Preferential Excitation of the Hybrid Magnetic-Electric Mode as a Limiting Mechanism for Achievable Fundamental Magnetic Resonance in Planar Aluminum Nanostructures

Tobing, Landobasa Yosef Mario; Zhang, Dao Hua

2016

Tobing, L. Y. M., & Zhang, D. H. (2016). Preferential Excitation of the Hybrid Magnetic-Electric Mode as a Limiting Mechanism for Achievable Fundamental Magnetic Resonance in Planar Aluminum Nanostructures. *Advanced Materials*, 28(5), 889-896.

<https://hdl.handle.net/10356/83583>

<https://doi.org/10.1002/adma.201504061>

© 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. This is the author created version of a work that has been peer reviewed and accepted for publication by *Advanced Materials*, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. It incorporates referee's comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at: [<http://dx.doi.org/10.1002/adma.201504061>].

Downloaded on 26 Apr 2023 15:14:30 SGT

DOI: 10.1002/ ((please add manuscript number))

Article type: Full Paper

Title Preferential Excitation of Hybrid Magnetic-Electric Mode as a Limiting-Mechanism for the Achievable Fundamental Magnetic Resonance in Planar Aluminum Nanostructures

Landobasa Y. M. Tobing¹ and D. H. Zhang^{1}*

¹Nanophotonics Lab, School of EEE, OPTIMUS, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798
Email: EDHZhang@ntu.edu.sg

Keywords: Nanophotonics, Ultraviolet, Aluminum plasmonics, Split-Ring Resonator

Aluminum nanostructures have been attracting much attention for their ability in confining light at the nanoscale in the UV-Vis frequency range. However the experimental investigation of their magnetic resonances remains challenging due to stringent dimensional requirements arising from the intrinsic loss caused by the aluminum interband transition. Here, we report interesting phenomena discovered from ultrasmall aluminum resonators. The first is the hybrid magnetic-electric mode whose preferential excitation in the ultraviolet becomes a limiting mechanism for the achievable fundamental magnetic resonance. The second is the resonance splitting arising from mode interaction with aluminum interband transition. We also demonstrate successful fabrications of ultra-small Al resonators with magnetic resonances as short as 376 nm. Our results support great potential of many applications in UV range, such as photocatalysis and light-harvesting.

1. Introduction

The excitation of magnetic and electric dipole resonances in the ultraviolet and visible frequency spectrum (UV-Vis) holds great promise for applications in light nanoantennas^[1-5], photocatalysis^[6-8], light-harvesting^[9-11], spectroscopy and biosensing^[12-17], ultrafast light emitting devices^[18], negative and near-zero refractive index^[19-25]. As the speed of collective oscillation of free electrons is fundamentally limited by kinetic inductance of the given metal, it is thus necessary to choose metal with high bulk plasma frequency for the above applications. Owing to its bulk plasma oscillation in the deep ultraviolet and higher free electron density, aluminum nanostructures has been shown to exhibit better plasmonic performance as compared to its gold and silver counterparts in the UV-Vis frequency range^[26, 27]. Different kinds of aluminum nanostructures have been explored^[28-30], and their electric dipole modes have been experimentally studied and mapped^[31]. Meanwhile, the magnetic dipole resonances have also been demonstrated at up to 532nm in planar split ring resonator (SRR) structure^[32], which also proved useful for enhancing Raman signal in the graphene^[33].

Interestingly, however, the realization of magnetic resonances in the deep visible spectrum remains challenging despite the fact that the fundamental kinetic inductance limitation has not yet occurred in such frequency range. This is mainly attributed to the aluminum interband transition (at 800 nm) that is known to impart red shifts of the resonance modes (Fig. S1, Supplementary Information). Thus, the existing size dependence of split ring resonators^[34], coupled with the need for compensating the red shift effects from the interband transition, has made the dimensional requirements of Al-based SRR more challenging than those based on other plasmonic metals. Other practical challenges include native surface oxidation of aluminum nanostructures, metal roughness, and most importantly cross-contamination during aluminum physical deposition step^[28] that has been shown to suppress plasmonic oscillations.

Here, we attempt to address these challenges by fabricating aluminum SRR structures in the *u*-shape and the *v*-shape geometries, whose magnetic, electric, and magnetic-electric resonances all fall within the UV-Vis-NIR frequency spectrum. We discuss the mode excitations based on longitudinal and transverse plasmons, where the former corresponds to the well known magnetic and electric modes in SRR, and the latter points to the unexplored hybrid magnetic-electric mode. In particular, we demonstrate that the preferential excitation of magnetic-electric mode over the fundamental magnetic mode becomes a limitation for the achievable magnetic resonances in aluminum SRR even before the fundamental kinetic inductance limitation sets in. Finally, we also discuss the interaction of these modes with aluminum interband transition, which results in the resonance splitting around 800 nm.

2. Results and Discussions

The working mechanism of an SRR is based on the interaction between accumulated charges at the SRR tips, which generates circulating current that produces localized magnetic fields in the SRR aperture. *U*-shaped SRR is the most widely used geometry for realizing a magnetic dipole^[34]. Other structures, such as cut-wire pairs, fishnet structures, and plasmonic nanoparticle clusters have also been proposed, where the accumulated electric charges interact in various ways, leading to the magnetic dipole generation^[35-38]. Recently, the use of spoof plasmon structures for realizing electric and magnetic dipoles has been theoretically and experimentally studied^[39,40], where cylindrical metal structures with grooves has been shown to generate localized magnetic surface plasmon with large cross-sections.^[39] In this work,, we fabricated SRRs in *u*-shape and *v*-shape geometries due to their relatively simple planar fabrication method as compared to other three dimensional counterparts^[35-38, 41]. The *u*-SRR

and v -SRR are schematically shown in Fig. 1a and Fig. 1b, respectively, with some of their smallest fabricated structures displayed in Fig. 1c.

