



Core-shell metallic alloy nanopillars-in-dielectric hybrid metamaterials with magneto-plasmonic coupling

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Combining plasmonic and magnetic properties, namely magneto-plasmonic coupling, inspires great research interest and the search for magneto-plasmonic nanostructure becomes considerably critical. Here we designed a nanopillar-in-matrix structure with core-shell alloyed nanopillars for both BaTiO₃ (BTO)-Au_{0.5}Co_{0.5} (AuCo) and BTO-Au_{0.25}Cu_{0.25}Co_{0.25}Ni_{0.25} (AuCuCoNi) hybrid systems, i.e., ferromagnetic alloy cores (e.g., Co or CoNi) with plasmonic shells (e.g., Au or Au/Cu). These core-shell alloy nanopillars are uniformly embedded into a dielectric BTO matrix to form a vertically aligned nanocomposite (VAN) structure. Both hybrid systems present excellent epitaxial quality and interesting multi-functionality, e.g., high magnetic anisotropy, magneto-optical coupling response, tailorable plasmonic resonance wavelength, tunable hyperbolic properties and strong optical anisotropy. These alloyed nanopillars-in-matrix designs provide enormous potential for complex hybrid material designs with multi-functionality and demonstrate strong interface enabled magneto-plasmonic coupling along with plasmonic and magnetic performance.

Keywords: Plasmonic nanostructure; Magnetism; Core-shell metallic nanopillar; Nanocomposite thin film; Optical anisotropy; Magneto-optical coupling

Introduction

Magnetic nanostructures have generated great scientific and technological interests, owing to their wide applications in the fields of biomedicine, thermal switches, energy efficient heat-assisted magnetic recording media, etc. [1–7] On the other hand, tremendous research efforts have been devoted to explore plas-

monic materials for their applications in nanosensors, biomedical, nanophotonics, etc. [8–11] Integrating magnetic nanostructures with plasmonic materials gives rise to the interplay of magnetic spins, plasmons and photons through magneto-optical (MO) coupling, including the Faraday effect (i.e., polarization rotation of transmitted light) and the Kerr effect (i.e., polarization rotation of reflected light) [12–14]. Such magneto-plasmonic design could result in enhanced MO response. Recent advances in magneto-plasmonic systems were

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mostly through the direct combination of magnetic and plasmonic materials, such as multilayer designs including bilayer stacking of plasmonic/magnetic layers or trilayer stacking of plasmonic/magnetic/plasmonic layers, such as Au/Co [15], Au grating/bismuth iron garnet [16], Au/[Co/Pt]_n/Au [17], etc. Other nanostructures such as Ag/FeCo core/shell nanoparticles [18], Ni nanodisks [19] and non-concentric ring disk (NCRD) hybrid Py/Au nanocavities [20] have also been demonstrated.

Recently, unique vertically aligned nanocomposite (VAN) systems with self-assembled metallic nanopillars in either a dielectric oxide matrix or a transition metal nitride matrix have been developed using a pulsed laser deposition (PLD) method [21–29]. VANs have been previously widely demonstrated in oxide-oxide systems with various two-phase combinations [30–32]. So far, both magnetic metallic nanopillars (such as Co [21,22], Ni [23], Fe [24,25]) and plasmonic metallic nanopillars (such as Au [26,27], Ag [28], Cu [29]) have been successfully deposited in different oxide or nitride matrices. Very interestingly, the metallic phase appears in the form of nanopillars vertically aligned in the oxide or nitride matrix with significantly enhanced magnetic anisotropy [21–25], optical anisotropy and nonlinearities [26–29] owing to the highly anisotropic morphologies. Most of the previous attempts involved the single element metal nanopillar incorporation, but incorporating multi-element metal alloys has not yet been demonstrated, largely due to the materials challenges and deposition complexity,

including vastly different growth kinetics between metals and oxides or nitrides.

In this study, a unique multi-phase hybrid material system consisting of highly epitaxial multi-element alloyed nanopillars in a dielectric oxide matrix has been demonstrated. Here, BaTiO₃ (BTO) is selected as the matrix, owing to its excellent lattice matching with the underlying substrate SrTiO₃ (STO), excellent chemical inertness, good thermal stability and immiscibility with the proposed metals, along with its interesting ferroelectric, piezoelectric and optical properties [33,34]. As illustrated in Fig. 1a, by combining magnetic and plasmonic metals in the alloyed nanopillars, an effective magneto-optical coupling is expected in this complex hybrid material form. Two systems (system I: BTO-AuCuCoNi and system II: BTO-AuCo) have been designed combining plasmonic (e.g., Au and Cu) and magnetic (e.g., Co and Ni) components. This demonstration provides a wide selection of material candidates and alloy combinations for complex plasmonic metamaterial designs beyond the conventional noble metals, as well as for multi-field coupling between the selected materials.

Results and discussion

Detailed microstructure characterization and growth mechanism

The microstructure and crystallinity of the BTO-alloy nanocomposite thin films were first investigated by a set of cross-sectional

