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Applications of Nanoporous and Metamaterials: An Unornamented Review

N. V. Krishna Prasad[1], T. Anil Babu[1], N. Madhavi[2], and S. Ramesh[2]

[1]*HOD&Chief Warden,*
Department of Electronics and Physics, G.S.S,
School of Science, GITAM (Deemed to be University),
NH 207, Nagadenehalli
Doddaballapur taluk
Bengaluru Campus, 561203 Karnataka, India
[2]*Department of Statistics,*
Government College Autonomous,
Rajamahendravaram, 533103 Andhra Pradesh, India

Materials with pore sizes less than hundred nanometres are considered nanoporous. Their organic/inorganic framework supports their porous nature, and the pores are filled with fluid. The pores of consistent shape and fixed diameter are essential for these materials in specific applications. They own certain magnetic, electrical, and optical properties, which signify them in various applications such as signal transmission, energy, medicine, *etc*. Apart from natural nanoporous materials in existence, fabrication of materials with required melting point through combining polymers is possible. Materials, which are tailored to achieve unnatural electromagnetic properties like negative dielectric constant, negative refractive index, electromagnetic index, *etc*., are known as metamaterials. They are microscopically built from conventional materials such as metals and dielectrics like plastics. Some of the metamaterials may be nanoporous but not all. Metamaterials find significant applications in designing of antennas, cloaking devices, sensing devices, *etc*. In view of the importance related to nanoporous and metamaterials, some of their applications are reviewed to the possible extent.

Матеріяли з розміром пор менше ста нанометрів вважаються нанопористими. Їхній органічно-неорганічний каркас підтримує їхню пористу природу, а пори заповнені рідиною. Пори узгодженої форми та фіксованого діяметра є важливими для цих матеріялів у конкретних застосуваннях. Вони мають певні магнетні, електричні й оптичні властивості, які пророкують їх у різноманітних застосуваннях, таких як передача сиґналу, енергетика, медицина тощо. Окрім наявних природніх нанопористих матеріялів, можливе виготовлення матеріялів із необхідною температурою топлення за допомогою комбінування полімерів. Матеріяли, створені для досягнення таких неприродніх електромагнетних властивостей, як неґативна діелектрична проникність, неґативний показник заломлення, електромагнетний показник тощо, відомі як метаматеріяли. Вони побудовані мікроскопічно зі звичайних матеріялів, таких як метали та діелектрики, такі як пластик. Деякі метаматеріяли можуть бути нанопористими, але не всі. Метаматеріяли знаходять значне застосування у розробці антен, маскувальних пристроїв, сенсорних пристроїв тощо. З огляду на важливість, пов'язану з нанопористими та метаматеріялами, деякі з їхніх застосувань розглядаються, наскільки це можливо.

Key words: nanoporous materials (NPM's), metamaterials (MM's), membranes, drug delivery, antenna design, gas storage, cloaking.

Ключові слова: нанопористі матеріяли, метаматеріяли, мембрани, доставка ліків, дизайн антени, зберігання газу, маскування.

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1. NANOPOROUS MATERIALS (NPM's)

A porous nanomaterial is signified by the existence of empty spaces with dimensions being controllable at nano-, atomic, and molecular scales. It can have micropores of diameter < 2 nm, mesopores of diameter between 2–50 nm and macropores of diameter $>$ than 50 mm. NPM's potential in areas related to Li-ion batteries, drug delivery, water purification, *etc.* gained much significance. Some examples of natural NPM's include zeolites, ceramic materials, and activated carbon. Application of NPM's depends on their porosity and surface area. Since NPM's are fabricated in laboratories from organic/inorganic templates, their porosity depends on structure of organic template or pore size of inorganic template. Greater number of NPM's are divided into membranes or bulk materials. It is reported that NPM with pore of standard dimension passes particular matter while hindering others [1]. Based on the relation between property and structure, designing of NPM's with required hindrances was taken up for particular applications. More emphasis was laid towards emerging applications such as photonics, energy storage, drug delivery, *etc.* by using NPM's. One of the useful applications was water treatment, in which water purification with nanoporous crystals adjoining graphene membranes was reported. Minimised 2*D* graphene oxide nanosheets were used to construct two-dimensional channels for filtering. 3*D* nanoporous crystals were converted to 2*D* graphene laminates for enhanced performance in water purification with higher permeability [2]. Exploration of NPM's leads to identification of new materials and applications. Recent developments in fabrication of nanoporous materials along with their applications were reported [3–9]. However, societal applications of NPM's in water purification, medicine and electronics are of more significance.