2.1. U-shape aluminum split ring resonator

We first present the resonance properties of u -SRRs where the extinction cross sections (σ_{ext}) were calculated by finite difference time domain method (FDTD) for x and y polarizations, as shown in Fig. 2a and Fig. 2b, respectively. The substrate in this calculation is assumed to be silica (SiO_2). As expected for u -SRR structures, there are two resonance peaks excited under x polarization, i.e., the fundamental magnetic mode (m_0) and the higher order magnetic mode (m_1). The m_0 mode corresponds to a strong horizontal electric dipole in the SRR gap and circulating currents along the wire, while m_1 mode corresponds to a horizontal electric dipole in the SRR bottom arm accompanied by anti-parallel vertical electric dipoles in the SRR arms [42, 43]. As resonator size is increased from 40 nm to 100 nm, the expected size dependence can be seen for m_0 and m_1 modes. However, towards the interband transition at $\lambda = 800$ nm, the m_0 mode splits into m_{01} and m_{02} modes. Likewise for the electric resonance (Fig. 2b), the electric mode (e_0) splits to e_{01} and e_{02} modes as the resonator size increases from 120 nm to 180 nm. Such a resonance splitting is in fact a consequence of Kramers-Kronig relations around the interband transition (Fig. S1, Supplementary Information), where there exists more than one frequencies for the resonance conditions as a result of the inflection point in the real permittivity. The electromagnetic field profiles corresponding to the two split modes were also numerically studied (Fig. S2, upper panel, Supplementary Information), where the two have the same electromagnetic field profiles except for the fact that their phases differ by $\pi/2$ from each other.

Unlike in our previous works where the u -SRRs were fabricated in fourfold rotationally symmetric lattice to enhance resonance magnitude under unpolarized light illumination [43, 44],

the aluminum u -SRRs in this work were instead fabricated in a square lattice with the purpose of studying the magnetic and electric resonance splitting near the interband transition. To reduce the native oxidation, the sample was coated with 2 nm thick nickel on top of 30 nm thick aluminum during the e-beam evaporation process. The experimentally measured transmissions of u -SRRs under x and y polarizations are presented in Fig. 2c and Fig. 2d, respectively. Note that the measured resonance positions are red shifted from their calculated values. This results from the native oxidation of aluminum which leads to an increase in the resistance (due to a reduction in the feature width) and a red shift from the cladding effects (due to few nanometers of oxide formation). In addition, a thin layer of conductive Indium Tin Oxide (ITO) also plays part in further red shifting the resonances due to slightly higher refractive index than silica. By considering the presence of a thin ITO film and ~ 4 nm thick aluminum oxide layer (Al_2O_3) on the SRR sidewalls, we also show the FDTD calculations of the u -SRR structures, as denoted by the dashed lines in Fig. 2c and Fig. 2d. The fundamental and higher order magnetic modes are denoted by circles and triangles, respectively. As resonator size is decreased, it can be seen that the magnetic mode moves from ~ 1663 nm ($s = 150$ nm) to ~ 1271 nm ($s = 70$ nm), before interacting with the interband transition at $s = 60$ nm, giving split resonances at ~ 766 nm (m_{01} mode) and ~ 1042 nm (m_{02} mode). Meanwhile, at increasing resonator size, the higher order magnetic mode moves from ~ 452 nm ($s = 60$ nm) to ~ 530 nm ($s = 70$ nm) before interacting with the interband transition at $s = 80$ nm, resulting in split resonances at ~ 657 nm (m_{11} mode) and ~ 961 nm (m_{12} mode). The m_{11} mode then moves asymptotically around 800 nm at larger sizes, while m_{12} mode moves from ~ 961 nm ($s = 80$ nm) to ~ 1119 nm ($s = 200$ nm). The same observation is found under the y -polarization incidence (Fig. 2d), where the electric mode moves from ~ 558 nm ($s = 60$ nm) towards the interband transition, and results in resonance splitting at ~ 713 nm (e_{01} mode) and ~ 943 nm (e_{02} mode). The e_{01} mode then follows the same asymptotic path around 800 nm, while the e_{02} mode moves from ~ 943 nm ($s = 80$ nm) to ~ 1324 nm ($s = 200$ nm). As expected from the red

shift from the aluminum interband transition, the achievable magnetic resonance frequencies remain lower than the gold and silver counterparts^[43, 44], in spite of the higher free electron density in aluminum.

2.2. V-shape aluminum split ring resonator

As the SRR size from our previous works is constrained to $s = 60 \text{ nm}$ ^[43, 44], a different SRR geometry is needed to further push the magnetic frequency into the short visible wavelength spectrum. This is accomplished by a ν -shape SRR (Fig. 1b), which we believe can effectively reduce the SRR area (or SRR inductance) within the same dimensional constraints. In addition, the magnetic resonance can be more flexibly tuned in the ν -SRR by virtue of its opening angle (θ) and size (s), as compared to that in the u -SRR which is tunable only by its resonator size (s). In another perspective, the tuning of resonance wavelength via the opening angle can also be understood as changing the SRR capacitance between SRR arms, which in turn leads to the tuning of SRR effective refractive index.^[45] In contrast to the u -SRR that has two magnetic modes (from x -polarized incidence) and one electric mode (from y -polarized incidence), the calculated cross sections in Fig. 3a reveal that the ν -SRR only has one magnetic mode (from x -polarized incidence) and one electric mode (from y -polarized incidence). This is due to the absence of a bottom arm in the ν -SRR, which precludes the formation of anti-parallel electric dipoles in m_1 mode in the u -SRR. Meanwhile, the interactions with the interband transition are clearly observed for magnetic and electric modes, where the split modes have the same electromagnetic field profiles with $\pi/2$ phase difference just as the case of the u -SRRs (Fig. S2, lower panel, Supplementary Information). The traces of split magnetic modes (m_{01} and m_{02}) at decreasing opening angles (Fig. 3b) show noticeable blue shifts. This is mainly caused by a reduction of the SRR inductance resulting from reduced SRR area associated with decreased opening angle. Similar to the u -SRR case, we also observed split magnetic modes (m_{01} and m_{02}) in ν -SRR structures, with resonance

magnitude progressively reduced as the mode moves towards the interband transition.