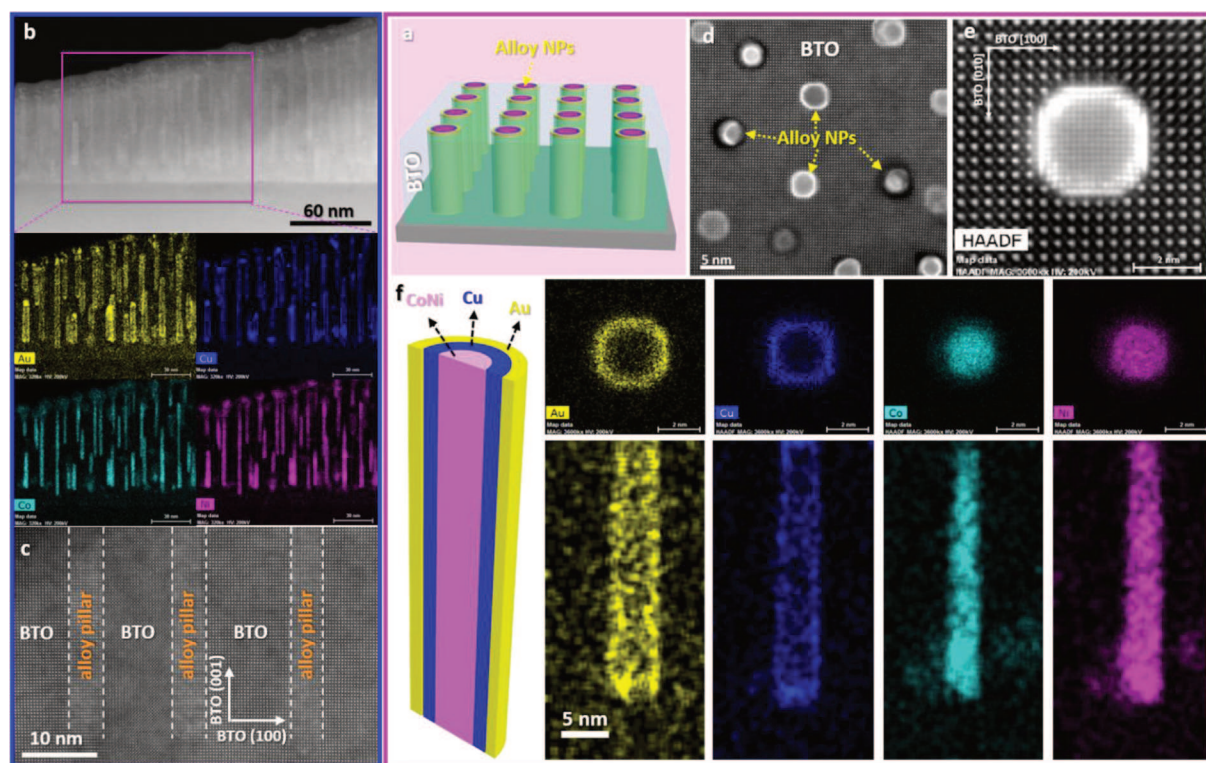
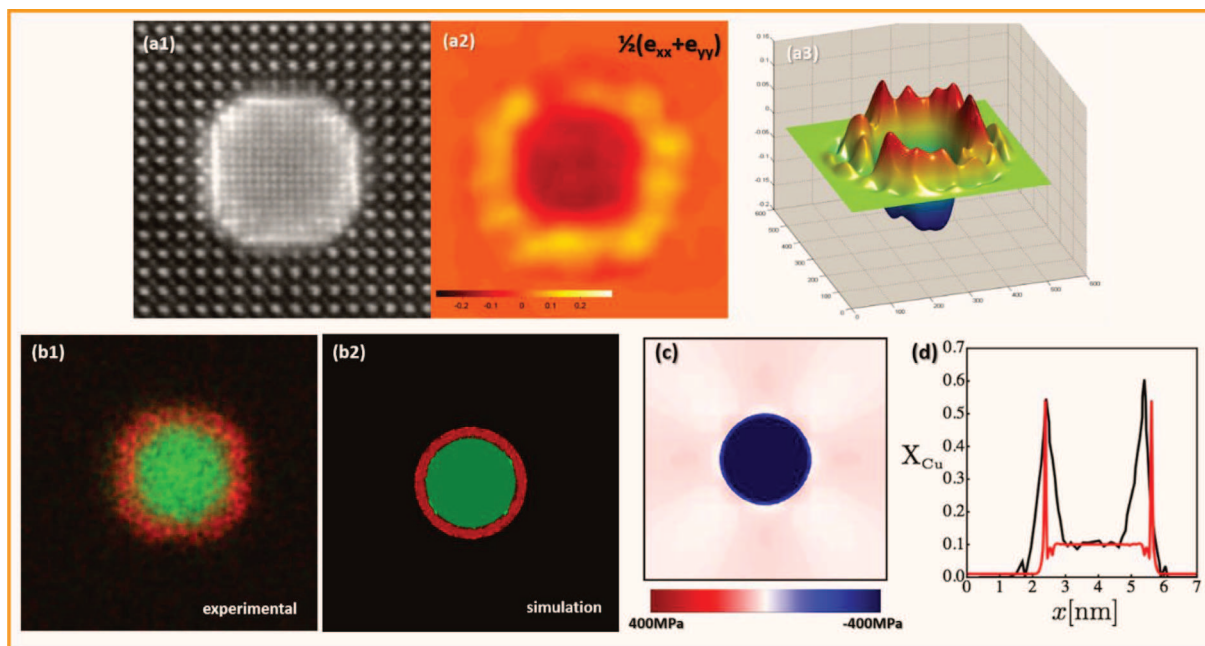


FIGURE 1

Microstructure study on the BTO-AuCuCoNi nanocomposite thin film. (a) Schematic illustration of the sample; (b) Low-mag cross-sectional STEM image with corresponding EDS mapping of Au, Cu, Co and Ni; (c) High-resolution cross-sectional STEM image of a typical area; (d) A representative plan-view STEM image and (e) high-resolution STEM image of a representative alloy nanopillar; (f) Schematic illustration of one single nanopillar (left panel) and right panels are the EDS mapping of Au, Cu, Co and Ni (both plan-view and cross-sectional).

**FIGURE 2**

Detailed strain mapping analysis by GPA analysis, EDX mapping of a representative nanopillar, and the corresponding phase field modeling. (a1) An atomic-scale STEM image with its corresponding (a2) 2-D GPA $\frac{1}{2}(\epsilon_{xx} + \epsilon_{yy})$ mapping and (a3) 3-D GPA mapping; (b1) STEM micrograph of BTO-alloy nanocomposite thin film and (b2) predicted solute distribution; (c) Simulated hydrostatic stress distribution for the BTO-alloy nanocomposite thin film; (d) Direct comparison of the EDS measurement (black) and phase field prediction (red) of the Cu distribution in the alloyed core-shell nanopillars. The interface accumulates Cu due to the driving forces imposed by the gradients of the composition dependent lattice parameter-induced chemical stresses between the BTO matrix and the alloy nanopillar.

