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Article

Keywords: Bimetallic Fe-Ag arrays, nonlinear refraction, nonlinear Faraday rotation, telecommunication wavelength, magneto-optical materials and devices

Posted Date: September 28th, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-79014/v1>

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Bimetallic Fe-Ag arrays with extraordinary nonlinear refraction and nonlinear Faraday rotation at telecommunication wavelength (1550 nm)

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There is a pressing need to discover magneto-optical materials and devices with better performance and lower cost that operate at telecommunication wavelengths. Here we report the discovery of giant negative nonlinear refraction and nonlinear Faraday rotation at 1550 nm using an array of bimetallic Fe-Ag nanopyramids. This system exhibited a very large third order nonlinear refractive index ($n_2 = -2.32 \text{ cm}^2/\text{GW}$) and nonlinear figure of merit ($F = 2.3$). The same system also exhibited an extraordinarily large magneto-optical susceptibility ($\chi_i^4 = 6.5 \times 10^{-12} \text{ esu}$) and photoinduced nonlinear Faraday rotation up to 2.5 radian/ μm at a magnetic field of 0.5 T. The nonlinear response was dependent on the degree of overlap of the Fe nanopyramid on the Ag nanopyramid which influences the strength of plasmon induced dipoles on the Ag nanopyramid. This nanoscale system opens up a rich new set of possibilities in utilizing magneto-plasmonic materials to miniaturize future multifunctional devices at telecommunication wavelengths.

MAIN

The wavelength-dependent optical and magneto-optical properties of metal nanostructures are an area of active research due to a variety of potential applications. One area of particular interest is their nonlinear optical (NLO) and nonlinear magneto-optical (NLMO) properties at or near the telecommunication wavelengths (such as between 1530 nm -1570 nm), that result from utilizing suitably engineered materials design [1–3]. Large and ultrafast optical and magneto-optical nonlinearity are generally desired for optical communication functionalities like all-optical switching, optical isolation, pulse limiting, multiplexing, demultiplexing, high sensitive magnetometry and quantum information processing [4–13]. Silicon has been considered to be a promising material for all-optical logic at telecommunication wavelength due to its linear optical transparency and a large nonlinear refractive index of $n_2 = 4 \times 10^{-5} \text{ cm}^2/\text{GW}$. However, its ultimate performance is limited by a weak nonlinear figure of merit of $F = 0.35$ defined by $F = \frac{n_2}{\beta \lambda}$, where β is the nonlinear absorption coefficient and λ is the wavelength of the incident light [14]. Graphene has also been regarded as a promising material due to the very high n_2 of $102 \text{ cm}^2/\text{GW}$ at the telecommunication wavelength. However, it is unlikely to address the current demand of high performance optical devices due to the challenges with making large area graphene for mass production as well as its zero band gap which results on broad-band optical absorption [15]. Many other 2D materials have been proposed for all-optical devices, including hexagonal Boron Nitride (h-BN), metal oxides, perovskites and metal dichalcogenides [16–23]. Despite exciting advances, outstanding challenge remain in the large-area-growth of low defect materials along with intrinsic materials limitations, such as a Faraday rotation limited by the cyclotron frequency of the system. The current state-of-the-art in the field of strong Faraday rotators at telecommunication wavelengths are based on linear response of bulk synthetic materials and solely driven by Yttrium Iron Garnet (YIG) [24]. Nonlinear Faraday properties have been generally investigated for cold atoms and atomic vapors at or near the laser wavelengths (energies) of their hyperfine transition energies regions, and for some dilute magnetic semiconductors like CdMnTe at or near their optical band gap energies, which are far from the telecommunication wavelength [12, 25, 26]. To the best of our knowledge, the nonlinear Faraday process has not been studied on the material systems at or near the telecommunication wavelengths. Partially motivated by these limitations, and the many unusual plasmonic and magneto-plasmonic properties of metallic nanostructures that have been discovered recently, there is continuing interest among the nonlinear optics and magneto-optics community to explore plasmonic nanostructures at the important 1550 nm [27–31].