However, there is another mode (at $\lambda \sim 200$ nm) whose resonance position is almost independent of SRR shapes and sizes. This is the hybrid magnetic-electric mode originating from transverse plasmons, which will be discussed in the following.

Thus far, the magnetic and electric mode excitations shown in the u -SRRs and the v -SRRs are based on longitudinal plasmons. Borrowed from the case of the metal nanorod, the term longitudinal plasmon refers to a collective oscillation of electrons along the nanorod long axis, where electric charges are accumulated at the nanorod tips^[46]. The mode excitation mechanism of magnetic and electric modes through longitudinal plasmons is illustrated in Fig. 4a. As the nanorod is bent into an SRR geometry, the electric charges at the tips interact capacitively, producing displacement current (in the SRR gap) and circulating current (along the SRR), which then results in a localized magnetic field perpendicular to the SRR plane. This is shown in Fig. 4a for m_0 mode, which produces a strong H_z -fields accompanied by a strong electric dipole across the SRR gap. Meanwhile, for the electric mode, one can see e_0 mode as a higher order longitudinal plasmons consisting of two parallel electric dipoles along the SRR arms. As the H_z -fields between two parallel dipoles cancel each other, the H_z -field for e_0 mode is rather delocalized from the SRR. Indeed, the qualitative difference between the magnetic and the electric modes lies in the fact that their magnetic fields are localized (for magnetic mode) and delocalized (for electric mode) from the SRR.

The localized magnetic fields (or magnetic dipole) can also be generated from transverse plasmons. The interaction between electric charges occurs on the SRR sidewalls instead of on the SRR tips, producing circulating current and localized magnetic fields in the same way as the longitudinal plasmon case. However, the same electric charges also produce electric dipoles across the v -SRR arms, resembling the behavior of electric mode. The illustration of

such a hybrid magnetic-electric mode (me_0) is given in Fig. 4b. Analogous to magnetic and electric modes generated via longitudinal plasmons, the “magnetic” part of me_0 produces localized H_z -fields inside the SRR, while the “electric” part of me_0 produces H_z -fields outside the SRR. The calculated electromagnetic field profiles for this hybrid mode is presented in Fig. 4b, for the ν -SRR ($s = 70$ nm with $\theta = 90^\circ$ and $\theta = 60^\circ$) at $\lambda = 200$ nm, where the phases of the “electric” and the “magnetic” parts of the (E_x, E_y) fields differ by $\pi/2$, suggesting that they coexist and are orthogonal to each other. The quiver plot of the “electric” (E_x, E_y) fields is consistent with the illustrated electric dipole distributions of the “electric” part, while that of the “magnetic” (E_x, E_y) is consistent with the illustrated electrical current distributions of the “magnetic” part. The mixed magnetic responses are revealed in the magnitude of H_z -fields, where the “magnetic” part is apparently more dominant than the “electric” part as the H_z -field is stronger inside than outside of the SRR. The magnetic dipole of me_0 mode is weaker than that of the m_0 mode for the longer visible wavelength, but becomes progressively stronger at decreasing wavelength. This is evident from Fig. 3b which shows that the cross sections become more comparable at shorter visible wavelength.

The experimental measurements are presented in Fig. 5, where the ν -SRRs were fabricated by the same patterning process except for the 2-nm thick coating layer that was changed to titanium instead of nickel. This is because we found that titanium prevents native oxidation better than nickel. The experimental transmission spectra are shown in Fig. 5a and Fig. 5b for x and y polarizations, with their FDTD calculations denoted by dashed lines based on the same considerations as those in the u -SRR cases. The existence of m_{01} (squares) and m_{02} (circles) modes is again observed for $\theta = 90^\circ$ and $\theta = 60^\circ$ under the x polarization, where these modes are going into and out of interband transition at decreasing resonator sizes. For $\theta = 90^\circ$, the m_{01} moves from ~ 781 nm ($s = 100$ nm) to ~ 654 nm ($s = 70$ nm), while the m_{02} moves from ~ 1275 nm ($s = 100$ nm) to ~ 1035 nm ($s = 80$ nm). Likewise, for $\theta = 60^\circ$, the m_{01} moves from

~ 764 nm ($s = 100$ nm) to ~ 533 nm ($s = 70$ nm), while the m_{02} moves from ~ 1124 nm ($s = 100$ nm) to ~ 880 nm ($s = 80$ nm). Meanwhile, the me_0 mode (triangles) is observed around ~ 400 nm, which are more pronounced at decreasing resonator size for both opening angles. This is in excellent agreement with the fact that the extinction cross sections of m_0 and me_0 become comparable towards the blue-end of the visible spectrum (Fig. 3b), which should translate into a comparable transmission contrast of m_0 and me_0 modes in Fig. 5a. In addition, the lack of size dependence of me_0 positions supports the hypothesis that this is indeed the hybrid magnetic-electric mode illustrated in Fig. 4b. For $\theta = 90^\circ$, the me_0 positions are ~ 445 nm (for $s = 80$ nm) and ~ 410 nm (for $s = 70$ nm); while for $\theta = 60^\circ$, the me_0 positions are at ~ 437 nm (for $s = 80$ nm) and ~ 386 nm (for $s = 70$ nm), which already enters the ultraviolet regime.

For completeness, we also present the results of ν -SRRs under the y polarization incidence (Fig. 5b), which show the traces of electric modes (denoted by triangle markers) at decreasing SRR size. For $\theta = 90^\circ$, the e_0 mode moves from ~ 630 nm ($s = 100$ nm) to ~ 454 nm ($s = 70$ nm), while for $\theta = 60^\circ$ the e_0 mode moves from ~ 619 nm ($s = 100$ nm) to ~ 446 nm ($s = 70$ nm). There are also subtle transmission dips around ~ 300 nm which likely originate from transverse plasmons along the y-direction. However, the resonance magnitude is independent of the resonator size, indicating that such a resonance dip comes from isolated transverse plasmons in the y-direction. This is in contrast to the me_0 mode which originates from the interaction between transverse plasmons in the x-direction. In addition to the fact that the ITO refractive index increases at short wavelengths^[47], the non-idealities from the lift-off pattern transfers including the sidewall angle and metal roughness also contribute to the differences between experimental and calculated me_0 mode positions. FDTD calculations (Fig. S3, Supplementary Information) reveal that me_0 mode does red shifts when sidewall angle and artificial roughness (see Methods) is introduced into the aluminum nanostructure, making our calculation results closer to the experimental findings in Fig. 5a.