and plan-view analyses. Fig. 1b presents a low-mag STEM image (upper panel) and corresponding EDS mapping (lower panel) of a cross-sectional sample, which shows nanopillars embedded in BTO matrix and all the metals (i.e., Au, Cu, Co and Ni) coexisting in the nanopillars, i.e., alloyed nanopillars. It is noted that the nanopillar length varies gradually in the STEM image in Fig. 1b due to the thin TEM foil edge effects by ion milling thinning process. Overall, the pillar lengths are mostly uniform throughout the sample which is primarily determined by the overall film thickness. The high-resolution STEM image in Fig. 1c reveals the excellent epitaxial quality of the nanocomposite film for both BTO and alloy phases, which can be further confirmed by the XRD characterizations in Fig. S1. The nanocomposite film is relatively robust with the annealing process (at 600 °C for 1 h in vacuum of 0.2 Torr), despite the fact that the strain starts to relieve, as shown in the XRD results in Fig. S2a, while a similar microstructure has been observed in the low-mag STEM image (Fig. S2b) and its corresponding EDS mapping (Fig. S2c). The size of the alloy nanopillars can be identified as fine as ~ 3 nm, which is difficult to be achieved by direct template growth or nanofabrication methods [35,36]. To further explore the microstructure of the film, plan-view TEM study has been carried out. Fig. 1d exhibits a representative plan-view STEM image of the BTO-alloy nanocomposite thin film, where uniformly distributed alloy nanoparticles can be clearly observed over a large area, which can be further confirmed in a low-mag STEM image in Fig. S3. The atomic-resolution STEM image in Fig. 1e reveals the local area of a typical alloy nanopillar, i.e., a highly strained

matrix-nanopillar interface has been generated, while both the alloy and oxide phases present high epitaxial quality. EDS mappings of Au, Cu, Co and Ni in the representative nanopillar (in both plan-view and cross-sectional form) are presented in Fig. 2f (right panel). To our surprise, instead of a uniform alloyed metal pillar, a unique core-shell structure has been observed. It is noted that core-shell nanopillars have been previously reported using focused electron beam induced deposition (FEED), however with much larger pillar diameters (~ 100 nm) [37]. In our work, Au and Cu exist in the shell with Co and Ni in the core. To demonstrate the uniformity of this core-shell structure in the entire sample, a large-scale EDS mapping shown in Fig. S4 presents all of the alloy nanopillars with the clear core-shell structure. Fig. S5 presents EDS mapping of all metal elements with a line-scan across an alloy nanopillar. More interestingly, a double-shell structure with Au in the outer shell and Cu in the inner shell has been further confirmed by the high-resolution EDS mapping, and both Au and Cu layers are extremely thin of less than 1 nm. Meanwhile, CoNi alloy has been formed and located in the core with a very fine diameter of ~ 2 nm. The double-shell structure is clearly shown in the schematic diagram in Fig. 1f (left panel). The simplified two element system of BTO-AuCo has also been deposited to demonstrate the feasibility of this method for other multi-element metallic systems. Both plan-view and cross-sectional STEM and EDS mappings are characterized and shown in Fig. S6, which present core-shell nanopillars with Au in the shell and Co in the core.

TABLE 1

Lattice parameter (standard bulk constant) and surface energy (quoted from literatures) of all the metals, BTO and STO.

Material	Lattice parameter (Å)	Surface energy (J m ⁻²)
Co (001)	3.5447	2.595–3.19 [38,39]
Ni (001)	3.5238	2.462 [40]
Cu (001)	3.615	3.615 [40]
Au (001)	4.072	4.072 [40]
BTO (001)	4.031	1.24 [41]
STO (001)	3.905	1.26 [41]

The overall alloy nanopillar-in-BTO matrix structure is a result of interfacial energetic interactions of different phases during deposition. Here, the surface energy for Co (001), Ni (001), Cu (001), Au (001), BTO (001) and STO (001) is 2.595–3.19 J m⁻² [38,39], 2.462 J m⁻² [40], 3.615 J m⁻² [40], 4.072 J m⁻² [40], 1.24 J m⁻² [41] and 1.26 J m⁻² [41], respectively, as listed in Table 1. The interfacial energy (γ_{MS}) of the metallic phases is higher than that of the oxides, the metallic phases follow the Volmer-Weber 3D island growth mode, i.e., the metallic nuclei forms and grows into nanopillars. Simultaneously, as the low interfacial energy (γ_{BS}) between BTO and STO is comparable, BTO follows layer-by-layer growth to form the matrix. To further understand the formation and stability mechanisms of the resultant core-shell structures in the alloyed nanopillars, we conducted a detailed microstructure analysis and coupled it with theoretical simulations. Fig. 2a1 presents an atomic-scale plan-view STEM image of a representative nanopillar. The BTO matrix exhibits high epitaxial quality while a highly strained alloy nanopillar is embedded in the matrix. Such a highly strained interface area can be confirmed by the strain mapping via geometric phase analysis (GPA) in Fig. 2a2 and 2a3. It is clear that, near the pillar-matrix interface, the lattices are highly distorted with misfit dislocations nucleated. The strain mapping also shows a highly tensile strain (bright colored area) near the pillar-matrix interfaces and compressive strain inside the alloy nanopillar, thus suggesting that the abrupt strain distribution from the pillar core to the pillar-matrix interface is coupled to the Au and Cu segregation at the interface forming the unique atomically sharp shell structure. The interfacial strain is mainly determined by the lattice mismatch between the selected materials in the nanocomposite systems, and the system favors the core-shell structure formation as it gives rise to the lowest energy in the system. Phase field modeling was conducted to explore the formation and stability mechanisms of the core-shell nanopillar. To simplify the calculation, and without loss of generality, we simulated the Cu-Ni contributions to the free energy of mixing, including the elastic energy of the core-shell structure (detailed information can be found in supplemental), in agreement with recent works [42,43]. Fig. 2b shows a direct comparison of the experimental and predicted spatial distribution of Cu in BTO-alloy nanocomposite thin film. Calculations demonstrate that the larger lattice parameter resulting from alloying Cu in Ni induces a high compressive stress in the nanopillar followed by a tensile stress of 70 MPa in the vicinity of the BTO matrix (see Fig. 2c). The stress difference between the BTO matrix and the alloy nanopillar, induced by the difference in composition-dependent epitaxial strain between the alloy nanopillar and

surrounding BTO matrix, favors Cu segregation at the BTO-alloy interface. In order to minimize the combined chemical and mechanical contributions to the free energy of the system, the abrupt change of stress at the BTO-alloy interface enhances the accumulation of Cu at the interface, in agreement with EDS results in Fig. 2d. The observed discrepancy could result from the limitations of measuring the chemical composition of solute, and the entropic and mixing effects imposed by the Au-Ni and Cu-Au interactions, as spatially resolved by EDS.

