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Metamaterials for Advanced Sensing Platforms

Luigi La Spada*

Abstract

The work is focused on the use of metamaterial as sensors. The interaction of the electromagnetic wave with planar (meta-surface), 3D (nano-) and near-zero structures will be studied and the related (sensitivity and selectivity) enhancement effects analyzed. It will allow us to use them as advanced sensing devices for diagnostic applications. To this regard, specific geometries will be proposed for cancer detection, biological tissue characterization and chemical analysis (i.e. glucose concentration measurements and blood diseases monitoring).

Keywords

Metamaterials; Electromagnetic Theory; Telecommunications

Introduction

Despite the classic electromagnetic theory and its main fundamental principles can be referred to the past [1], important developments have recently been made in theoretical and numerical aspects of applied electromagnetics, affecting all the related applications, such as sensing and telecommunications. The requirement of going beyond the limitations (anisotropy, narrow/single-bandwidth, high losses) that standard materials present in nature has become an important issue, due to the increasing demands that the nowadays technology requires for enhancing the electromagnetic devices performances.

A new class of artificial materials that can go beyond these limitations is currently investigated by several research groups, and they are called metamaterials. Such new materials are defined as artificial structures, engineered to provide unusual electromagnetic properties not easily found in nature [2]. A basic design consists of an array of electrically small electromagnetic scatterers, called inclusions, embedded into a dielectric host material. Here we consider the 3D version, the so-called nanoparticles (Figure 1a) and the 2D version, named metasurfaces (Figure 1b) Such inclusions are located at mutual distance, typically a small fraction of the wavelength. If an electromagnetic wave impinges on this structure, all the local fields scattered from inclusions will be summed up to the incident field, resulting in a change of the net field distribution. Since the phase shift across volume occupied by a single particle (unit cell) is small, the diffraction effects can be considered negligible. Thus, the structure behaves as a continuous effective material. This material would have new (homogenized) values of constitutive parameters (permittivity ε and permeability μ), generally different from the parameters of the host material and the inclusions. The equivalent permittivity and permeability are primarily dependent on the geometrical properties of an inclusion shape and mutual distance between them (the so-called lattice constant). Thus, it is possible to tailor the related electromagnetic response, by appropriate design, and to achieve desired new values of equivalent permittivity and permeability [3-4].

In this regard, materials can be categorized according to the scheme of Figure 1c: if both the permittivity and permeability have positive real parts, as most of the materials in nature do, they may be called “double positive (DPS)” media [5]; whereas if both quantities are negative, third quadrant of Figure 1c, the corresponding materials may be called “double-negative (DNG)” media [6]. Due to their anomalous wave refraction [7,8], such materials have been the subject of great interest in the engineering and physics communities. Media with a negative real part of the permittivity, but a positive permeability, second quadrant, are named as “ε-negative (ENG)” materials [9] and they include plasma and plasmonic materials (noble metals, polar dielectrics and some semiconductors) below their plasma frequencies. In the fourth quadrant, we have the “μ-negative (MNG)” media [9], which can be realized with ferromagnetic materials or synthesized with suitable inclusions in a host background [10]. The artificially realized MNG materials are essential, basic constituents in the construction of DNG materials. In analogy with DNG materials, ENG and MNG materials can be labeled as “single negative (SNG)” media [9].

Metamaterials with all these unusual values of constitutive parameters (SNG, DNG, SNZ, DNZ) offer many unexpected and counter-intuitive physical phenomena such as backward-wave propagation, negative refraction, and ‘amplification’ of evanescent waves [2-5]. During the past decade, huge research efforts worldwide have been put into possible application of these phenomena for novel