2. NPM's IN WATER PURIFICATION

Water is one of the prime sources of human existence. It is evidenced that humankind, out of available water on the Earth, can use only 0.03% of fresh water. Anthropogenic activity leads to water pollution and reduced water resources [10]. This pollution affects human health, and purification of water through efficient methods is of prime concern. Apart from existing technologies for purifying wastewater, membrane filtration gains more attention due to its high efficiency, simple operation and low cost. In this context, nanoporous membranes, which filter pollutants ranging between 1–10 nm with high performance, are of importance in water purification [11, 12]. High-performance nanoporous membranes designed from materials of organic–inorganic hybrid materials [13, 14] were reported. Water purification with single-layer graphene nanoporous membrane with diameter less than 10 nm was reported [1, 15]. Late review on design and role of nanoporous membranes in water purification was reported, which might be useful in developing novel NPM's useful for efficient water purification [16–21]. In general, water purification includes techniques like Reverse Osmosis (RO), Nano Filtration (NF) or Ultra Filtration (UF). Nanoporous membranes used in these techniques use various processes like phase inversion (conversion of pure solution to solid) [22], interfacial polymerization [23], monomer action [24], track etching [25, 26], and electrospinning [27, 28].

3. NPM's IN ORGANIC ELECTRONICS

Materials used in electronic devices are evaluated in terms of size, cost and effectiveness. In this regard, electronic devices developed with organic materials gain significance due to their low cost as they replace regular devices of inorganic nature with solution. This technique makes them highly potential in integrated circuits, energy storage devices, biomedical electronics, *etc.* [29–33]. Latest review was reported regarding performance enhancement in these devices inserted with nanoporous configuration [34]. Nanofabricated components used in organic electronic devices are being reported to perform better [35]. At present, basic units, which include nanotubes and nanowires, are of significance in the growth of optoelectronic devices. Reports indicated that usage of metallic nanodots in organic photovoltaic device increases its photocurrent, and organic nanopillars enhanced their performance [36–39]. Modulation of performance and charge trapping was reported in organic memory devices [40].

The role of nanoporous structures in organic electronic devices was continuously increasing due to their specific advantages [34].

4. NPM's IN NANOMEDICINE

An important NPM in nanomedicine is nanoporous silicon (Psi), which is a silicon element of exceptional design obtained from silicon substrate by electrochemical etching [41, 42]. These elements are mainly used in health care, biosensors and drug delivery [43]. As these elements are highly biocompatible with body during interaction [44, 45], they find significant applications related to drug delivery and drug loading [46]. Nanosize Psi materials are reported to overcome the problems faced by traditional therapeutic administration [47]. Variation in adsorption capacity of Psi, its pore size, uniformity in porous structure and flexible functionalization of surface make it significant in drug movement [48]. These particles allow wide range of drugs to be loaded and protected from degradation [49, 50].

The shape and size of pore can be tuned by changing the current density, electrolyte concentration through etching [51]. Large surface enhances adsorption capacity and favour loading of biomolecules with higher molecular weights [52, 53]. Increase in current density and decrease in HF electrolyte concentration increase pore size [54, 48]. Pores are created in Si particles and powders through stain etching [55–59]. They should be inert and nontoxic in biological environment for them to be used in drug delivery. Since silicon is nontoxic, variation in physical properties at nanoscale may lead to negative response [60]. Usage of Psi nanoparticles in testing of therapeutic, antitumour and gene deliveries is of significance [61–68]. Combination of molecular units into switches makes these particles improve drug delivery regulation for better effectiveness in cancer treatment [69].

