(16):3073-7.

Cao J, Sun T, Grattan KT. Gold nanorod-based localized surface plasmon resonance biosensors: A review. *Sensors Actuators B: Chem.* 2014;195:332-51.

Okuno M, Tokimoto T, Eguchi M, Kano H, Ishibashi T-a. Intensity enhancement of vibrational sum frequency generation by gap-mode plasmon resonance. *Chem Phys Lett.* 2015;639:83-7.

Chau Y-F, Jiang Z-H, Li H-Y, Lin G-M, Wu F-L, Lin W-H. Localized resonance of composite core-shell nanospheres, nanobars and nanospherical chains. *Progress In Electromagnetics Research.* 2011;28:183-99.

Chau Y-F, Yeh H-H, Tsai DP. Near-field optical properties and surface plasmon effects generated by a dielectric hole in a silver-shell nanocylinder pair. *Appl Opt.* 2008;47(30):5557-61.

Chau Y-F, Jiang Z-H. Plasmonics effects of nanometal embedded in a dielectric substrate. *Plasmonics.* 2011;6(3):581-9.

Chau Y-F, Tsai DP. Three-dimensional analysis of silver nano-particles doping effects on super resolution near-field structure. *Opt Commun.* 2007;269(2):389-94.

Kats MA, Yu N, Genevet P, Gaburro Z, Capasso F. Effect of radiation damping on the spectral response of plasmonic components. *Opt Express.* 2011;19(22):21748-53.

Govorov AO, Richardson HH. Generating heat with metal nanoparticles. *Nano today.*
2007;2(1):30-8.

[27] Bhosale RR, Takalkar G, Sutar P, Kumar A, AlMomani F, Khraisheh M. A decade of ceria based solar thermochemical H2O/CO2 splitting cycle. *Int J Hydrogen Energy*. 2019;44(1):34-60.

[28] Tian Y, Tatsuma T. Plasmon-induced photoelectrochemistry at metal nanoparticles supported on nanoporous TiO2. *Chem Commun*. 2004(16):1810-1.

[29] Johnson PB, Christy R-W. Optical constants of the noble metals. *Physical review B*. 1972;6(12):4370.

[30] Okamoto T. Near-field spectral analysis of metallic beads. *Near-field optics and surface plasmon polaritons*. 2001:97-123.

[31] Gresho PM, Sani RL. Incompressible flow and the finite element method. Volume 1: Advection-diffusion and isothermal laminar flow. 1998.

[32] Janicki V, Zorc H. Refractive index profiling of CeO2 thin films using reverse engineering methods. *Thin Solid Films*. 2002;413(1-2):198-202.

[33] Malitson IH. Interspecimen comparison of the refractive index of fused silica. *Josa*. 1965;55(10):1205-9.

[34] Engineering Toolbox. Air - Density at varying pressure and constant temperatures 2004 [Available from: https://www.engineeringtoolbox.com/air-temperaturepressure-density-d_771.html.

[35] Idris MNSS, Chiang H-P, Muslim N, Chau Y-FC, Mahadi AH, Voo NY, et al. Raman Spectrometry of Scattering of Nano-Gold Ceria Films. *Advanced Science Letters*. 2018;24(11):8940-3.

[36] Tian Y, Tatsuma T. Mechanisms and applications of plasmon-induced charge separation at TiO2 films loaded with gold nanoparticles. *J Am Chem Soc*. 2005;127(20):7632-7.

[37] Zhao Z, Uddi M, Tsvetkov N, Yildiz B, Ghoniem AF. Redox kinetics study of fuel reduced ceria for chemical-looping water splitting. *The Journal of Physical Chemistry C*. 2016;120(30):16271-89.

[38] Schefle JR, Welte M, Steinfeld A. Thermal reduction of ceria within an aerosol reactor for H2O and CO2 splitting. *Ind Eng Chem Res*. 2014;53(6):2175-82.

[39] Trovarelli A. Catalytic properties of ceria and CeO2-containing materials. *Catalysis Reviews*. 1996;38(4):439-520.

[40] Chueh WC, Falter C, Abbott M, Scipio D, Furler P, Haile SM, et al. High-flux solar-driven thermochemical dissociation of CO2 and H2O using nonstoichiometric ceria. *Science*. 2010;330(6012):1797-801.