PLASMONICS

An ultrafast plasmonic tuning knob

Near- and mid-infrared plasmonics are exciting research areas with applications in nanoscale energy concentration, sensing or ultrafast switching for telecommunication. Now, a new efficient way to manipulate plasmon resonances in semiconductor nanoarrays at ultrafast timescales has been found.

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Finding a 'tuning dial' for easy control of the optical properties of materials with ultrafast precision is one central topic in contemporary plasmonic and photonic research. In recent years, plasmonic control has been realized in a diverse range of solid-state systems including metals[1], semiconductors[2], graphene[3] and topological insulators[4]. Besides modulation efficiency, however, the challenge in many of these materials is to obtain good tunability over a wide spectral range, especially in the technologically important mid- to near-infrared frequency region. The difficulty largely arises from an inflexible carrier density. With a better switching scheme, exciting applications that rely on the spatial confinement of plasmons to length scales far below the diffraction limit, such as nanoplasmonic circuits, photovoltaics, modulators, and bio- and chemical sensors[5], await new discoveries.

Now, writing in *Nature Photonics*[6], Peijun Guo and co-workers report that they can turn such a plasmonic tuning knob in a new semiconductor structure. They have accomplished broadband modulation at near- and mid-infrared frequencies in an efficient and ultrafast way using femtosecond optical excitation. Whereas some previous works relied on photoexcitation with above-bandgap photon energies, here the researchers have realized a large optical modulation depth with relatively low photon energies. The ingredient for introducing such a modulation is the non-parabolicity of the conduction band in the indium tin oxide (ITO) semiconductor nanoarrays that they used. This non-parabolicity accounts for extraordinary, pump-induced carrier temperatures of 10,000 K, resulting in subpicosecond modulation with up to 300% transmission change, and operation at telecom wavelengths and in the mid-infrared fingerprint region.

It is well known that one of the most important optical properties of a material is the dielectric permittivity, ε, which is a function of frequency. At high enough frequencies, ε can be solely determined by the plasma frequency ω_p (if loss is negligible). The plasma frequency represents the natural resonant frequency of a collective oscillation, or plasmon, of a free-electron gas. For frequencies below ω_p, the material can behave like a reflective metal (ε is negative), whereas it acts like a transparent dielectric (ε positive) for frequencies above ω_p. Therefore, ω_p represents an effective 'knob' that allows tuning of optical material properties and plasmon resonances.

Many ways exist to change ω_p. In its simplest form, $\omega_p^2 = ne^2/m$ (with electron charge e), ω_p is insensitive to the electron temperature for a constant effective electron mass m and can be altered by tuning the electron density n. Whereas metals are characterized by a constant carrier density that fixes the plasma resonance frequency (typically visible or near-infrared frequencies), in semiconductors n is adjustable. This is most commonly realized by photoexcitation above the bandgap with intense laser pulses. But ω_p can depend on temperature in cases where the parabolic band-structure approximation fails — that is, where the electrons in a solid no longer follow the parabolic energy–momentum relation observed at band extrema. This non-parabolicity results in a momentum dependence of the effective mass, $m = m(k)$, which can significantly alter the plasma frequency even for a constant density of free electrons. This is the unique condition realized in the experiment by Guo and co-workers.

The team investigated a metamaterial array consisting of ITO nanorods (Fig. 1a). Although plasmonic resonances in noble metal nanostructures have long been under investigation, ITO nanorods have only recently attracted attention as plasmonic

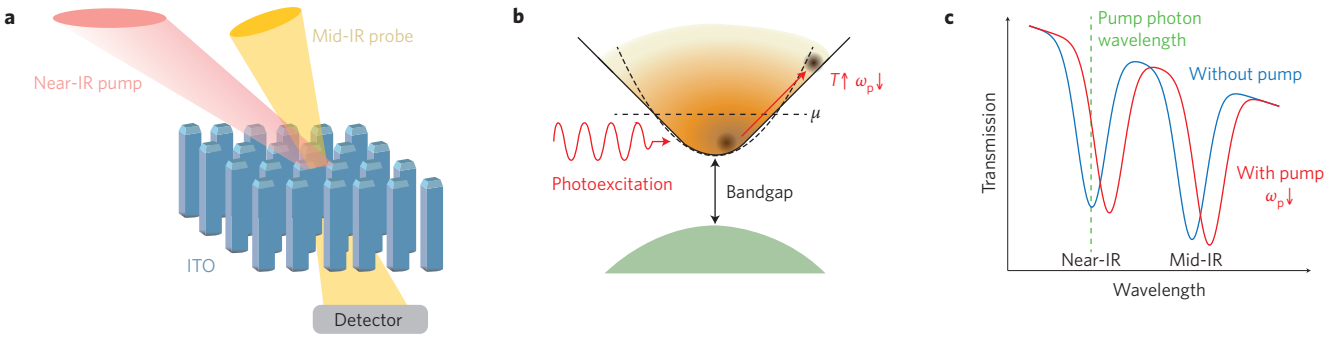

Figure 1 | Metamaterial array of ITO nanorods. **a**, Schematic of the ultrafast infrared (IR) pump–probe experiment for probing localized surface plasmons in ITO nanoarrays. **b**, Near-infrared intraband photoexcitation creates conduction electrons of exceptionally high temperature without modifying the carrier density. The transient hot carrier distribution is sensitive to the non-parabolic nature of the conduction band (solid line), resulting in a temperature-dependent plasma frequency ω_p. μ, electron chemical potential; T, electron temperature. **c**, The reduction in plasma frequency is observed as a redshift of the localized surface plasmon resonance in transmission measurements. Panel **b** adapted from ref. 6, Nature Publishing Group.