Magnetic anisotropy and magneto-optical coupling

To demonstrate the multi-functionality of this unique core-shell nanopillar structure, we first explored its magnetic properties. Fig. 3a shows the M-H hysteresis loops of the film measured at temperatures from 10 K to 300 K, with the applied field out-of-plane (OP, parallel to the nanopillars, schematically shown in the inset of Fig. 3b). A typical M-H loop for hard magnets has been observed at low temperatures with a saturation magnetization (M_s) of ~ 50 emu/cm³. A high coercivity (H_c) value of ~ 5000 Oe has been obtained at 10 K, and it decreases with increasing temperature, which reveals a thermally activated magnetization reversal process. Furthermore, the magnetization-temperature (M-T, 5–380 K) measurements under field cooling (FC, applied magnetic field of 50 Oe, 100 Oe, 200 Oe and 500 Oe; typically, a small field is applied to differentiate the FC and ZFC curves) and zero-field cooling (ZFC) have also been carried out, as shown in Fig. 3b. Under the FC condition, the magnetization monotonically decreases with increasing temperature. Under the ZFC condition, it increases gradually to a maximum value (blocking temperature: T_B) before decreasing monotonically as temperature increases, and the T_B value increases with increasing applied field. In addition, a bifurcation between the ZFC and FC curves has been observed at an irreversibility temperature (T_{irr}). The value of T_B is lower than T_{irr} in all the cases, which has also been observed in many other magnetic nanostructures [44–46]. At low temperatures of $T < T_B$, the magnetization of the nanopillars is randomly oriented to some degree (but the moments inside a single nanopillar are not disordered). While $T > T_B$, the anisotropy energy is overcome by thermal energy and the magnetization of the nanopillars starts to rotate towards the field direction, and the system becomes superparamagnetic. When the applied magnetic field is in-plane (IP, perpendicular to the nanopillars), however, the magnetic properties are very different as compared to those discussed above under OP condition (shown and compared in the inset of Fig. 3a and Fig. S7), which indicates anisotropic magnetization in the alloy nanopillars. In addition, the M-H loops of the annealed BTO-AuCuCoNi sample were also measured and compared with the as-grown film at 10 K (see Fig. S8). No obvious changes for the M_s and H_c values have been observed, while there are some differences in the shape of the loops. This might be caused by the strain relaxation after the annealing process, which consequently changes the magnetic anisotropy of the film. The magnetic properties of BTO-AuCo thin film have also been explored and shown in Fig. S9. It is noted that the M_s value of ~ 50 emu/cm³ for BTO-AuCuCoNi and ~ 65 emu/cm³ for BTO-AuCo is estimated based on the volume of the entire film, instead of the actual CoNi or Co pillar volume. If the actual volume is considered, the M_s of crystalline Co