One class of interesting metallic systems are bimetallic plasmonic nanostructures which show either improved materials stability and/or unusual optical and magneto-optical properties in terms of activity and

stability arising from synergetic effects. In the past, metals like Fe, Co, Ni, Pt, Pd and Al have been combined with the noble metals Ag, Au and Cu to enhance the plasmonic and magneto-plasmonic properties. For example, ferroplasmons have been discovered in Ag-Co bimetallic nanoparticles, in which strong surface plasmons have been observed in the Co side of the metallic system while preserving its ferromagnetism [32, 33]. Additionally, the Ag-Co and Ag-Fe system have also demonstrated reduced degradation rate of plasmonic signals due to oxidation of silver thus leading to very stable plasmonic behavior over long periods of time [33, 34]. Fe₂O₃-Au core shell nanoparticles have been reported to have a high Faraday rotation at resonant frequency ascribed to spectral overlap of magneto-optical transition to plasmonic resonance [35].

In this article, we report the discovery of giant third order nonlinear refractive index and photo-induced nonlinear Faraday rotation at 1550 nm from a hexagonal array of partially overlapped Fe-Ag truncated nanoppyramids. This nanoppyramidal system exhibited a very large third order nonlinear refractive index ($n_2 = -2.32 \text{ cm}^2/\text{GW}$) and nonlinear figure of merit ($F = 2.3$). The same system also exhibited a photoinduced nonlinear Faraday rotation of magnitude of 2.5 radian/ μm at a magnetic field of 0.5 T. We found that these effects are strongly dependent on the plasmon induced dipole strength from Ag nanoppyramids across the Fe nanoppyramids and which in turn depends on the overlapping extent of Fe nanoppyramids on Ag nanoppyramids.

RESULTS

Nonlinear optical properties

We studied nonlinear optical properties of nanoppyramidal systems viz. pure Ag, pure Fe and Fe-Ag (with 30% and 90% overlap) at 1550 nm whose surface plasmons induced resonant absorption was at 750 nm (except for pure Fe pyramidal system). The third order optical nonlinearities were studied by f-scan methods, particularly transmission f-scan and reflection f-scan, which are modifications of the conventional z-scan method [36–38]. These methods allow us to measure the nonlinear index of refraction (n_2) in reflection and the nonlinear absorption or two photon absorption coefficient (β) in transmission modes. The electric field ($\mathbf{E}$) dependent polarization ($\mathbf{P}$) of a nonlinear system can be expressed as

$$\mathbf{P} = \chi_E^{(1)} \mathbf{E} + \mathbf{P}_{\text{NL}} = \chi_E^{(1)} \mathbf{E} + \chi_{EE}^{(2)} \mathbf{E}\mathbf{E} + \chi_{EEE}^{(3)} \mathbf{E}\mathbf{E}\mathbf{E} + \chi_{EEEE}^{(4)} \mathbf{E}\mathbf{E}\mathbf{E}\mathbf{E} + \dots \quad (1)$$

where, $\chi^{(i)} (i=1,2,3,\dots)$ is the i^{th} order nonlinear susceptibility of the nonlinear system. The real part of the $\chi_{EEE}^{(3)}$ is related to n_2 while imaginary part is related to β . A schematic of experimental set up to calculate the value of n_2 and β is shown in Fig. 1 (a). First, for the open aperture configuration, we used a 1550

nm fiber laser with a pulse duration of 64 fs, and an average power of 20 mW which was incident on an electrically focused tunable lens (EFTL). The samples were placed at distance f_s from the EFTL. The output of the lens impinged in the sample and the intensity in the sample was controlled by changing the focal length of the EFTL with applied current. The transmitted laser beam was detected with a Ge-photodetector, and the normalized transmittance was used to calculate the value of β using the relation as,

$$T(f) = \frac{1}{B(f)} \int \ln\{1 + B(f)\text{sech}^2(\rho)\} d\rho, \rho \rightarrow 0, \infty \quad (2)$$

with

$$B(f) = \beta(1 - R)I_o(f)L_{eff} \quad (3)$$

Here, L_{eff} is the effective sample thickness given by $L_{eff} = \frac{(1 - e^{-\alpha L})}{\alpha}$, L being sample thickness and α being linear absorption coefficient. Also, R is reflection coefficient and I_o is peak intensity of the beam which is function of focal length. Also, ρ is expressed as $\rho = \frac{2\ln(1 + \sqrt{\tau})}{\tau}$ with τ being full width at half maximum pulse duration.