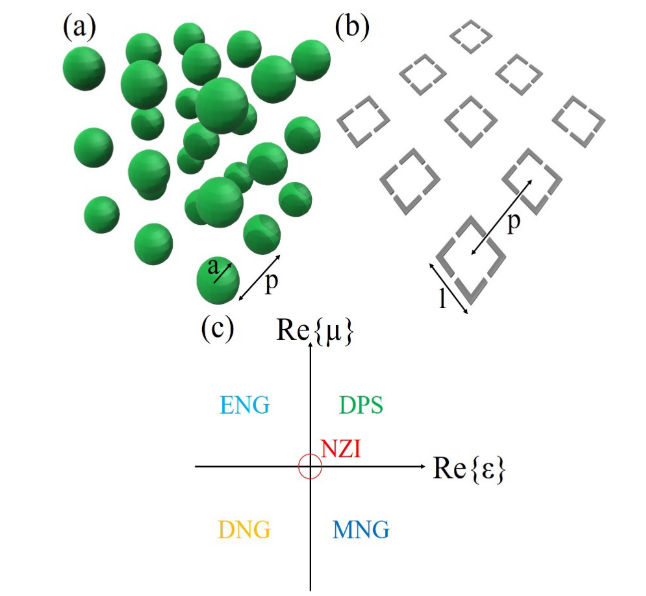

Figure 1: Metamaterial arrangement in: (a) 3D version, nanoparticles (radius *a*); (b) 2D version, metasurfaces (length *l*). (c) Classification of metamaterial structures as a function of permittivity and permeability real part.

***Corresponding author:** Dr. Luigi La Spada, School of Computing, Electronics and Mathematics, Faculty of Engineering, Environment and Computing Coventry University Priory St, Coventry, CV1 5FB, United Kingdom, Tel: +44 7584100162; E-mail: luigi.laspada@coventry.ac.uk

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devices such as miniaturized antennas and waveguides [11], the resolution-free lenses [12,13], invisibility cloaks [14-16] and sensing [17].

There are two main problems that prevent wide use of metamaterials in practical engineering systems: a significant loss and a narrow operating bandwidth, compared to ordinary dielectrics [3-5]. It is important to stress that these two drawbacks are not mutually independent. They are the consequences of inherent change of the permittivity/permeability with frequency, in other words their dispersion behavior. Ordinary dielectrics are usually considered as being frequency independent (dispersion less) across the entire electromagnetic spectrum. It would be very convenient to have similar behavior in the case of metamaterials. Unfortunately, the values of constitutive parameters of all SNG, SNZ, DNZ or DNG metamaterials do change significantly with frequency. This change is, in general, described by Lorentz dispersion model [5].

All the types of passive metamaterials are highly dispersive comparing to the conventional dielectrics, and all of them are intrinsically narrowband. How much the inherent dispersion affects the operational bandwidth of the metamaterial-based device depends on a particular application: the narrowband operation is the inherent drawback of all passive metamaterials. Nowadays, advances in simulation and fabrication technologies allow a rather broad flexibility in designing metamaterials and their electromagnetic responses [18]. The potential ability to engineer these responses for a wide variety of applications has inspired great interest in metamaterials. Interestingly and related to this work, the recent advances in nanotechnology and molecular bioengineering are leading researchers to speculate about the possibility of bringing these metamaterial concepts back to the visible frequencies and about the proper design of artificial molecular shapes to achieve artificial optical metamaterials to tailor their electromagnetic properties at infrared and visible frequencies [19].

Metamaterials for Sensing Applications

The main advantages in using metamaterials as bio-electromagnetic sensors are the following:

• A significant reduction in the structure size and the related enhancement of the sensitivity sensor.

• The possibility to optimize the sensor response by tailoring its geometrical and electromagnetic properties as a function of the application required.

• They are able to detect higher (permittivity/refractive index) variation in the output signal, in response to small changes of the input signal. This, combined with the high electric field focalization and real-time monitoring, permit to improve the sensing performances and to detect really small amount of compounds.

Electric properties of materials can be described by their dispersive complex dielectric permittivity (real and imaginary part) as a function of the frequency. In general, biological tissue dielectric properties and their frequency response are the results of the interaction between the electromagnetic radiation and their constituents, covered by two different mechanisms that influence the shape of the permittivity as a function of the frequency:

• The relaxation effects associated with permanent and induced molecular dipoles. The mechanism of dipoles relaxing is called dielectric relaxation and for biological tissue is described by classic Debye relaxation (Microwave regime).

• The resonance effects, which arise from the rotations or vibrations of atoms, ions, or electrons. These processes are observed near their characteristic absorption frequencies (Infrared and Visible regime).

Tissue diseases typically induce structural, biochemical and mechanical changes. These variations imply significant changes in their electromagnetic properties, in other words their permittivity values can be significantly different. The main aim of an electromagnetic biosensor is to reveal such differences, by correlating the substance dielectric properties to its resonant properties. The output signal must have the resonant characteristics (resonance position, magnitude and bandwidth) depending on such modifications.