(metal-like) media[7]. ITO is a degenerate semiconductor of low carrier density compared with metals (10^{20}–10^{21} cm^{-3}) and is ubiquitous as a transparent electrode material for light-emitting diodes, solar cells or liquid-crystal displays. In contrast to the noble metals with fixed carrier densities, ITO is characterized by a tunable carrier density and mobility that is achieved by doping or post-synthesis processing[7]. Hence, plasmons in ITO can access the infrared fingerprint region for material identification and chemical sensing. In addition, ITO has a large bandgap of ~4 eV. As a consequence, infrared or low-energy plasmons in ITO experience much less damping than those in noble metals, where the interband transitions are close in energy to the plasmon resonances.

Previous work on ITO nanorod photonics showed distinct localized surface plasmon resonances (LSPR)[7], that is, surface charge oscillations confined to the nanostructure. These resonances are in the near- or mid-infrared, depending on whether the light polarization is oriented perpendicular or parallel, respectively, to the nanorod axis. In their experiment, Guo *et al.* modify the LSPR on an ultrafast, subpicosecond timescale. The high-energy LSPR is resonantly pumped with near-infrared photons below the bandgap of ITO (schematically shown in Fig. 1b,c). Owing to the absence of the interband excitation, the carrier density in ITO remains constant. Consequently, the change in plasma frequency observed in transmission at the LSPR (Fig. 1c) with a near- or mid-infrared probe does not stem from a carrier-density-induced modulation of plasma frequency as previously reported in other types of semiconductor[2]. In a detailed theoretical treatment, the researchers attribute the pronounced pump–probe signal to the conduction-band non-parabolicity of ITO in combination with a low carrier density and low heat capacity. These characteristics create a condition in which electrons in the conduction band are heated by the pump pulse to an astonishingly high carrier temperature of 10,000 K. For comparison, gold, one of the most investigated plasmonic materials, exhibits far lower carrier temperatures of 2,000 K (ref. 8) under similar pumping conditions. The exceptionally high carrier temperature in ITO ensures an electron distribution with a pronounced high-energy tail that is especially sensitive to the deviation of the conduction band from the parabolic form. The increase in effective mass at elevated energy states leads to a transient reduction in ω_p by up to 20%. This is accompanied by relative transmission changes in the mid-infrared (Fig. 1c) of the order of 300% for moderately high excitation intensities (6.5 mJ cm^{-2}). The modulation depth is 1–2 orders of magnitude larger than in metals or semimetals (for example graphene) and comparable to other semiconductors[2–4]. Furthermore, the timescale of the transient modulation is in the subpicosecond range, much faster than those observed in metals or semiconductors and on a par with single-layer graphene[3].

Spectral tuning of the plasmonic resonances in the near- and mid-infrared range can be achieved in different ways, for example by adjusting the carrier density, the pump fluence or the photon energy by which a different LSPR mode can be excited. Additional flexibility is offered by shifting the resonances by means of the incidence angle and the geometry of the ITO nanorods. This allows one to target specific frequency windows with a broadband response. Electrical gating can, in principle, be included for adjusting the carrier density and hence ω_p (ref. 9). The compatibility of the presented ITO device with semiconductor processing technology is certainly an advantage over competing schemes, for instance graphene devices, and electrical gating would add only moderate complexity.

The ITO nanorod approach, using conduction-band non-parabolicity for all-optical control, points to a very interesting direction for plasmonic media. One current limitation of the work is the required moderate to high pump intensities that call for sophisticated laser amplifier systems. Low-cost, turn-key systems with high repetition rates such as fibre lasers are preferred, but currently lack sufficient pulse energies. Band-structure engineered materials such as strained samples or heterostructures that have significant band non-parabolicities[10] as a starting point might help to amplify the transient signals and solve these obstacles. Using field enhancement provided by nanostructures or metamaterials could additionally relax the requirements on pump intensities, but at the expense of sample complexity. The ultimate performance limitations of the proposed ultrafast 'plasmonic tuning knob' remain a fascinating open question. ❐

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IMAGING

Making sensing of incoherence

Obtaining information about an object or medium with an unknown, random scattering potential is notoriously difficult. The projection of random illumination patterns as probe is now shown to help.

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Noise is usually considered to be the enemy of signal. There are many cases, however, where noise is an ally, either by revealing structure in its variations or by acting as a source of free energy for amplification. Applications range from basic physics and chemistry to dynamical systems and communications[1,2].

Writing in the OSA journal *Optica*, Milad Akhlaghi and Aristide Dogariu from the University of Central Florida CREOL report a method they call 'stochastic optical sensing' that leverages the power of noisy probes[3]. The scheme, which essentially creates a moiré pattern between signal and