Second, the samples were tilted at an angle of θ with respect to the laser beam direction and the light reflected by the sample surface was analyzed to measure the n_2 . The normalized reflected beam intensity can be expressed as

$$R_N(f, \theta) = 1 + Re \left[\frac{2n_o^3 \cos \theta - 4n_o^2 \sin^2 \theta \cos \theta}{n_o^4 \cos^2 \theta - n_o^2 + \sin^2 \theta} \right] \left[\frac{(n_2 + ik_2)I_o}{\sqrt{n_o^2 - \sin^2 \theta}} \right] \left\{ \frac{1}{1 + (\frac{f_s - f}{Z_0(f)})^2} \right\} \quad (4)$$

Here, f , $Z_0(f)$, θ , n_o and k_2 are the focal length of EFTL, Rayleigh range, angle between normal to the incident beam and sample surface, linear refractive index and extinction coefficient respectively.

Fig. 1(b) and (c) show results for transmission and reflection f-scans for the pure Fe, pure Ag and Fe-Ag nanopyramidal systems. Two immediate features are evident from Fig. 1(b) and (c). First, the Fe-Ag system exhibited significantly enhanced nonlinear absorption and refraction as compared to the pure Ag, which in turn was much higher than pure Fe. Second, the Fe-Ag system showed the opposite sign for the nonlinear refraction as compared to pure Ag. A very large value for the nonlinear refraction of $n_2^{Fe-Ag} = -2.32 \text{ cm}^2/\text{GW}$ and nonlinear absorption coefficient of $\beta^{Fe-Ag} = 6.5 \times 10^3 \text{ cm/GW}$ were obtained for the Fe-Ag system with 30 % overlap. For the Fe-Ag system with 90 % overlap, $n_2^{Fe-Ag} = -1.02 \text{ cm}^2/\text{GW}$ and $\beta^{Fe-Ag} = 9.5 \times 10^3 \text{ cm/GW}$ were obtained. Whereas, for the pure Ag system, the nonlinear refraction of $n_2^{Ag} = 0.19 \text{ cm}^2/\text{GW}$ and nonlinear absorption coefficient of $\beta^{Ag} = 6.7 \times 10^2 \text{ cm/GW}$ were obtained. For the pure Fe system the nonlinear response was negligible. The n_2^{Fe-Ag} value is 3 to 4 orders of magnitude larger than those typically reported in the literature for metallic nanostructures, which range in the order of $10^{-4} \text{ cm}^2/\text{GW}$ to $10^{-1} \text{ cm}^2/\text{GW}$ [2, 39–41].

(a)

(b)

(c)

Figure 1. (a) Schematic diagram for experimental setup of f-scan method (b) normalized transmission and (c) normalized reflection of Fe, Ag and Fe-Ag nanopyramidal arrays.

Plasmonics and microstructure

In order to understand the origin of giant optical nonlinearity observed in the Fe-Ag nanopyramidal system, we investigated the plasmon induced linear optical behavior and electron energy-loss behavior. The plasmon induced linear optical absorption properties of the nanopyramidal system [pure Ag, pure Fe, Fe-Ag (30 % and 90 % overlap)] were measured using normally incident broadband light. We saw that the pure Ag has a sharper dipole resonance curve followed by Fe-Ag (~ 30 % overlap) and Fe-Ag (~ 90 % overlap) at 750