We further reduced the ν -SRR size by decreasing the SRR opening angle to $\theta = 30^\circ$ (for $s = 70$ nm), with 14 nm lateral offset between the SRR arms to minimize e-beam proximity effects. From SEM inspection, the gap separation and the feature width are 28 nm and 21 nm, respectively, which we believe mark the smallest fabricated aluminum split ring resonator so far. Their measurements are presented in Fig. 6, where for clarity the inverse transmission spectra are plotted in log scale. For $s = 80$ nm, the resonance positions are ~ 604 nm (for m_{01} mode), ~ 481 nm (for e_{01} mode), and ~ 425 nm (for me_0 mode); while for $s = 70$ nm, ~ 469 nm (for m_{01} mode), ~ 429 nm (for e_{01} mode), and ~ 376 nm (for me_0 mode). It is interesting to note that m_{01} mode is progressively overshadowed by me_0 mode at decreasing SRR size, and that the m_{01} almost entirely diminishes in Fig. 6b. This clearly shows me_0 is more preferred to m_0 in the short visible wavelength, and we believe such a preferential excitation could serve as the other limitation for the achievable fundamental magnetic mode apart from the well known kinetic inductance limitation^[48, 49].

3. Conclusions

We have presented the experimental realization of aluminum split ring resonator with fundamental magnetic ($\Delta\lambda = 469 - 1663$ nm), electric ($\Delta\lambda = 429 - 1324$ nm), and magnetic-electric ($\Delta\lambda = 376 - 445$ nm) resonances in the UV-Vis-NIR spectrum. Compared to gold and silver SRRs in the same geometry, the resonance positions of the aluminum SRR are generally red shifted due to higher damping loss of aluminum in the Vis-NIR frequency range, suggesting the need to have smaller SRR size. For that reason, we have introduced an SRR based on the ν -shape geometry that has more tuning flexibility in terms of its opening angle and resonator size, which can effectively reduce the SRR area under the same dimensional constraints. Compared to the smallest fabricated u -SRR, the nominal SRR area has been reduced as much as $\sim 40\%$ in the ν -shape geometry, pushing the magnetic resonance

wavelength from 671 nm to 469 nm. We have also demonstrated the resonance splitting of magnetic and electric modes in the u -SRR and the v -SRR that result from their interactions with the interband transition. The magnetic dipole generation based on longitudinal and transverse plasmons has been discussed and demonstrated, where the magnetic response of the latter has the character of both magnetic and electric resonances. Due to the decreasing damping loss at decreasing wavelength, it is shown that the hybrid magnetic-electric mode will eventually dominate over the fundamental magnetic mode. This could serve as another limitation for the achievable magnetic frequencies other than the well known kinetic inductance limitation, which is derived from the preferential excitation of the hybrid magnetic-electric mode at short visible wavelengths.

4. Methods

Fabrication of aluminum split ring resonators: The SRR structures corresponding to different shapes and sizes were fabricated on 1 cm x 1 cm ITO coated glass substrate, where each SRR structure occupies 100 μ m x 100 μ m footprints with markers denoting its orientation. The patterning of u -SRR and v -SRR structures were done by electron beam lithography (Raith e_LiNE) using high contrast sonicated cold development process^[50] with 20 keV beam energy and 30 pA beam current. The writing time for each SRR structure (of 100 μ m x 100 μ m footprint) is 4 minutes. A 30-nm thick Al was deposited (Ohmiker-60BL, at 0.05 nm/s rate), followed by deposition of 2-nm thick nickel or titanium film (Ohmiker-60BL, at 0.01 nm/s) for coating purposes. For lift-off pattern transfers, the samples were immersed in warm n -methyl pyrrolidone (NMP) solution for 10-20 minutes.

Numerical calculation: Finite difference time domain (FDTD solutions, Lumerical Inc) was used to calculate the scattering properties of u -SRR and v -SRR structures. The scattering properties were calculated in total-field-scattered-field module, where the inward and outward

power flows were calculated to deduce absorption (σ_{abs}) and scattering (σ_{scat}) cross sections.

The extinction cross section (σ_{ext}) is $\sigma_{\text{ext}} = \sigma_{\text{abs}} + \sigma_{\text{scat}}$. The transmission spectra were obtained from an observation plane 30-40 nm below the SRR structure. All FDTD simulations were performed at the minimum mesh grid of 2 nm, with the mesh accuracy of 6-7 and auto shut-off value of 10^{-5} . The refractive index of Al and SiO_2 are obtained from software database. The refractive index of ITO depends on the film conductivity, thickness, and roughness. In addition, the value of ITO refractive index in the near infrared spectrum is not yet available. In the fitting, the substrate refractive index is chosen between 1.8 and 2.2 in order to taken into account ITO substrate and the coating layer, and the calculated transmission contrast is adjusted to take into account the effect of array density. The native oxide layer on the SRR sidewall is assumed to be Al_2O_3 , with its refractive index taken from software database. The actual resonator sizes are also investigated through SEM inspection, where the actual arm length could be smaller due to fabrication non-idealities due to e-beam proximity effects. The 5° off-normal metal sidewall angle was obtained from our previous work on nanofabrication^[51], which was deduced from the difference between the as-patterned nanodot size and the nanodot size after lift-off for the same e-beam exposure dose. The artificial surface roughness was introduced by defining fixed mesh size in the v-SRR structure, where larger mesh size gives higher metal “roughness”. The impact of metal roughness was stronger when the sidewall angle was also incorporated. The magnetic-electric resonance is further suppressed when the sidewall angle is increased to 10° . For the σ_{ext} plots in Fig. 2a and Fig. 2b, the vertical shifts are as follows. For Fig. 2(a), the vertical shifts ($\Delta\sigma$) are $\Delta\sigma = 0$ ($s = 40$ nm), $\Delta\sigma = 1.2 \times 10^4 \text{ nm}^2$ ($s = 50$ nm), $\Delta\sigma = 4 \times 10^4 \text{ nm}^2$ ($s = 60$ nm), $\Delta\sigma = 5 \times 10^4 \text{ nm}^2$ ($s = 70$ nm), $\Delta\sigma = 6.3 \times 10^4 \text{ nm}^2$ ($s = 80$ nm), $\Delta\sigma = 7.8 \times 10^4 \text{ nm}^2$ ($s = 90$ nm), $\Delta\sigma = 9 \times 10^4 \text{ nm}^2$ ($s = 100$ nm). For Fig. 2(b), $\Delta\sigma = 0.5 \times 10^4 \text{ nm}^2$ ($s = 120$ nm), $\Delta\sigma = 1.5 \times 10^4 \text{ nm}^2$ ($s = 140$ nm), $\Delta\sigma = 3 \times 10^4 \text{ nm}^2$ ($s = 150$ nm), $\Delta\sigma = 4.5 \times 10^4 \text{ nm}^2$ ($s = 160$ nm), $\Delta\sigma = 6 \times 10^4 \text{ nm}^2$ ($s = 180$ nm)