Metasurfaces

As stated before, metamaterials are macroscopic composites of (non-)periodic structure whose function is due to both the architecture as well as the chemical composition. The 3D concept of metamaterials can be extended by arranging electrically small scatterers into a two-dimensional pattern at a surface or interface. This metamaterial surface version is called metasurface [20]. They can be of arbitrary shape, not necessarily of zero thickness, and can have dimensions and periodicity smaller compared to the operative wavelength in the surrounding medium. Metamaterials generally exhibit some properties which are not very suitable for most of the practical applications, especially their sharp resonant peaks and very strong spectral dispersion. This results in a narrow operating bandwidth. While this is obviously not convenient for communications applications, it is useful for sensors because it ensures larger change of the output signal with small changes of the input stimulus, reaching an increased sensitivity. Such a narrow operating ranges behavior can be utilized in some applications, such as in the areas of controllable surfaces [21], chemistry [22], and biomedical sensors [23].

The electromagnetic fields strong localization, confinement and enhancement allow us to use them to improve the sensors performance to enable detection of extremely small amounts of analytes for chemical and biological sensors. Such structure can be engineered and optimized in terms of its response (resonant frequency position, amplitude and bandwidth) to obtain high sensitivities and high selectivity properties, by changing its geometrical and electromagnetic properties. Any perturbations to the electromagnetic response of the metasurface, modify the effective material response. In general, apart from the specific geometry, the polarizabilities of these metallic inclusions can also be controlled by affecting the capacitive and or inductive properties [24].

In the microwave frequency range can be used for the detection of cancer [25], water content [26] (Figures 2a and 2b, respectively) and blood diseases [27].

On the other hand, a typical intrinsic property of the compound under study is its absorption spectrum in the IR and visible regions. Mid-infrared (MIR) and near infrared (NIR) sensors have been increasingly studied for noninvasive measurements in medicine, and also in food technology and biotechnology. The electromagnetic absorption phenomena of the material under test are detected by the changes in the biosensor signal output amplitude/bandwidth. The sensor must be tuned to the main absorption peaks of specific molecular bonds. The IR spectrum can be exploited to monitor glucose concentration [28] in whole blood or during fermentation or

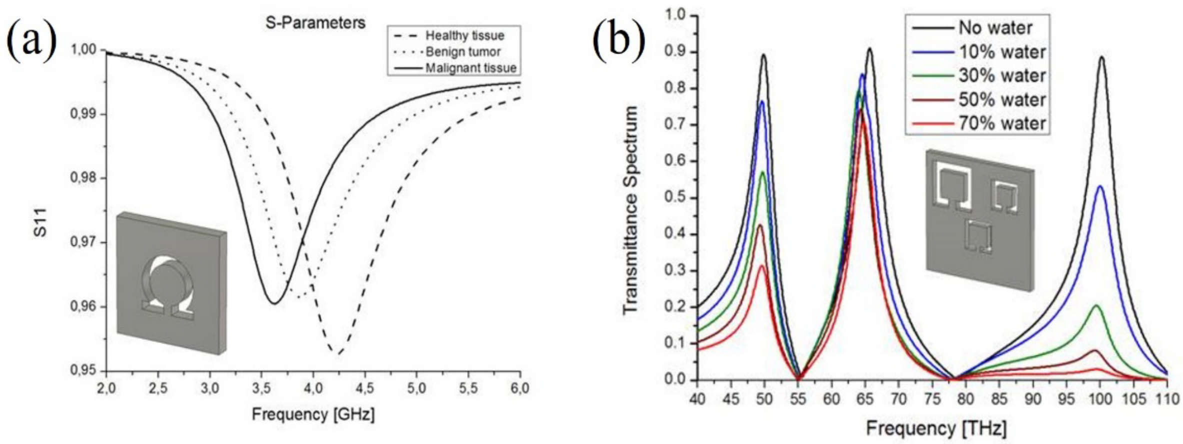

Figure 2: Meta-surfaces used as sensors for: (a) cancer tissue detection and (b) water content recognition.

to monitor hemoglobin fractions and oxygen saturation [29], due to the different optical absorption spectrum of deoxyhemoglobin (Hb) and oxyhemoglobin (HbO_2).