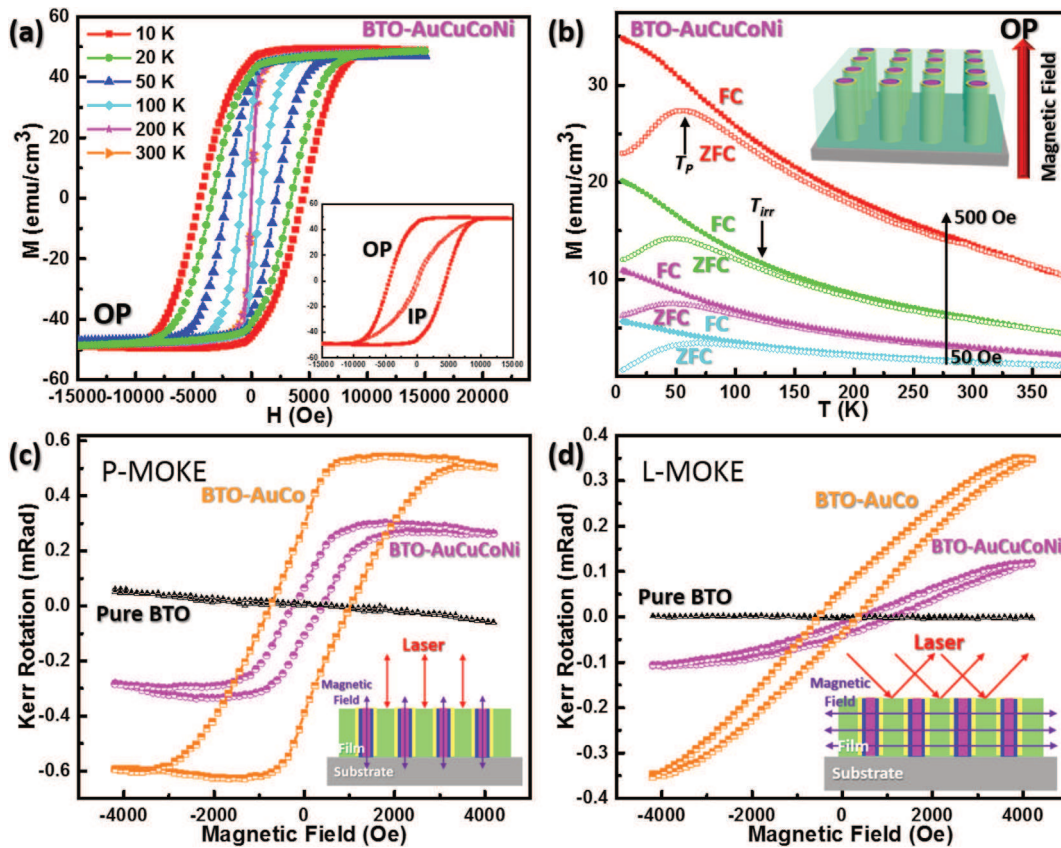


FIGURE 3

Magnetic and magneto-optic properties of the alloy core-shell nanopillars. (a) M-H hysteresis loops measured at multiple temperatures (10–300 K). The inset compares the out-of-plane (OP) and in-plane (IP) MH curves at 10 K; (b) M-T curves measured under field cooling (FC) and zero-field cooling (ZFC), in which the applied field (50 Oe, 100 Oe, 200 Oe, 500 Oe) points in OP direction. The inset is a schematic image exhibits the field direction. Comparison of the magnetic-optical response of BTO-AuCuCoNi, BTO-AuCo and pure BTO in different experimental configurations of (c) Polar-MOKE (P-MOKE) and (d) Longitudinal-MOKE (L-MOKE) measured at room temperature. The insets show the schematic of the experimental setup.

would be much larger and estimated to be around 1400 emu/cm³. Generally, the anisotropic magnetization is attributed to both magnetocrystalline anisotropy (as well as the stress anisotropy if the magnetic nanopillars are strained) and shape anisotropy. The uniaxial anisotropy could be determined as $K_u = H_k M_s / 2$ (here $H_k = H_s + 4\pi M_s$, where H_s is the saturation field) [47]. Here, K_u (at 10 K) is calculated to be $\sim 4.13 \times 10^6$ erg cm⁻³ and $\sim 3.71 \times 10^6$ erg cm⁻³ for BTO-AuCuCoNi and BTO-AuCo, respectively. The shape anisotropy can be estimated by $E_s = 2\pi N M_s^2$ (N is the demagnetizing factor, given by $N^{-1} \approx 1 + 1.6 \frac{c}{a}$ for cylinder, c and a are the height and the radius of the nanopillars, respectively) [48]. Then, E_s can be estimated to be $\sim 3 \times 10^5$ erg cm⁻³ and $\sim 7.24 \times 10^5$ erg cm⁻³ for BTO-AuCuCoNi and BTO-AuCo, respectively. Therefore, magneto-crystalline anisotropy (or stress anisotropy) is the major factor for such fully strained magnetic nanopillars. These ultra-thin CoNi alloy nanopillars are of great interest for various applications, such as quantized magnetic disk (QMD) [49,50], where one magnetic nanopillar can be defined as one bit.

The magneto-optical Kerr effect (MOKE), wherein linearly polarized light rotates and becomes elliptically polarized upon reflection from certain material's surface, could be of great interest for these ultra-thin magnetic nanopillars. More interestingly,

the Au and Cu shells are known to be plasmonic [29,51], and the correlation of plasmonic nanostructure and magnetic material is believed to enable enhanced magneto-optical (MO) response, which has been realized in multiple metal/metal multilayer systems [16,52]. To demonstrate the MO effect enhanced by the unique magnetic core-plasmonic shell structure in these alloy nanopillars, MOKE measurements have been conducted in two experimental setups (shown in the insets of Fig. 3c and 3d) at room-temperature, namely Polar-MOKE (P-MOKE) and Longitudinal-MOKE (L-MOKE). Fig. 3c and 3d present polar and longitudinal Kerr rotation hysteresis loops of pure BTO and BTO-alloy nanocomposite thin films at $\lambda = 632$ nm. Both of the BTO-AuCuCoNi and BTO-AuCo samples present obvious MOKE response in both P-MOKE and L-MOKE, while no MOKE signal has been observed in the pure BTO film. It is worth-noting that the applied field is in the range of -4200 Oe to 4200 Oe, due to the limitation of the equipment. BTO-AuCo exhibits stronger MOKE signals than BTO-AuCuCoNi in both polar and longitudinal setups, which is consistent with the above magnetic property results. Furthermore, in P-MOKE, the switching (coercive) field for BTO-AuCo is ~ 925 Oe, while BTO-AuCuCoNi obtains a smaller value of ~ 350 Oe. It is worth mentioning that an obvious difference has been observed for the MOKE loops compared to the

forementioned M-H curves for both BTO-AuCuCoNi and BTO-AuCo films. This could be due to the surface sensitivity of the MOKE measurement. At the surface, the magnetic behavior could be different from the bulk region due to the reduced magnetic coordination, change of strain state, as well as the contribution of the surface anisotropy [53]. Since the MOKE measurements were only probed over a small region of the film surface, the results indicate that the superparamagnetic limit has not been reached. To further explore the magneto-plasmonic coupling, L-MOKE measurements at different wavelengths were carried out using a home-built MOKE system with a tunable laser source (note that due to the limitation of the instrument only L-MOKE can be measured). The L-MOKE measurements of BTO-AuCuCoNi at 550 nm, 590 nm, 640 nm and BTO-AuCo at 535 nm, 580 nm, 590 nm are presented in Fig. S10a and S10b, respectively. For BTO-AuCuCoNi, the MOKE loop at 550 nm shows a stronger MO response (a larger coercivity value as highlighted in the inset of Fig. S10a), and for BTO-AuCo, a stronger MO response is obtained at 580 nm and 590 nm (as highlighted in the inset of Fig. S10b). These results clearly show that the stronger MO response occurs at wavelengths closer to the plasmonic resonance wavelength of 510 nm for BTO-AuCuCoNi and 580 nm for BTO-AuCo (see Fig. 4a), which indicates resonantly enhanced magneto-plasmonic coupling in these nanocomposite thin films.

Plasmonic resonance and anisotropic optical performance

Another key feature of the BTO-alloy nanocomposite thin films is their anisotropic optical properties. We thus first carried out the transmission measurements and the spectra are shown in Fig. 4a. For the BTO-AuCo film, obvious surface plasmon resonance (SPR) has been attained at the wavelength of ~580 nm (from Au nanoshells), which has been confirmed by COMSOL simulated optical field enhancement maps shown in Fig. S11. For the more complicated BTO-AuCuCoNi system, two pronounced SPR wavelengths at ~510 nm and ~740 nm have been observed. From COMSOL simulations (Fig. 4b), the first resonance is attributed to both Au/Cu nanoshells, while the latter could be from the outmost Au nanoshell. The shift of the SPR positions can be caused by the shape, size and composition of the metallic nanostructures [54,55].