Characterization: The measurements of *u*-SRR and *v*-SRR structures were carried out by CRAIC spectrophotometer using unpolarized broadband source (UV-Vis-NIR) at normal incidence. The light signal from 80 μ m x 80 μ m aperture was collected through 15x Objective lens (NA = 0.28), which was then normalized with the background spectrum of ITO glass (for transmission) or of aluminum pad (for reflection). The characterization of different polarization responses was done by introducing off-the-shelf polarizer between the sample and the condenser during sample measurements.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors thank the reviewers for their valuable inputs in improving this manuscript. The

authors thank Luo Yu for fruitful discussions and Qihua Xiong for facilitating microspectrophotometer measurements. The authors acknowledged the financial support from Ministry of Education (RG86/13), A*Star (1220703063), Economic Development Board (NRF2013SAS-SRP001-019) and Asian Office of Aerospace Research and Development (FA2386-14-1-0013)

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

- [1] J. N. Farahani, D. W. Pohl, H.-J. Eisler, B. Hecht, "Single quantum dot coupled to a scanning optical antenna: A tunable superemitter," *Phys. Rev. Lett.* **2005**, 95, 017402.
- [2] H. Mertens, J. S. Biteen, H. A. Atwater, A. Polman, "Polarization-selective plasmon-enhanced silicon quantum-dot luminescence," *Nano Lett.*, **2006**, 6, 2622–2625.

- [3] A. G. Curto, G. Volpe, T. H. Taminiau, M. P. Kreuzer, R. Quidant, N. F. van Hulst, “Unidirectional emission of a quantum dot coupled to a nanoantenna,” *Science* **2010**, 329, 930–933.
- [4] A. Kinkhabwala, Z. Yu, S. Fan, Y. Avlasevich, K. Müllen, W. E. Moerner, “Large single-molecule fluorescence enhancements produced by a bowtie nanoantenna,” *Nature Photonics* **2009**, 3, 654–657.
- [5] O. L. Muskens, V. Giannini, J. A. Sánchez-Gil, J. Gómez Rivas, “Strong enhancement of the radiative decay rate of emitters by single plasmonic nanoantennas,” *Nano Lett.* **2007**, 7, 2871–2875.
- [6] S. Mukherjee, F. Libisch, N. Large, O. Neumann, L. V. Brown, J. Cheng, J. B. Lassiter, E. A. Carter, P. Nordlander, N. J. Halas, “Hot Electrons do the Impossible: Plasmon-Induced Dissociation of H₂ on Au,” *Nano Lett.* **2013**, 13, 240–247.
- [7] I. Thomann, B. A. Pinaud, Z. B. Chen, B. M. Clemens, T. F. Jaramillo, M. L. Brongersma, “Plasmon Enhanced Solar-to-Fuel Energy Conversion,” *Nano Lett.* **2011**, 11, 3440–3446.
- [8] S. C. Warren, E. Thimsen, “Plasmonic Solar Water Splitting,” *Energy Environ. Sci.* **2012**, 5, 5133–5146.
- [9] H. A. Atwater, A. Polman, “Plasmonics for Improved Photovoltaic Devices,” *Nat. Mater.* **2010**, 9, 205–213.
- [10] S. Linic, P. Christopher, D. B. Ingram, “Plasmonic-Metal Nanostructures for Efficient Conversion of Solar to Chemical Energy,” *Nat. Mater.* **2011**, 10, 911–921.
- [11] T. F. Villesen, C. Uhrenfeldt, B. Johansen, A. N. Larsen, “Self-Assembled Al Nanoparticles on Si and Fused Silica, and Their Application for Si Solar Cells,” *Nanotechnology* **2013**, 24, 275606.