Nanoparticles

For what concerns the detection in the visible, the phenomenon of Localized Surface Plasmon Resonance (LSPR) has been heavily utilized for sensing applications [30]. The resonant spectral response of LSPR to a variation in external refractive index plays a critical role in chemical [31] and biological sensing technology [32]. It offers interesting characteristics, advantageous in using them for sensitive and label-free biochemical purposes. Plasmonic sensors are of great interest due to the rapidly progress in micro- and nano-fabrication technology [33]. As manufacturing processes have rapidly developed, the recent sensor technologies are being used for reading DNA bases [34] as well as detecting interactions between proteins [35], surface membrane binding events [36], antigen-antibody recognition events [37], and cellular imaging, acting as transducers that convert small changes in the local refractive index into spectral shifts in the intense nanoparticle extinction and scattering spectra [38]. The demand for LSPR-based nano-scale bio-sensing has increased due to the advantage of label-free, minimal interference, and real-time monitoring performance [39].

The extremely intense and highly confined electromagnetic fields induced by the LSPR can realize a highly sensitive probe to detect small changes in the dielectric environment around the nanostructures. When molecules get close to the surface of a noble metal nanostructure, the refractive index of immediate environment surrounding the nanostructure is increased. Thus, molecular interactions at the surface of the nanostructures directly lead to local refractive index changes; these changes can then be monitored via the SPR peak wavelength shift. This can allow for the detection of extremely low concentrations of molecules [40]. Hence, the ideal LSPR nanosensor should have a high spectral shift along the alteration of surrounding material and a narrow line-width of spectral response [41].

In the last few years several researches have paid attention to glycerol measurements in aqueous solution due to the importance in several application fields. From a biomedical point of view, it is well known that glycerol is the basis of triglycerides and it plays an important role in energy metabolism. Glycerol concentration measurement is crucial for several application fields, such as biomedical engineering, medicine and biofuels fabrication. Glycerol measurement in aqueous solutions is not simple because its permittivity varies (not too much) by changing its chemical concentration [42], as shown in Figure 3a.

Iovine, et al. developed a metamaterial-based sensor consisting of an array of nanorods is proposed. The sensor can detect the presence of glucose and its concentration in aqueous solutions [43]. Nanorods particles exhibit optimal performances for sensing applications [44].

It is well known that the permittivity of water solutions increases with increasing the chemical species concentration. Therefore, it would be possible to sense the presence of either organic or inorganic compounds in a water solution, with possible applications in food [45] and medical diagnostics [46]. In this way nanorods can be used for quantitative analysis of a large number of substances such as the alcohol content [47], acidity [48], and extractable substances with and without sugar [49].

Haematological diseases induce structural, biochemical and mechanical changes in Red Blood Cells (RBCs) [50]. The structural variations imply significant changes in cell electromagnetic properties. The refractive indices of different kind of RBCs, in the optical frequency range, differ in their real and imaginary part [51]. The scattering coefficients properties of the sensor change their position, depending on the different RBCs structural modifications. As a result, the sensor is capable to detect human red blood cells structural modifications, allowing us to detect different blood diseases, by refractive index measurements [52].

Park MH, *et al.* structures, exploiting different LSPR enhancement phenomena proposed to detect healthy and tumor tissues [53-58]. An example is depicted in Figure 3b. Structural modifications of chromophores and pigments in skin produce variations of the optical properties of skin layers. A change in the electromagnetic properties, related to the size and shape variation of chromophores and pigments, can be a useful tool for the recognition of different skin diseases. If the resonances of the sensor are designed to coincide with the skin compounds spectral characteristics, in case of diseases the response of the sensor is greatly modified in terms of magnitude and amplitude width. A change in the frequency amplitude of the sensor response is related to the different absorption rate of skin chromophores and pigments [59,60].

Near-Zero-Index Materials

Near the two axes of Figure 1c, where the real part of one of the constitutive parameters is near zero, the materials may be termed as "ε-near-zero (ENZ)" and "μ- near-zero (MNZ)" materials. Materials with both constitutive parameters equal (or close) to zero, which fall at the origin of Figure 1c, have been termed as "near-zero-index (NZI)" materials [61]. Such materials possess several interesting applications such as tailoring the phase-front of an electromagnetic wave and designing filters [62], obtaining directive antennas [61], implementing optical nano-circuits [63], confining electromagnetic fields [64], enhancing transmission [65], obtaining anomalous tunneling effects [66,67], focusing the electromagnetic field [68], cloaking objects [69,70], improving sensing systems [71-73], new types of guiding systems [74], optical antennas [75], and absorbers [76].