nm (near the energy of two photons at 1550 nm) as shown in Fig. 2(a). The dipole resonance peak at 750 nm was achieved in each pyramidal system by controlling the thickness of the Ag pyramids which was ~ 17 nm while the height of the Fe pyramids in each case was ~ 9 nm. The representative SEM image of pure Ag and 30 % overlapped Fe-Ag nanopyramidal system is shown in Fig. 2(b) and (c). The pure Fe nanopyramidal system didn't show any significant absorption features in the wavelength region studied here. Moreover, we didn't see any linear absorption feature in the 1550 nm in all nanopyramidal systems as evident from the inset of Fig. 2(a). The enhancement in optical nonlinearity observed in the pure Ag or the Fe-Ag system compared to that of the pure Fe system was attributed to matching of the two photon resonance conditions. The plasmonic systems (Ag and Fe-Ag) had plasmon induced resonance peak wavelengths at 750 nm which is near the fundamental frequency for two photons at 1550 nm. However, the giant enhancement in the Fe-Ag system over the Ag system was completely unexpected since the plasmon induced dipole resonance is more damped in the Fe-Ag system compared to the Ag system, as evident from Fig. 2(a). Nevertheless, this analysis firmly established that the matching of two photon resonance conditions partially contributed to the observed optical nonlinearity, as pure Ag, and Fe-Ag nanopyramidal system had significantly higher optical nonlinearity than pure Fe.

One of the reasons for the very large nonlinear optical responses from Fe-Ag nanopyramidal array could be a synergistic effect between Fe metal and Ag metal nanopyramids. To explore the system further, we investigated the electron energy-loss spectra from those nanostructures as shown in Fig. 3(a), (b) and (c). The dipole induced electron energy-loss peaks were observed at 1.60 ± 0.02 eV in each case, slightly shifted from the observed optical absorbance at 1.65 ± 0.01 eV (750 nm). This difference in observed electron energy-loss and optical absorbance peak comes from their observed part of the dielectric function. In case of EELS, we observe $\text{Im}(\frac{\epsilon-1}{\epsilon+1})$, while in optical absorption we observe $\text{Im}(\epsilon)$, ϵ being the complex dielectric function of the system [42]. To analyze the energy-loss behavior from the corner of Ag nanopyramids, the features in electron energy-loss peak from Ag corners [marked as A, B, C in Fig. 3] of each Ag, Fe-Ag (30 % overlap) and Fe-Ag (90 % overlap) were quantified in terms of peak intensity and area [in parts per million (ppm)]. We found that the peak intensity of pure Ag nanopyramids were higher than that of Fe-Ag, and the Fe-Ag (30 % overlap) had higher peak intensity than Fe-Ag (90 % overlap). Further, peak intensity and peak area of Ag corners (B and C) adjacent to the Fe overlap were smaller than free corner (A). Moreover, 30 % overlapped Fe-Ag nanopyramids had significantly larger intensity and area (at B and C corners) than 90 % overlapped Fe-Ag nanopyramids as summarized in Table I.

What was apparent from the optical and EELS analysis of nanopyramidal system was that the surface plasmon dipoles are stronger for the 30 % overlapped as compared to the 90 % overlapped case. The plas-

Figure 2. (a) Normalized plasmon induced linear absorption spectra of Fe, Ag and Fe-Ag (30 % and 90 % overlap) nanopyramidal systems. Inset shows the linear absorption of the Fe-Ag system from 400 to 2000 nm. (b) A representative scanning electron micrograph (SEM) image of pure Ag and (c) Fe-Ag (30 % overlapped system) (the scale bar is 500 nm) (d) The schematic of oscillating displacement field $D(t)$ in the Fe pyramid induced by surface plasmon dipoles of a Ag nanopyramid

mon induced oscillating dipole causes an induced electric displacement field across the Fe as in Fig. 2(d). The magnitude of displacement field is proportional to the plasmonic dipole strength. The displacement field developed across the ferromagnetic medium could control the magnetization of ferromagnetic material through magneto-electric effect. In other words, the dipole induced local field act on the electrons of the ferromagnetic material which produces magneto-electric (M-E) effect with moment $\mathbf{T} \sim \mathbf{P} \times \mathbf{M}$, where $\mathbf{P}$

Figure 3. (i) High-angle annular dark-field images and (ii) EELS intensity mapping of (a) pure Ag, (b) Fe-Ag (30 % overlapped), (c) Fe-Ag (90 % overlapped) nano pyramids at peak value of 1.60 ± 0.02 eV.