- [12] A. W. Clark, A. Glidle, D. R. S. Cumming, J. M. Cooper, "Plasmonic split-ring resonators as dichroic nanophotonic DNA biosensors," *J. Am. Chem. Soc.* **2009**, 131, 17615-17619.
- [13] A. W. Clark, A. Glidle, D. R. S. Cumming, J. M. Cooper, "Nanophotonic split-ring resonators as dichroics for molecular spectroscopy," *Appl. Phys. Lett.* **2008**, 93, 023121.
- [14] B. Paivanranta, H. Merbold, R. Giannini, L. Buchi, S. Gorelick, C. David, J. F. Löffler, T. Feurer, Y. Ekinici, "High aspect ratio plasmonic nanostructures for sensing applications," *ACS Nano* **2011**, 5, 6374-8382.
- [15] B. Lahiri, A. Z. Khokhar, R. M. De La Rue, S. G. McMeekin, N. P. Johnson, "Asymmetric split ring resonators for optical sensing of organic materials," *Opt. Express* **2009**, 17, 1107-1115.
- [16] Y. Gu, Q. Li, J. Xiao, K. Wu, and G. P. Wang, "Plasmonic metamaterial for ultrasensitive refractive index sensing at near infrared," *J. Appl. Phys.* **2011**, 109, 023104.
- [17] A. V. Kabashin, P. Evans, S. Pastkovsky, W. Hendren, G. A. Wurtz, R. Atkinson, R. Pollard, V. A. Podolskiy, and A. V. Zayats, "Plasmonic nanorod metamaterials for biosensing," *Nature Mater.* **2009**, 8, 867-871.
- [18] M. S. Eggleston, K. Messer, L. Zhang, E. Yablonovitch, M. C. Wu, "Optical Antenna enhanced spontaneous emission" *Proc. Nat. Acad. Sci.* **2014**, 112, 1704-1709.
- [19] T. A. Klar, A. V. Kildishev, V. P. Drachev, V. M. Shalaev, "Negative-Index Metamaterials: Going Optical," *IEEE J. Sel. Top. Quant. Electron.* **2006**, 12, 1106-1115.
- [20] S. Xiao, U. K. Chettiar, A. V. Kildishev, V. P. Drachev, V. M. Shalaev, "Yellow-light negative index metamaterials," *Opt. Lett.* **2009**, 34, 3478.
- [21] G. Dolling, M. Wegener, C. M. Soukoulis, S. Linden, "Negative-index metamaterial at 780 nm wavelength," *Opt. Lett.* **2007**, 32, 53.

- [22] D. R. Smith, W. J. Padilla, D. C. Vier, S. C. Nemat-Nasser, S. Schultz, "Composite medium with simultaneously negative permeability and permittivity," *Phys. Rev. Lett.* **2000**, 84, 4184.
- [23] D. R. Smith, J. B. Pendry, and M. C. K. Wiltsgire, "Metamaterials and negative refractive index," *Science* **2004**, 305, 788.
- [24] C. Soemphol, A. Sonsilphong, and N. Wongkasem, "Metamaterials with near-zero refractive index produced using fishnet structures," *J. Opt.* **2014**, 16, 015104.
- [25] B. Zhou, T. J. Cui, "Directivity enhancement to Vivaldi antennas using compactly anisotropic zero-index metamaterials," *IEEE Antennas Wirel. Propag. Lett.* **2011**, 10, 326–329.
- [26] P. R. West, S. Ishii, G. V. Naik, N. K. Emani, V. M. Shalaev, A. Boltasseva, "Searching for better plasmonic materials," *Laser Photonics Rev.* **2010**, 4, 795-808.
- [27] P. Tassin, T. Koschny, M. Kafesaki, C. M. Soukoulis, "A comparison of graphene, superconductors and metals as conductors for metamaterials and plasmonics," *Nat. Photon.* **2012**, 6, 259-264.
- [28] M. W. Knight, N. S. King, L. Liu, H. O. Everitt, P. Nordlander, N. J. Halas, "Aluminum for Plasmonics," *ACS Nano* **2014**, 8, 834-840.
- [29] I. Zoric, M. Zach, B. Kasemo, C. Langhammer, "Gold, Platinum, and Aluminum Nanodisk Plasmons: Material Independence, Subradiance, and Damping Mechanisms," *ACS Nano* **2011**, 5, 2535– 2546..
- [30] Y. Ekinici, H. H. Solak, J. F. Loffler, "Plasmon Resonances of Aluminum Nanoparticles and Nanorods," *J. Appl. Phys.* **2008**, 104, 083107.
- [31] M. W. Knight, L. Liu, Y. Wang, L. Brown, S. Mukherjee, N. S. King, H. O. Everitt, P. Nordlander, N. Halas, "Aluminum Plasmonic Nanoantennas," *Nano Lett.* **2012**, 12, 6000-6004.

- [32] B. Lahiri, S. G. McMeekin, A. Z. Khokhar, R. M. De La Rue, N. P. Johnson, “Magnetic response of split ring resonators (SRRs) at visible frequencies,” *Opt. Express* **2010**, 18, 3210–3218.
- [33] G. Sarau, B. Lahiri, P. Banzer, P. Gupta, A. Bhattacharya, F. Vollmer, S. Christiansen, “Enhanced Raman Scattering of Graphene using Arrays of Split Ring Resonators,” *Adv. Opt. Mater.* **2013**, 1, 151-157.
- [34] S. Linden, C. Enkrich, G. Dolling, M. W. Klein, J. Zhou, T. Koschny, C. M. Soukoulis, S. Burger, F. Schmidt, M. Wegener, “Photonic metamaterials: magnetism at optical frequencies,” *IEEE J. Sel. Top. Quant. Electron.* **2006**, 12, 1097-1105.
- [35] J. A. Fan, C. Wu, K. Bao, J. Bao R. Bardhan, N. J. Halas, V. N. Manoharan, P. Nordlander, G. Shvets, F. Capasso, “Self-Assembled Plasmonic Nanoparticle Clusters,” *Science* **2010**, 328, 1135-1138.
- [36] F. Shafiei, F. Monticone, K. Q. Le, X.-X. Liu, T. Hartsfield, A. Alu, X. Li., “A Subwavelength plasmonic metamolecule exhibiting magnetic-based optical Fano Resonance,” *Nat. Nanotechnol.* **2013**, 8, 95-99.
- [37] V. M. Shalaev, W. Cai, U. K. Chettiar, Ho-K. Yuan, A. K. Sarychev, V. P. Drachev, A. V. Kildishev, “Negative index of refraction in optical metamaterials,” *Opt. Lett.* **2005**, 30, 3356–3358.
- [38] G. Dolling, C. Enkrich, M. Wegener, C. M. Soukoulis, S. Linden, “Simultaneous negative phase and group velocity of light in a metamaterial,” *Science* **2006**, 312, 892–894.
- [39] P. A. H. Huidobro, X. Shen, J. Cuerda, E. Moreno, L. Martin-Moreno, F. J. Garcia-Vidal, T. J. Cui, J. B. Pendry, “Magnetic Localized Surface Plasmons,” *Phys. Rev. X* **2014**, 4, 021003.
- [40] X. Shen, T. J. Cui, “Ultrathin plasmonic metamaterial for spoof localized surface plasmons,” *Laser Photonics Rev.* **2014**, 8, 137-145.