5. NPM's IN ENERGY AND GAS STORAGE

Energy production from non-renewable resources raises concerns on environmental issues. To address this concern, it is required to use renewable energy sources. In this condition, heterogeneous catalysts play an important role, which converts renewable sources into fuels and chemicals. It is a known fact that surface area influences efficiency of heterogeneous catalysts, and hence, nanoporous heterogeneous catalysts play a vital role [70]. Review on the uses of three-dimensional nanoporous metals and their composites in converting renewable sources into chemicals and fuels mainly focussed on material fabrication based on metals as they are used as efficient electrocatalysts. Dealloying in aqueous media is an important process of manufacturing nanoporous metal catalysts, in which highly active element is being separated from parent alloy. Sometimes, an external voltage is used to accelerate dealloying process subjected to non-spontaneous reactions [71]. Electrocatalytic process that includes water oxidation, methanol and CO_2 [72–74] reductions can produce fuel. However, nanoporous electrocatalysts are disadvantageous in terms of cost and stability. Nanoporous structures obtained through leaching serve to be high-performance electrocatalysts. Conventional 2*D* thin-film water-oxidation electrocatalysts perform well with limited use. Hence, bulk nanoporous materials are an alternative as it is possible to combine materials' quality with nanostructures' electrocatalytic properties. It is reported that 3*D* nanoporous graphene can be synthesized from nanoporous nickel template along with adjusting pore size using solid-state growth approach at low temperatures [75, 76]. Alteration of nanoporous Ni templates alters pore size on nanoscale leading to manufacture of nanoporous graphene for designing of electrochemical-energy storage devices.

Utilization of fossil fuels and associated harmful gases leads to environmental pollution forcing us to use technology of renewable energy. This includes hydrogen gas as an alternative energy for vehicles in terms of safe and commercial aspect [77]. Porous carbon is one of the materials being tested for hydrogen adsorption [78–81]. CNG is one of the alternatives containing compressed methane at normal temperature that emits low pollution [82]. Some of the drawbacks suggest ANG with porous materials in place of CNG [83]. At the same time, huge utilization of fossil fuels emitting dangerous gases (CO_2) forced developing adsorbents, which can arrest and stock carbon [84]. Activated carbons and zeolites are sorbents, which store H_2, CO_2 and CH_4 with high porosity and of low cost [85–88]. Reports indicated carbon powder, which may be used to synthesize activated carbon for membranes and thin films [89]. In this context, carbon cloth was reported to be an efficient gas adsorbent [89–91]. Materials of required adsorption capacity were designed using different approaches and reported [92, 93].

Machine learning and data science technology were used for hydrogen storage in materials [94].

6. METAMATERIALS (MM's)

Metamaterials are materials whose natural electromagnetic properties can be altered. If natural materials like glass or diamond, which exhibit positive refractive index, permittivity and permeability, are tailored for negative values, they are called negative index materials and exhibit reverse Doppler effect. Four and half decades earlier from now, it has been realized that materials tailored in a suitable extent exhibit the property of negative refraction, and materials with negative permittivity and permeability values exhibit properties of lenses [95]. Prior to this report, such material was prepared after thirty years [96]. Tailoring of materials to exhibit negative permittivity and/or permeability continued with fast rate in spite of their novel applications. These applications include cloaking, antenna design, electronics, *etc.* The metamaterials with negative permittivity and permeability will be having negative refractive index and be called as Left Handed Material.

It is not possible to have both values negative simultaneously. Hence, these materials are to be modified for abnormal properties required as mentioned above.

7. ANTENNA DESIGNING

High gain, efficiency, large bandwidth, small size, large power and lightweight are some of the important characteristics in antenna design. These characteristics can be obtained from antennas designed with MM's [97].

Hence, metamaterials' usage in antenna design makes the antenna exhibit specific characteristics different from routine. Metamaterial antenna consists of one or more layers of metamaterial substrates. Depending on the design and application, selection of metamaterial is done.

To start with metamaterials to be used in, antenna consists of one or more unit cells whose permittivity, permeability and resonance frequency (ε, μ, f_r) depend on size and structure of each unit cell [98, 99].

Less cell size when compared with wavelength makes a metamaterial satisfy homogeneity condition. As per the previous reports, simulation of unit cell numerically could not obtain required results. Therefore, continuous modification in cell size was taken up until required structure as per simulation was attained. Optimization techniques yield good results in determining the size of unit cells. It is reported that usage of AMC's (artificial magnetic conductors as a class of applied metamaterials) improves antennas' radiation properties in microwave applications. Improvement in radia-

