Bringing tunability to ultrafast nanoplasmonics

Malik Maaza and Beye Aboubakar Chedikh

By using a thermally-induced change in the host structure, the operating wavelength of nanoplasmonics can be reversibly tuned.

The nanosciences are stimulating the possibility of engineering novel nanophotonics with tunable, tailored properties. In particular, nanocomposites with metallic nanoparticles embedded in an insulating host matrix (as shown in Figure 1), represent a distinctive class of nanoplasmonics: they have specific nonlinear characteristics due to enhancement of the local field. The cost effectiveness of these materials could open up photonic applications in wave mixing, heterodyning, and modulation, and could expand their role in laser applications.

In addition, nanoplasmonics could be an integrated component of nonlinear optical (NLO) devices: the global market for NLO materials was estimated at $856.1 million in 2005 and is expected to grow to $1,656 billion by 2009. Since nanoplasmonics are macroscopically isotropic, their nonlinear response is of the third order. The $\chi^{(3)}_{\text{composite}}(\omega)$ enhancement—which takes place in the neighborhood of the plasmon frequency $\omega_p$—has been confirmed experimentally. In addition, they are fast: degenerate four-wave mixing and Z-scan in Au, Ag, and Cu-based nanoplasmonics have given values of about $10^{-7} - 10^{-9}$ esu with response times on the picosecond scale. Further, because the notions of centro-symmetry and phase matching are not major concerns with these new materials, they should open up new possibilities for NLO nanophotonics.

One of the technological challenges has been to fabricate these nanoplasmonics with the additional feature of reversible $\chi^{(3)}_{\text{composite}}(\omega)$ frequency tunability: tuning $\omega_p$ via an external stimulus. As $\omega_p$ is proportional to $n_{\text{eff}}^2/m_{\text{eff}}(\omega)$, one could anticipate its tunability via the carrier density ($n$), the effective electronic mass ($m_{\text{eff}}$) of the metallic nanoparticles, or through the dielectric function of the dielectric host matrix ($\omega_{\text{host}}$). While the first two of these parameters can be varied by changing the nature of the nanoparticles, the third option requires a radical change in the host matrix. The latter is more effective, as has been illustrated experimentally. Results with gold nanoparticles embedded in different host matrices—including Fe$_2$O$_3$, SiO$_2$, TiO$_2$, and Nb$_2$O$_5$—have exhibited plasmon tunability via the variation of the refractive index of these different host matrices. The variation of $\omega_p$ is substantial: from 2.4eV to 1.7eV. Such a variation entails an explicit host-matrix change. This is not a practical way to achieve plasmon-frequency tunability and a possible externally-driven $\chi^{(3)}_{\text{composite}}(\omega)$ modulation within the same nanodevice.

We have developed an elegant method for the preparation of tunable and reversible nanoplasmonics where both the nature of the metallic nanoparticles and the host matrix remain fixed. This allows us to thermally and reversibly tune $\omega_p$ and $\chi^{(3)}_{\text{host}}(\omega)$ in a controllable manner for both linear and nonlinear applications. The new idea is based on using vanadium dioxide (VO$_2$) as an intelligent host matrix because it exhibits a reversible, thermally-induced metal-semiconductor phase transition when heated above its critical value of 68°C. This concurs with an optical transition, and hence a variation in the material’s optical constants. This reversible change in $\epsilon(T)$ is pronounced in the infrared. The limit dielectric constants $\epsilon(0)$ and $\epsilon(\infty)$ are 43 and 10.0 in the dielectric regime, respectively, and 18.3 and 9.0 in the metallic regime.
Figure 2. Shown is the optical transmission of the Au-VO$_2$ nanoplasmonic structure below and above the critical temperature of $T_c \approx 68^\circ$C. The minimum in the 600-650nm range corresponds to the plasmon absorption of the nanostructured gold.

In the near infrared, $\varepsilon(\omega)$ has values of approximately 8.64 and 5.7 in the dielectric and metallic states respectively. To demonstrate the utility of this approach, we laser-deposited Au-VO$_2$ nanoplasmonics onto Corning glass. The embedded Au nanocrystallites were $\approx 13$nm in diameter. Figure 2 depicts the ultraviolet–visible–near-infrared transmission profiles at different temperatures. We limited our interest to the 425-750nm spectral range in order to focus on the shift of the nanostructured gold $\omega_p$. Initially, the Au-VO$_2$ wavelength was about 648nm with the temperature below $T_c \approx 68^\circ$C (i.e. with the host matrix in its dielectric state). However, as the temperature increased past the transition point, changing the material into its metallic state, the wavelength shifted towards the blue (to $\approx 603$nm). This sizeable variation of $\approx 45$nm confirms the tunability of $\omega_p(T)$ through temperature change.

In Figure 3, we can see the evolution of $\omega_p(T)$, with the thermal cycling over the 25-120$^\circ$C range: this result confirms its thermal reversibility with a jump-like change. Such a sharp transition with a hysteresis of $\approx 16$C is inherent to the first order transition of the VO$_2$, which lasts $\approx 500$fs. Such an ultrafast temperature change in the refractive index should enable ultrafast nanoplasmonics. As shown in Figure 2, the ultraviolet-visible transmission is low: about 22.5 and 19.7% at $\approx 525$nm (below and above $T_c$ respectively). As a result, such Au-VO$_2$ nanoplasmonics would be impractical in their current form for tunable third-order frequency $\chi^3$ composite generation. What is required is that the optical ultraviolet-visible transmission be enhanced using an optimal optical design: for example, by sandwiching Au-VO$_2$ nanoplasmonics between thin layers of TiO$_2$.

Figure 3. The nanostructured-gold plasmon wavelength is shown versus versus the external temperature. Note the reversibility of the process as the temperature moves above and below 68$^\circ$C.

Author Information

Malik Maaza
Nanosciences Laboratories
Materials Research Group
National Research Foundation
iThemba labs
Somerset West, Western Cape Province, South Africa
http://www.tlabs.ac.za

Dr. M. Maaza is the initiator of the South African Nanotechnology initiative and is currently the chairman of the Nanosciences African Network (NANOAFNET), supported by ICTP and IPPS. He holds a PhD from Paris VI with a research background in surface-interface, x-ray, and neutron optics. His current research at iThemba Labs is on nanophotonics and nanomaterials for renewable energy. He has had three publications on neutron and x-ray optics in SPIE proceedings.

Beye Aboubakar Chedikh
Physics Department
Dakar, Senegal

A.C. Beye is an expert in materials sciences, and is the founding president of the African Materials Research Society. He is a member of the board of directors of the African Laser Centre as well as of the Nelson Mandela–World Bank African Institutes of Science and Technology. He is the initiator of the US–Africa initiative in materials sciences. His research encompasses materials sciences and laser spectroscopy.

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References