- [41] A. I. Kuznetsov, A. E. Miroshnichenko, Y. H. Fu, V. Viswanathan, M. Rahmani, V. Valuckas, Z. Y. Pan, Y. Kivshar, D. S. Pickard, B. Lukyanchuk, “Split-ball resonator as three-dimensional analogue of planar split-rings,” *Nat. Commun.* **2014**, 5, 3104.
- [42] C. Enkrich, M. Wegener, S. Linden, S. Burger, L. Zschiedrich, F. Schmidt, J. F. Zhou, Th. Koschny, C. M. Soukoulis, “Magnetic metamaterials at telecommunication and visible frequencies,” *Phys. Rev. Lett.* **2005**, 95, 203901.
- [43] L. Y. M. Tobing, L. Tjahjana, D. H. Zhang, Q. Zhang, Q. Xiong, “Deep subwavelength fourfold rotationally symmetric split-ring-resonator metamaterials for highly sensitive and robust biosensing platform,” *Sci. Rep.* **2013**, 3, 2437.
- [44] L. Y. M. Tobing, L. Tjahjana, D. H. Zhang, Q. Zhang, Q. Xiong, “Sub-100-nm Sized Silver Split Ring Resonator Metamaterials with Fundamental Magnetic Resonance in the Middle Visible Spectrum,” *Adv. Opt. Mater.* **2014**, 2, 280-285.
- [45] K. Kishor, M. N. Baitha, R.K. Sinha, B. Lahiri, “Tunable negative refractive index metamaterial from V-shaped SRR structure: fabrication and characterization,” *J. Opt. Soc. Am. B* **2014**, 31, 1410-1414.
- [46] J. A. Schuller, E. S. Barnard, W. Cai, Y. C. Jun, J. S. White, M. L. Brongersma, “Plasmonic for extreme light concentration and manipulation,” *Nat. Mater.* **2010**, 9, 193-204.
- [47] T. A. F. König, P. A. Ledin, J. Kerszulis, M. A. Mahmoud, M. A. El-Sayed, J. R. Reynolds, and V. V. Tsukruk, “Electrically tunable plasmonic behavior of nanocube–polymer nanomaterials induced by a redox-active electrochromic polymer,” *ACS Nano* **2014**, 8, 6182-6192.
- [48] M. W. Klein, C. Enkrich, M. Wegener, C. M. Soukoulis, S. Linden, “Single-slit split-ring resonators at optical frequencies: limits of size scaling,” *Opt. Lett.* **2006**, 31, 1259.
- [49] J. Zhou, Th. Koschny, M. Kafesaki, E. N. Economou, J. B. Pendry, C. M. Soukoulis, “Saturation of the magnetic response of split-ring resonators at optical frequencies,” *Phys. Rev. Lett.* **2005**, 95, 223902.

- [50] L. Y. M. Tobing, L. Tjahjana, D. H. Zhang, "Direct patterning of high density sub-15-nm gold dot arrays using ultrahigh contrast electron beam lithography process on positive tone resist", *Nanotechnology* **2013**, 24, 075303.
- [51] L. Y. M. Tobing, L. Tjahjana, D. H. Zhang, "Sub-10-nm size and sub-40-nm pitch metal dot patterning for low-cost bit patterned media application," *IEEE Trans. Nanotechnol.* **2014**, 13, 496-501.
- [52] A. D. Rakić, A. B. Djurišić, J. M. Elazar, and M. L. Majewski, "Optical properties of metallic films for vertical-cavity optoelectronic devices," *Appl. Opt.* **1998**, 37, 5271-5283.

Figure 1. Aluminum split ring resonators (SRR) on ITO glass substrate. (a) Schematic representations of u -SRRs and v -SRRs with lattice constant a . (b) SEM images of the fabricated u -SRRs [1st column, (1)-(3)] and v -SRRs [2nd and 3rd column, (4)-(9)] with different resonator sizes (s) and opening angles (θ). The scale bar corresponds to 100 nm. The resonator sizes for the u -SRRs are 100 nm (1), 80 nm (2), and 60 nm (3); while for the v -SRRs are 100 nm (4, 7), 80 nm (5, 8), and 70 nm (6, 9). For all SRR structures, the lattice constant is designed to be two times the resonator size ($a = 2s$), and the feature width is 20-25 nm.

Figure 2. The resonance modes of aluminum *u*-SRR and their interactions with aluminum interband transition at $\lambda_{\text{int}} = 800$ nm. Near the interband transition, the fundamental magnetic mode (m_0) splits into m_{01} and m_{02} while the electric mode (e_0) splits into e_{01} and e_{02} . Finite difference time domain calculation of extinction cross-section (σ_{ext}) of *u*-SRRs on SiO_2 substrate under normal incidence for (a) *x*-polarization, $s = 60$ -100 nm and $w = 25$ nm; and (b) *y*-polarization, $s = 120$ -200 nm and $w = 40$ nm. The experimental (solid) and calculated (dashed) transmission spectra of *u*-SRRs on ITO glass for (c) *x*-polarization, $s = 60 - 100$ nm, $w = 25$ nm, and (d) *y*-polarization, $s = 120 - 200$ nm, $w = 40$ nm. The fundamental magnetic modes are indicated by filled (m_{01}) and hollow (m_{02}) circles, while the higher order magnetic modes are indicated by filled (m_{11}) and hollow (m_{12}) triangles. The electric modes are indicated by filled (e_{01}) and hollow (e_{02}) squares.

Figure 3. The resonance modes of v-SRR and their interactions with aluminum interband transition. (a) The excitation of magnetic (m_{01} and m_{02}) and electric (e_{01} and e_{02}) modes in v-SRR with $\theta = 90^\circ$ under x-polarized and y-polarized light illumination for two v-SRRs with $s = 100$ nm and $s = 70$ nm. (b) The traces of split magnetic modes at decreasing SRR opening angle (from $\theta = 90^\circ$ to $\theta = 30^\circ$) for $s = 80$ nm and $s = 70$ nm, and the magnetic-electric mode (me_0) at locations around 200 nm almost independent of opening angle.