This unique design of embedding alloy nanopillars in a dielectric BTO matrix results in anisotropic optical response, thus angular-dependent ellipsometry measurements have been taken for the BTO-AuCuCoNi film and its optical complex dielectric functions have been derived by fitting the ellipsometric ϕ (ϕ) values (Fig. S12), from 300 nm to 2500 nm. Because of the anisotropic nature of the sample, a uniaxial model has been utilized to fit the dielectric functions in both directions ($\parallel$: parallel and $\perp$: perpendicular to the film surface), with the real part (ϵ') and imaginary part (ϵ'') plotted in Fig. 4c and Fig. S13a, respectively. The results show that $\epsilon'_{\parallel}$ is positive throughout the measured wavelength range, however, $\epsilon'_{\perp}$ changes sign from positive to negative at ~705 nm, suggesting a hyperbolic metamaterial behavior. The transverse-positive dispersion in this film could be potentially used for various optical components, such as a hyperlens [56]. The effective complex refractive index (refractive

index n , extinction coefficient k) is plotted in Fig. S13b. Because of the uniaxial anisotropy nature of this nanocomposite film, i.e., $\epsilon_{[100]} = \epsilon_{[010]} \neq \epsilon_{[001]}$, the light propagation (k -wavevector) can be extracted by the dispersion relation:

$$\frac{k_x^2 + k_y^2}{\epsilon_{\perp}} + \frac{k_z^2}{\epsilon_{\parallel}} = \frac{\omega^2}{c^2} = k_0^2$$

where k_x , k_y and k_z are the wave vector components in [100], [010] and [001] directions, respectively; ω is the frequency and c is the speed of light. The optical iso-frequency surface in k -space at 1000 nm is shown in the inset of Fig. 4c, in which a hyperbola with two sheets is obtained, suggesting a class one hyperbolic metamaterial. To further explore the optical anisotropy of the film, angle-dependent and polarization-resolved reflectivity has been measured and fitted at incident angles of 55°, 65° and 75°. The experimental and fitted reflectivity are plotted in Fig. 4d and 4e, respectively. Features at the wavelength of ~550 nm are observed for all the measured angles, which is caused by the plasmonic resonance of the metal nanopillars and consistent with the above transmittance spectrum. Basically, in the case of s-polarized light (electric field is parallel to the film surface, as schematically illustrated in inset of Fig. 4d), the reflectivity increases with increasing incident angle, which is expected from classical electromagnetic theory [57]. However, in the case of p-polarized light, the reflectivity is reduced while the incident angle increases. The optical measurements of the BTO-AuCo system have also been performed and the spectra are shown in Fig. S14, which exhibit negative $\epsilon'_{\perp}$ at wavelengths larger than 1310 nm. Overall, both of the BTO-alloy systems exhibit apparent optical anisotropy, which could be used for various photonic components such as hyperbolic metamaterials.

The design of this BTO-alloy nanocomposite thin film could be extended to various selections of material systems, for both of the dielectric matrix and the metallic nanopillars. To demonstrate the versatile materials selections under this platform, we have grown another two oxide-alloy pillar systems, i.e., BTO-CuCo and BTO-CoNiFe systems, as shown in Figs. S15 and S16, respectively. For the case of BTO-CuCo, a Co core-Cu shell structure was formed. Interestingly, the Co nanopillars were either fully wrapped or partially sandwiched by the Cu shell depending on the specific orientation of the alloyed pillars. Further optimization on the pillar orientation could lead to more uniform core-shell pillars. For the case of BTO-CoNiFe, the three metals form nearly perfect alloy nanopillars without obvious core-shell structure observed, because the formation of CoNiFe alloy results in the lowest energy in the system. Such nanostructures might also be achieved by magnetron sputtering as this technique has been applied to grow single metal-oxide nanocomposite thin films [58,59], despite the fact that the crystal quality of the films might not be as good as those deposited by PLD. By designing different metallic combinations (e.g. Au, Ag, Cu, Fe, Co, Ni, Pt, Pd, Al), certain physical and/or chemical properties could be achieved. For the selection of the oxide matrix, besides BTO in this study, other oxides can also be applied, such as BaZrO₃, CeO₂, etc., as long as the oxides are immiscible and have excellent lattice matching with the metals. Furthermore, the density and size of the alloy nanopillars could be tailored by controlling