Other than their rich ability as a platform to study fundamental electromagnetic wave theory, metamaterial-based absorbers (Figure 4a) offer a wide variety of practical applications. Although many of these applications are still in their youth, a major goal since the creation of them has been to integrate them into existing devices to boost their performance.

Today, electromagnetic wave absorbers continue to have many relevant uses. One of the most widespread uses is for radar cross section (RCS) reduction. The basic goal of RCS reduction is

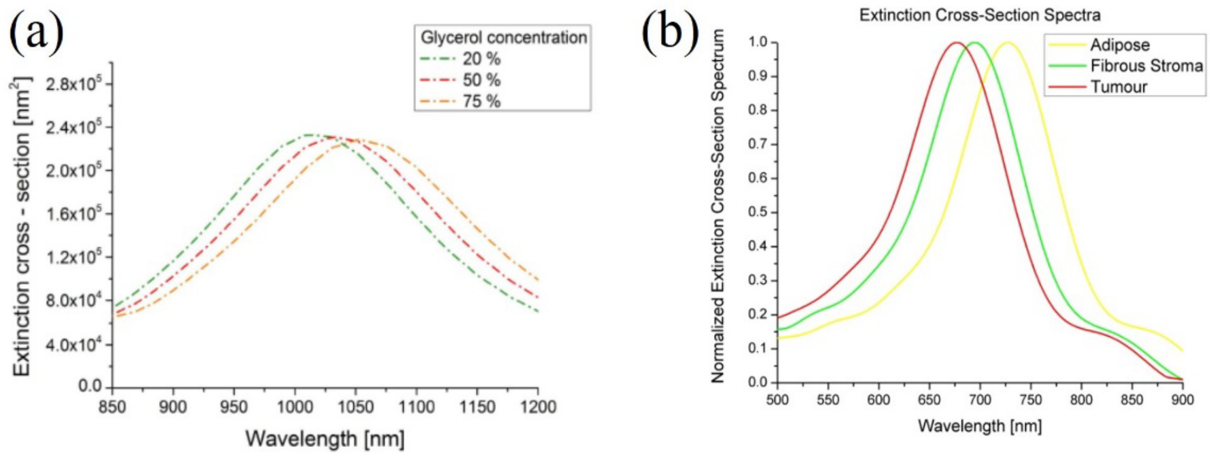

Figure 3: Nanoparticles used as sensors for: (a) glycerol measurements and (b) skin-cancer detection