Peak at 1.60 ± 0.02 eV	Pure Ag			Fe-Ag (30 % overlap)			Fe-Ag (90 % overlap)		
	A	B	C	A	B	C	A	B	C
Peak intensity (ppm)	232.2	235.5	240.0	180.2	165.4	168.2	120.2	86.9	90.5
Area (ppm)	95.6	97.8	102.7	181.9	166.6	169.1	74.7	66.5	67.0

Table I. The measurement average EELS peak intensity and average EELS peak area from Ag and Fe-Ag nanopyramids as marked regions A, B, C in Fig. 3 (ppm stands for part per million)

and **M** are plasmon dipole induced electric polarization and magnetization of ferro-electrons in Fe nanopyramids. This moment is expected to control the third order optical nonlinearity in nanomaterials [43, 44]. So, the plasmon induced effect in ferromagnetic material like M-E effect could be an important factor, apart from matching of the two photon resonance conditions, for enhancement of the nonlinear optical behavior in Fe-Ag nanopyramidal system.

Nonlinear Faraday rotation

Given the above hypothesis, we explored the possibility of external magnetic effects on the nonlinear behavior of this system by employing both the f-scan and polarization rotation measurements simultaneously,

as suggested by Frey et al [45]. The Fe-Ag system, which showed the large value of n_2 (i.e. 30 % overlap Fe-Ag), the nonlinear Faraday rotation at 1550 nm was studied. In the presence of external static magnetic field, the polarization of the system can be expressed as

$$\mathbf{P} = \chi_E^{(1)} \mathbf{E} + \mathbf{P}_{NL}^H = \chi_E^{(1)} \mathbf{E} + \chi_{EH}^{(2)} \mathbf{E} \mathbf{H} + \chi_{EEE}^{(3)} \mathbf{E} \mathbf{E} \mathbf{E} + \chi_{EEEH}^{(4)} \mathbf{E} \mathbf{E} \mathbf{E} \mathbf{H} + \dots \quad (5)$$

Here, $\chi_{EH}^{(2)}$ is the second-order nonlinear susceptibility which is related to linear Faraday rotation/magnetic circular dichroism (MCD) while $\chi_{EEEH}^{(4)}$ is the fourth-order nonlinear susceptibility which describes nonlinear Faraday (polarization) rotation.

The schematic diagram for the experimental set up to measure nonlinear Faraday rotation is shown in Fig. 4(a). The laser with linear polarized light was focused on the sample by the EFTL and a regular f-scan was taken as a function of the applied magnetic field in the Faraday configuration where the static magnetic field varied from 0 up to 0.5 T in steps of 0.1 T. We recorded the transmission of the laser beam as a function of current in the EFTL at some fixed value of the magnetic field, after the beam was passed through a Thomson polarizer oriented at a 45° angle with respect to the incoming polarization when there was no magnetic field applied. The transmitted intensity of the beam can be expressed as

$$I(f) = \frac{I_o(f + f_s)}{1 + \beta I_o(f + f_s) L_{eff}} \quad (6)$$

and the polarization angle of rotation ($\Delta\Theta$) can be expressed as

$$\Delta\Theta = VHL_{eff} - \frac{\chi_i^4}{2\chi_i^3} H \ln \{1 + \beta I_o(f + f_s) L_{eff}\} \quad (7)$$

Where, H is the applied magnetic field and V is the Verdet constant, and χ_i^4 and χ_i^3 are the imaginary components of the fourth-order nonlinear and third-order nonlinear susceptibilities. The first term in equation 7 corresponds to the linear Faraday effect, while the second term is the photo-induced contribution to the nonlinear rotation. The transmittance of the beam passing through the analyzer can be calculated using Malus's law in the small angle approximation and optimizing for sensitivity as,

$$T(f) = \{1 - \beta I_o(f + f_s) L_{eff}\} \left[1 + VHL_{eff} - \frac{\chi_i^4}{2\chi_i^3} H \ln \{1 + \beta I_o(f + f_s) L_{eff}\} \right] \quad (8)$$

At low intensity, we observed that all the scans showed the same value indicating that the linear Faraday rotation is negligible for the sample at 1550 nm (zero offset in the wings as a function of the B-field). This linear rotation behavior is expected due to the off-resonance condition (away from the plasmon resonance energy).