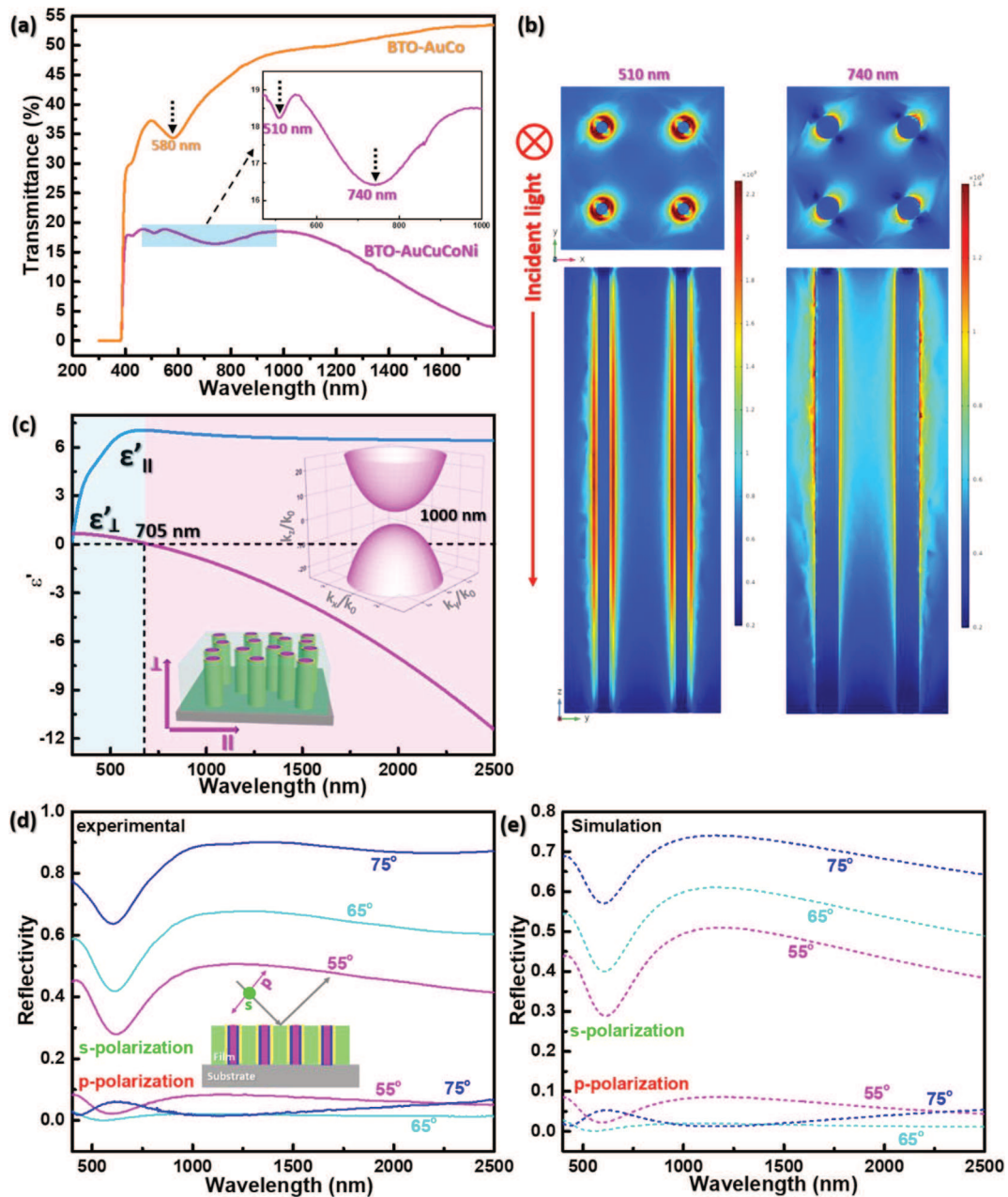


FIGURE 4

Optical properties of the BTO-Alloy nanocomposite thin films. (a) Transmittance spectral of BTO-AuCo and BTO-AuCuCoNi thin films; (b) Simulated optical field enhancement maps corresponding to incident illumination at 510 nm and 740 nm; (c) Real part of complex dielectric function of the BTO-AuCuCoNi thin film in in-plane (parallel to the film surface) and out-of-plane (perpendicular to the film surface) directions, inset is the extracted iso-frequency surfaces of the sample at 1000 nm; (d) Experimental and (e) simulated reflectivity spectra of BTO-AuCuCoNi at different angles of incidence (55°, 65°, 75°) for p-polarized and s-polarized incident lights.

the target composition and deposition parameters, such as deposition frequency and temperature [23,60]. Further work could focus on the ordered growth of the alloy nanopillars. Different from the recently reported nitride-metal-oxide 3-phase nanocomposite thin film which involves three classes of materials, i.e., Au-NiO-TiN, and a two-step growth of the layers [61], the core-shell alloy pillars in this work were processed in a simple one-step self-assembly process by combining multiple metals as the core-shell pillars and one oxide phase as the matrix. It is

noted that the magnetic-optical coupling happens within the alloyed core shell nanopillars, magnetic Co (or CoNi) core and the plasmonic Au (or AuCu) shell. The specific pillar diameters, magnetic, optical and MOKE properties are compared between the core-shell alloy structures in this work and the three-phase system and summarized in Table S2. Compared to the conventional magneto-plasmonic materials design (multilayer or core-shell nanoparticles), the one-step PLD growth of the core-shell metal alloyed nanopillars in oxide matrix provides more flexibil-

ity on complex materials integration, materials selection and microstructure tuning. Such flexibility in alloy designs and materials selections also allow more sophisticated multi-field coupling between the metal phases and the oxide phase. For example, in the BTO-AuCuCoNi and BTO-AuCo systems, BTO is ferroelectric, while Au is plasmonic, and Co is magnetic. Therefore, in this system, a ferroelectric-magnetic-plasmonic coupling (e.g., ferroelectric domain switching of BTO could be affected by the magnetic field or plasmon resonance) could be achieved and further exploration of the oxide-metal alloy VANs could present enormous opportunities in complex multifunctional devices.

Conclusion

Alloyed metallic nanopillars consisting of multiple metal elements have been incorporated into the BTO matrix to form unique vertically aligned hybrid thin films (i.e., BTO-AuCuCoNi and BTO-AuCo). A very unique core-shell metal nanopillar structure has been observed, in which Co and/or Ni are located in the core while Au and/or Cu form atomically thin shells around the magnetic core. The diameter of the alloy nanopillars is as small as ~ 5 nm, with the shell layer of only ~ 1 nm. The effective combination of plasmonic and magnetic metals in the nanopillars produces multi-functionality, such as anisotropic magnetic properties, strong magnetic-optical coupling response, tunable plasmonic wavelength, hyperbolic performance, and anisotropic optical performance. These extraordinary properties could be further tailored by materials selection (e.g., different metals-matrix combinations) and alloy composition tuning. The core-shell alloy-oxide VAN designs provide great opportunities for magnetic data storage, plasmonic-magnetic devices and energy related applications.

Materials and methods

Target and thin film preparation

The BTO-alloy nanocomposite targets were prepared by a conventional solid-state mixing, followed by spark plasma sintering (SPS, Thermal Technology 10-3) at 200 °C and 30 MPa with no holding time. The deposition of the BTO-alloy thin films was conducted by the co-deposition process of all the phases using composite targets. The BTO-alloy thin films were deposited on STO (001) substrates using PLD technique with a KrF excimer laser (Lambda Physik, $\lambda = 248$ nm). Before deposition, the base pressure was below 1×10^{-6} Torr. The deposition was performed under vacuum condition with deposition temperature of 700 °C, the target-substrate distance of 4.5 cm, the deposition frequency of 5 Hz, and the sample was naturally cooled in vacuum after the deposition.