Figure 4. Mode characteristics of aluminum ν -SRR. The vector of the transverse electric fields is overlaid with the magnitude of longitudinal H_z -fields, with the representation of its electric dipole (red arrow), magnetic field (blue arrow), and circulating current (green arrow). (a) The modes emerging from the longitudinal plasmons, i.e., the magnetic (m_0) and the electric (e_0) modes. The opening angle is $\theta = 60^\circ$. (b) The mode emerging from transversal plasmons, i.e., the magnetic-electric (me_0) mode, for (1) $\theta = 90^\circ$ and (2) $\theta = 60^\circ$.

Figure 5. Mode excitation through longitudinal and transverse plasmons: (a) The x -polarized experimental (solid) and calculated (dashed) transmissions of v -SRRs of $\theta = 90^\circ$ and $\theta = 60^\circ$ for different sizes, where the split magnetic modes m_{01} (circles), m_{02} (squares), and the magnetic-electric mode me_0 (triangles) are all indicated; (b) The y -polarized experimental (solid) and calculated (dashed) transmissions of v -SRRs of $\theta = 90^\circ$ and $\theta = 60^\circ$ for different sizes, where the electric modes (e_0) are denoted by triangle markers.

Figure 6. Preferential excitation of magnetic-electric mode in the ultraviolet spectrum. The magnetic, electric, and magnetic-electric modes of ν -SRR ($\theta = 30^\circ$ with 14 nm lateral offset between the arms) for $s = 80$ nm and $s = 70$ nm. The insets show the fabricated ν -SRR, where the scale bars correspond to 100 nm. The gap separation and feature width are 28 nm and 21 nm, respectively.

Aluminum is a promising candidate for light at the nanoscale in the ultraviolet, however the realization of magnetic resonance in the UV range remains challenging due to stringent dimensional requirements arising from intrinsic loss caused by interband transition. Here, we report the mode interaction with aluminum interband transition and preferential excitation of hybrid magnetic-electric mode discovered in ultrasmall Al resonators.

Nanophotonics, Aluminum, Nanostructures, ultraviolet

L. Y. M. Tobing, D. H. Zhang, *

Title Preferential Excitation of Hybrid Magnetic-Electric Mode as a Limiting-Mechanism for the Achievable Fundamental Magnetic Resonance in Planar Aluminum Nanostructures

Supporting Information

Preferential Excitation of Hybrid Magnetic-Electric Mode as a Limiting-Mechanism for the Achievable Fundamental Magnetic Resonance in Planar Aluminum Nanostructures

*Landobasa Y. M. Tobing, Dao-Hua Zhang **

1. The complex permittivity plot of aluminum (Al), gold (Au), and silver (Ag)

Among noble metals, gold (Au) and silver (Ag) are the two most widely studied metals for plasmonic applications^[26, 27]. Gold is desired for its stability from oxidation, and for its compatibility with protein functionalization in biosensing applications. However, the damping loss increases significantly in the visible spectrum due to gold interband transition at $\lambda = 550$ nm, thereby quenching the magnetic resonance in the visible spectrum. Meanwhile, silver has much lower damping loss in the visible spectrum due to its interband transition at $\lambda = 350$ nm^[52], but suffers from rapid oxidation that leads to a degradation of its plasmonic properties. The plasma oscillation frequencies of gold (at 8.9 eV) and silver (at 9.2 eV) are actually quite comparable^[26], suggesting that the kinetic inductance remains the main limitation for the realization of magnetic resonance in the visible spectrum. Indeed, this is the main motivation to explore aluminum (Al) as a plasmonic material as it has much higher plasma oscillation frequency at 12.7 eV.^[26]

In contrast to gold and silver whose real permittivity rapidly decreases towards the visible spectrum, the real permittivity of aluminum remains largely negative even in the ultraviolet range (Fig. S1). This is due to the fact that aluminum produces three times more valence electrons than gold and silver, making a much higher conduction electron density leading to higher plasma oscillation frequency. In terms of damping loss, however, aluminum differs qualitatively from gold and silver due to its interband transition that lies in the NIR range (at 800 nm), making the damping loss for aluminum generally higher than gold and silver except in the deep visible and ultraviolet frequency range. Using damping loss as the gauge for plasmonic tunability range for each metal, it is thus apparent that aluminum is suitable for plasmonics in the UV-Vis range, while gold and silver is suitable for Vis-NIR spectrum^[26]. As damping loss imparts red shift to the resonance modes, in addition to linear dependence of resonance positions on resonator dimensions^[27, 42], it then becomes a challenge to realize aluminum split ring resonators with magnetic modes in the UV-Vis frequency range.

Fig. S1. The real (solid) and imaginary (dashed) permittivity of aluminum (blue), gold (green), and silver (red).

2. The phase relation of tranverse electric fields of the split-modes in u-SRR and v-SRR structures.

Fig. S2. The magnetic modes around aluminum interband transition for (upper panel) u -SRR with $s = 80$ nm and (lower) v -SRR with $s = 100$ nm and $\theta = 120^\circ$. The electric field distributions of m_{01} and m_{02} modes are qualitatively similar, with their amplitudes dependent on their resonance positions relative to the interband transition. The phase responses reveal that the two modes have $\pi/2$ phase difference from each other. The scales for all electric fields magnitudes are set from 0 to 10, while those for all electric field phases are set from $-\pi$ to π .

3. The effect of ITO layer, metal sidewall angle, and metal surface roughness on ν -SRR spectral characteristics

Fig. S3. The influence of ITO coating on the glass substrate, metal sidewall angle, and metal surface roughness to the magnetic-electric modes in Al ν -SRR ($\theta = 60^\circ$, $s = 70$ nm): (1) Al ν -SRR on SiO₂ substrate, (2) Al ν -SRR on ITO substrate, (3) Al ν -SRR on ITO substrate with 5° sidewall angle at 2nm roughness, and (4) Al ν -SRR on ITO substrate with 5° sidewall angle at 3 nm roughness.