Figure 4. (a) Schematic diagram for experimental setup of the Nonlinear-polarization rotation F-scan method, (b) normalized transmission at different B-field, inset shows the normalized transmittance for 0.5 T and the theoretical fitting using equation 9, and the experimental value found for χ_i^3 , (c) Nonlinear polarization rotation with respect to magnetic field at different laser intensities. The solid and dotted lines are the fitted curves using equation 10

The equation 8 contains information about the linear and nonlinear Faraday effects. As we didn't observe any linear Faraday rotation behavior, the observed rotation at higher intensities is due to pure photo-induced Faraday effect. In this case the above expression can be written as

$$T(f) = \{1 - \beta I_o(f + f_s)L_{eff}\} \left[1 - \frac{\chi_i^4}{2\chi_i^3} H \ln \{1 + \beta I_o(f + f_s)L_{eff}\} \right] \quad (9)$$

with

$$\Delta\Theta = \frac{\chi_i^4}{2\chi_i^3} H \ln \{1 + \beta I_o(f + f_s) L_{eff}\} \quad (10)$$

Fig. 4(b) (in inset) and (c) are the experimental transmittance at 0.5 T and photo-induced (nonlinear) Faraday rotation at different intensities along with fitted data using equation 9 and equation 10 respectively. For fit, first, we calculated the third-order nonlinear susceptibility in terms of the two photon absorption coefficient (β) which was obtained to be $\chi_i^3 = \beta \frac{n^2 c \lambda}{8\pi^3} = 9.4 \times 10^{-8}$ esu. Then, χ_i^4 was obtained by fitting equation 9 at 0.5 T. We found the value for the nonlinear fourth order susceptibility to be $\chi_i^4 = 6.5 \times 10^{-12}$ esu. The value obtained for χ_i^4 is six orders of magnitude larger than in dilute semiconductors [25].

DISCUSSION

The nonlinear optical processes in metallic nanostructures are generally governed by various excitations like multiphoton absorption, thermal scattering, interband and intraband transitions and geometry [46–48]. In our experiment, we ruled out the possibility of thermal scattering, by using a very low energy pulse of 0.4 nJ/pulse, with an average power of 20 mW on the sample, along with a repetition rate of 50 MHz, which put the system in a relatively low intensity regimen. Also the excitation wavelength of 1550 nm was far away from the plasmon resonance and therefore, low linear absorption and consequently low heating of the nanostructures is expected. Additionally, the enhancement of two photon absorption (by four times) of Fe-Ag nanoparticles over that of pure Ag nanoparticles in off-resonant wavelength was attributed to the interband and intraband transition of Fe-metals which subsequently reduced the absorption saturation effect of Fe-Ag system over pure Ag [49]. Surprisingly, we observed that the Fe-Ag nanopyramidal system has an enhancement of about 10 times that of the Ag system at lower photon energy (1550 nm). Another important observation of the optical nonlinearity of the Fe-Ag system over pure Ag was large as well as negative value of n_2 which was not reported in the previous study. It indicates the Fe-Ag system is self-defocusing while the pure Ag system is self-focusing. This is likely due to the difference in local optical response/polarization of Fe and Ag nanopyramids with incident laser fields as discussed above. Of particular interest was the same Fe-Ag system with the extraordinarily large value of nonlinear (photo-induced) Faraday rotation and nonlinear magneto-optical susceptibility at the same wavelength. While the EELS results strongly suggest a contribution from plasmon induced activity in the origin of the giant nonlinear properties of this metallic system, other mechanisms may still be important. For instance, one can expect the enhancement in the optical nonlinearity of the Fe-Ag system due to evanescent wave intensification at the magnetic/nonmagnetic interface through Schoch effect (magnetoelastic origin) and/or Goos-Hänchen effect (electromagnetic origin)

[50, 51]. The observation of large optical nonlinearity and strong nonlinear (photo-induced) polarization rotation effect on this system at the same wavelength of 1550 nm is very unique and clearly suggests an exciting system for further exploration.