Microstructure characterizations

The crystal structure and microstructure of the films were characterized by XRD (Panalytical X'Pert X-ray diffractometer). An FEI Titan™ G2 80–200 STEM with a Cs probe corrector and ChemiSTEM™ technology (X-FEG™ and SuperX™ EDS with four windowless silicon drift detectors) operated at 200 kV was used in this work. The microstructure of the films was characterized by STEM using a high-angle annular dark-field (HAADF) detector and energy-dispersive x-ray spectroscopy (EDS).

Magnetic and Magneto-optic measurements

Temperature dependence of magnetization and magnetic hysteresis curves were measured by a SQUID magnetometer (MPMS: Quantum Design). The magnetic field was applied either perpendicular (out-of-plane, OP) or parallel (in-plane, IP) to the film surface. The magneto-optic measurements were carried out by a home-built MOKE system equipped with a photoelastic modulator, a laser with wavelength of 632 nm, and applied magnetic field in the range of -4200 Oe to 4200 Oe. The linearly polarized light has been applied at normal incidence. The schematic of the experimental setup could be found in the insets of Fig. 3c and 3d for P-MOKE and L-MOKE, respectively.

Another MOKE system was set up for wavelength dependent measurements, as schematically shown in Fig. S15, the chopper and second lock-in were used to simultaneously monitor sample reflectivity, while taking MOKE data. An average laser power of $30 \mu\text{W}$ was used and the beam spot on the sample was approximately $50 \mu\text{m}$ in diameter. The voltage signal from the lock-in amplifier was mapped to the Kerr rotation angle using an achromatic half wave plate that was placed into the beam path before the sample (under no magnetic field). The lock-in signal was recorded as a function of the half wave plate's rotation, which allowed us to relate the change in polarization angle to the measured voltage signal. Data points were taken with a lock-in time constant of 3 seconds and a dwell time of 9 seconds or longer, at each magnetic field value to reduce the point-to-point noise.

Optical measurements and simulation

Transmittance measurements were conducted by UV-vis spectroscopy (Lambda 1050). Variable angle ellipsometry experiments were carried on a RC2 spectroscopic ellipsometer (J.A. Woollam Company). Two optical parameters of Psi (ψ) and Delta (Δ) were obtained by the ellipsometry measurements, which are related to the ratio of the reflection coefficients for the light of p-polarization r_p and s-polarization r_s : $r_p/r_s = \tan(\psi)\exp(i\Delta)$. Afterwards, the effective refractive index and optical dielectric functions were obtained by fitting the ellipsometry data using different models in the VASE software. In this study, a biaxial layer with general oscillator layer models consisting of hybrid Drude-Lorentz oscillators and two Lorentz oscillators have been applied to fit $\epsilon_{\perp}$ and $\epsilon_{\parallel}$, respectively.

COMSOL Multiphysics Wave Optics Module with electromagnetic waves, frequency domain (ewfd) was applied for the optical simulation. Optical constants for Ni, Co, Au, Cu and BaTiO₃ were directly taken from the software database and the simulated geometry was retrieved based on the plan-view and cross-sectional STEM images. The simulated optical unit cells were retrieved based on the average nanopillar diameter ($\bar{d}$), average nanoshell thickness ($\bar{t}$) and average interpillar distance ($\bar{l}$), which are $\bar{d} = 8$ nm, $\bar{t} = 1.5$ nm and $\bar{l} = 15.0$ nm for BTO-AuCo, and $\bar{d} = 4$ nm, $\bar{t}_{\text{Au}} = 0.5$ nm, $\bar{t}_{\text{Cu}} = 0.5$ nm and $\bar{l} = 10.0$ nm for BTO-AuCuCoNi. Normal incidence depolarized electromagnetic field was applied with two ports on the top and bottom of the model.

CRediT authorship contribution statement

Jijie Huang: Writing – original draft, Conceptualization, Methodology, Validation, Data curation, Formal analysis, Writ-

ing – review & editing, Investigation. **Xin Li Phuah:** Methodology, Investigation, Writing – review & editing. **Luke Mitchell McClintock:** Methodology, Data curation, Writing – review & editing. **Prashant Padmanabhan:** Methodology, Data curation. **K.S.N. Vikrant:** Data curation, Investigation, Software, Writing – review & editing. **Han Wang:** Methodology, Investigation, Writing – review & editing. **Di Zhang:** Methodology, Investigation, Writing – review & editing. **Hao-han Wang:** Methodology, Investigation, Writing – review & editing. **Ping Lu:** Methodology, Investigation, Writing – review & editing. **Xingyao Gao:** Methodology, Investigation, Writing – review & editing. **Xing Sun:** Methodology, Investigation, Writing – review & editing. **Xiaoshan Xu:** Supervision, Writing – review & editing. **R. Edwin García:** Supervision, Writing – review & editing. **Hou-Tong Chen:** Supervision, Writing – review & editing. **Xinghang Zhang:** Supervision, Writing – review & editing. **Haiyan Wang:** Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award DE-SC0020077. J.H. acknowledges the support from Guangdong Basic and Applied Basic Research Foundation (2019A1515111029). The authors acknowledge the support from the U.S. National Science Foundation (DMR-2016453 and DMR-1809520) for the microscopy work. H.H.W. and X.S.X acknowledge the support from the U.S. National Science Foundation (DMR-1454618). K.S.N.V. and R.E.G. acknowledge the support from US ONR (N00014-17-1-2087) and the U.S. National Science Foundation (DMR-BSF 1734763). Sandia National Laboratories is a multi-program laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. This work was performed, in part, at the Center for Integrated Nanotechnologies (CINT), an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. Los Alamos National Laboratory, an affirmative action equal opportunity employer, is managed by Triad National Security, LLC for the U.S. Department of Energy's NNSA, under contract 89233218CNA000001. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mattod.2021.10.024>.

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