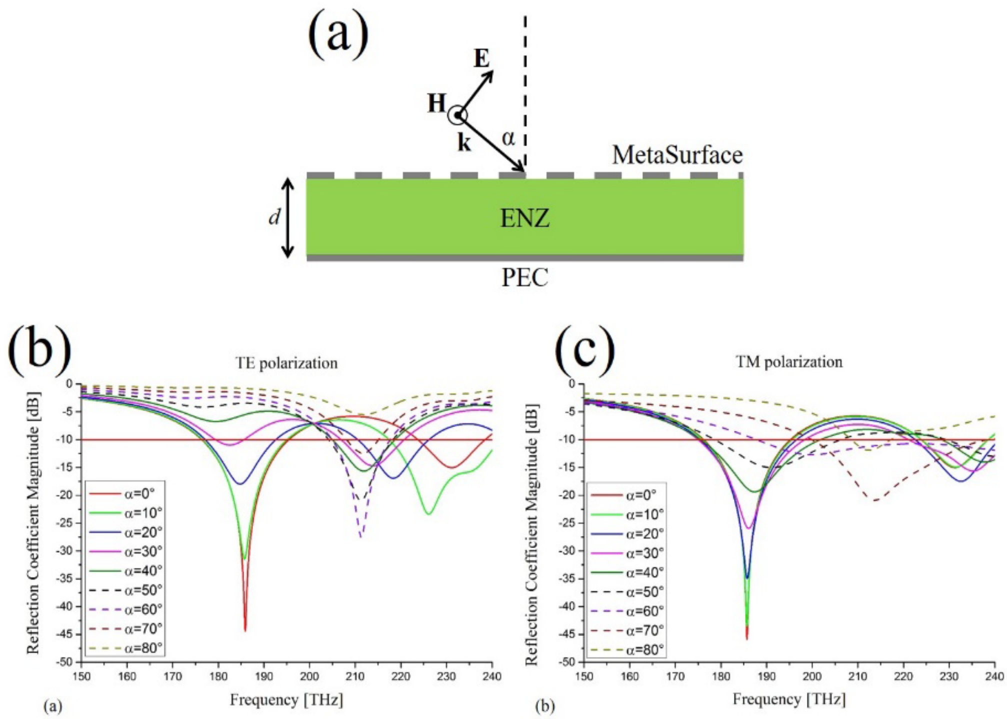

Figure 4: (a) Epsilon-Near-Zero absorber setup; Response to external impinging electromagnetic wave for (b) TE and (c) TM polarization.

to reduce radar echo so that objects can be hidden [77]. EM wave absorbers can also be used for antennas in reducing side lobe radiation or undesirable radiation from antennas [78]. Clearly, these applications have huge military and civilian potential. More recently, electromagnetic wave absorbers have been used in the reduction of electromagnetic interference by absorbing spurious electromagnetic radiation [78]. Along with preventing health risks due to exposure of specific electromagnetic radiation at frequencies, useful tool for wireless communications [79].

Because metamaterial-based absorbers are tunable with respect to their operational wavelength, they can be used as spectrally sensitive detectors or sensors. Much work has done in both integrating them into existing designs and creating novel devices based on metamaterials to provide detection and sensing throughout the electromagnetic spectrum. Microbolometers are a type of thermal detector in which incident electromagnetic radiation is absorbed by a material and then sensed by a thermometer [80]. In the pyroelectric detector, absorbed energy is sensed by a material that has a temperature dependent dielectric function, and the material forms a portion of a sensitive capacitive circuit [81]. These devices are of great interest in the IR wavelengths range and are particularly useful at THz frequencies. Theoretical work was done showing the possibility of adding a metamaterial-based absorber to conventional bolometer microbridges in the MIR region to introduce an element of spectral sensitivity [82]. In another example of metamaterial-based absorbers as detectors, in [83] it was shown that SRR's could be implemented on cantilever pixels to detect light. Utilizing metamaterial-based absorbers to provide heat upon absorption (through their loss) can cause mechanical displacement of the cantilever. By scaling the SRR design, this study could show photoresponsivity in the THz regime and in the microwave region. Rather than adding to an existing device, it is proposed that metamaterial-based absorbers themselves could act as plasmonic sensors in the NIR regime [84]. In addition to applications discussed above, there are many great options for future development of metamaterial-based absorbers. One is the advent of tunable, or active, metamaterial absorbers, making itself that could be dynamically tuned by means of external stimuli [85], as shown in Figure 4b and 4c for TE and TM polarization, respectively. One accessible application of tunable metamaterial-based absorber is in imaging. Some work has been done on THz imaging using compressive sensing [86]. Another possibility is the application of metamaterial-based absorbers as accurate, tunable and efficient thermal emitters over a specific frequency range to maximize efficiency [87]. There are a multitude of challenges in the future of metamaterial-based absorbers; one is overcoming fabrication issues, specifically in the visible regime, to make them as efficient as possible. Another challenge is to integrate them into practical devices. Despite the difficulties and challenges faced by metamaterial-based absorbers, they have a bright future with many potential applications which should have a significant impact on current science and technology.

Conclusions

This work was focused on the applications of metasurfaces, nanoparticles and near-zero materials for advanced sensing platforms.

New high sensitivity sensors were proposed, using 2D/3D structures whose frequency response is modified by the change of the surrounding dielectric environment or by exploiting the electromagnetic wave interaction with plasmonic structures. Several configurations and geometries were studied. The possibility to successfully use such structures as sensors in a broad electromagnetic spectrum (from microwave to the visible range) was demonstrated. It allowed us to develop diagnostic applications for biological compounds, cancer tissues and different health diseases.

Moreover, results here presented pave the way for new interesting and relevant use of metamaterials in a variety of fields such as optics, communications and nanodevices.

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Author Affiliation

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School of Computing, Electronics and Mathematics. Faculty of Engineering,Environment and Computing. Coventry University. Priory St, Coventry, CV1 5FB,United Kingdom.