CONCLUSION

To summarize, we investigated the nonlinear optical and magneto-optical properties of bi-metallic nanopyramidal systems in telecommunication wavelength. We found that the giant value of nonlinear optical and magneto-optical coefficients are due to two photon absorption phenomena which is further enhanced due to plasmon induced synergistic effect between two metallic systems. We further found that the partially overlapped Fe-Ag system exhibits a negative and extraordinarily large value of third order refractive index, two photon absorption coefficient and nonlinear Faraday rotation unlike pure Ag or Fe nanopyramidal system. Moreover, the nonlinear responses in Fe-Ag systems are strongly dependent on the overlapping extent and in turn the plasmon induced dipole strength across the ferromagnetic material. This strongly indicates the giant enhancement of third order nonlinearity in Fe-Ag nanopyramidal systems due to the plasmon induced activity in Fe metals like magneto-electric effect which depends on the plasmon induced polarization and magnetization of ferromagnetic material. All these properties in a single nanosystem brings many fold increase in the technological potentials such as for the realization of various miniaturized all-optical, magneto-optical, quantum-optical and integrated devices at telecommunication wavelengths.

METHODS

Angle-resolved nanosphere lithography

To fabricate the pyramidal metallic nanostructures from the nanosphere lithography, the polystyrene beads of diameter 500 nm were used to mask the quartz substrates by the technique used by Prasad et al [34]. The partial overlapping in nanopyramids was achieved by tilting the masked substrates on the sample holder away to the metallic vapor direction. To achieve 90 % overlapped in between Fe and Ag sample holder was tilted away by 1° to vapor direction, while to achieve 30 %, the sample holder was tilted away by 5° .

EELS fit

In order to quantify the plasmon peak position and peak area- Gaussian peaks and Lorentzian peaks were fit to the data. A multiplication of the Lorentzian functions was used to approximate the zero loss peak. A fit of zero loss peak is shown in Fig. 5.

Figure 5. Fit spectra of zero-loss spectrum peak (black solid line) taken from red box.

The summation of gaussian peaks were used to produce noise free models of the electron energy-loss spectra. Inelastic scattering in ppm (parts per million) was calculated using the relation: $\frac{I \times 10^6}{I_0}$ Where I is the beam current in a pixel from the spectrum and I_0 is the incident beam current. The Gaussian peak corresponding to the dipole plasmon peak position was used to analyze the area and peak intensity (in ppm) of plasmon loss for corresponding position (A, B and C). A representative of fit data is shown in Fig. 6.

Figure 6. A representative of fitting of plasmon-loss peak for the spectrum data taken from the red box

ACKNOWLEDGMENT

The authors want to acknowledge support by NSF Grant ECCS-1607874. HG acknowledges financial support from SIUE. GD acknowledges support by U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division

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Figures

(a)

(b)

(c)

Figure 1

(a) Schematic diagram for experimental setup of f-scan method (b) normalized transmission and (c) normalized reflection of Fe, Ag and Fe-Ag nanopyramidal arrays.

Figure 2

(a) Normalized plasmon induced linear absorption spectra of Fe, Ag and Fe-Ag (30 % and 90 % overlap) nanopyrnidal systems. Inset shows the linear absorption of the Fe-Ag system from 400 to 2000 nm. (b) A representative scanning electron micrograph (SEM) image of pure Ag and (c) Fe-Ag (30 % overlapped system) (the scale bar is 500 nm) (d) The schematic of oscillating displacement field $D(t)$ in the Fe pyramid induced by surface plasmon dipoles of a Ag nanopyrnidal

Figure 3

(i) High-angle annular dark-field images and (ii) EELS intensity mapping of (a) pure Ag, (b) Fe-Ag (30 % overlapped), (c) Fe-Ag (90 % overlapped) nano pyramids at peak value of 1.60 ± 0.02 eV.

(a)

Figure 4

(a) Schematic diagram for experimental setup of the Nonlinear-polarization rotation F-scan method, (b) normalized transmission at different B-field, inset shows the normalized transmittance for 0.5 T and the theoretical fitting using equation 9 , and the experimental value found for χ_3^i , (c) Nonlinear polarization rotation with respect to magnetic field at different laser intensities. The solid and dotted lines are the fitted curves using equation 10

Figure 5

Fit spectra of zero-loss spectrum peak (black solid line) taken from red box.

Figure 6

A representative of fitting of plasmon-loss peak for the spectrum data taken from the red box