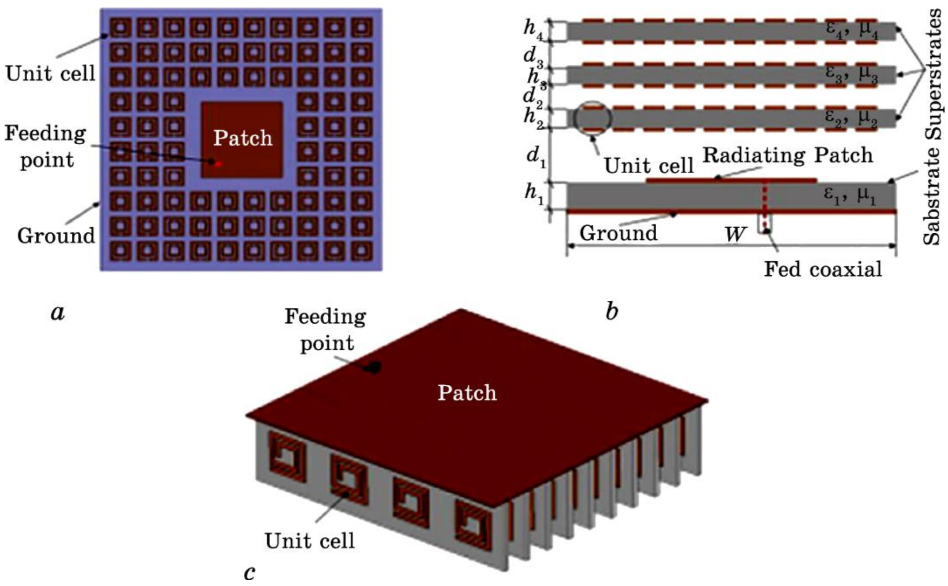

Fig. 1. Usage of metamaterials to improve power gain: (*a*) radiated patch surrounded by unit cells; (*b*) metamaterials as superstrate; (*c*) antenna load [3].

tion properties of metamaterial antennas was achieved through placement of antenna above reflector such that radiation is along only single direction that reduces reverse radiation [100]. AMC's are widely used metamaterials, which simulate perfect magnetic conductors (PMC's) in antenna design [101]. Metamaterials of high permeability can be used to design a patch antenna without reducing the efficiency (Fig. 1) [102, 103].

8. GAIN AND BANDWIDTH IN METAMATERIAL ANTENNAS (MMA's)

Metamaterials in antenna design improve gain. Low gain is the main drawback of small planar antenna, which may be addressed through usage of metamaterials. Improvement in power gain is a function of superstrate number, unit cell and the distance between radiation element and superstrate. Placing of unit cells round the radiation elements loads the substrate. Hence, unit cell size must be estimated so that MM's exhibit particular characteristics, which match resonant frequency of the antenna. Therefore, the antenna gain depends on number of unit cells and resonant frequency [104]. Antennas, if designed with metamaterial superstrates, increase gain, size and antenna thickness. Figure 2 shows plane fractal an-

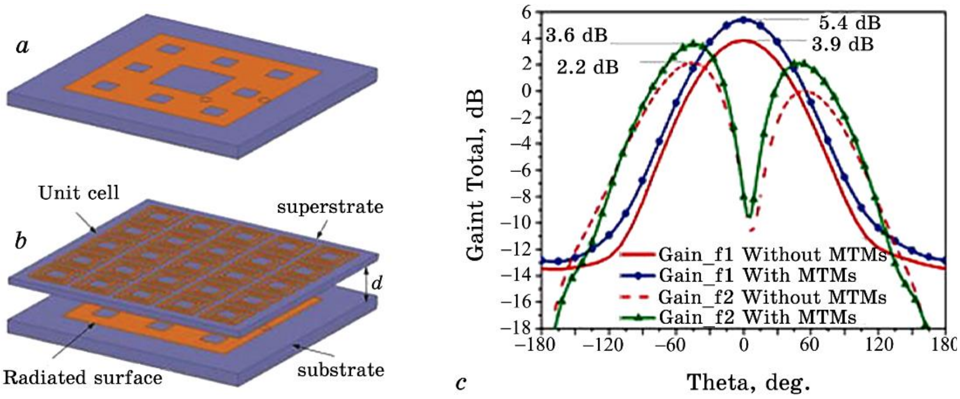

Fig. 2. (*a*) Plane fractal antenna, (*b*) antenna covered with AMC metamaterial, (*c*) power gain for two resonant frequencies [3].

tenna along with power gain.

Compact antennas designed with dielectric substrates can be replaced with less size MMA having defected ground structures (DGS) exhibiting unusual properties at resonant frequency [105]. In addition, usage of metamaterials increases antenna bandwidth.

Figure 3 displays the antennas' S-parameters with and without metamaterials. Unit cells situated at superstrate influence bandwidth based on cell number and closeness between superstrate and radiation surface.

Metamaterials can also be used to integrate multiple systems on a single device [106], and the designed antennas exhibit multiband behaviour with highly correlated results [107].

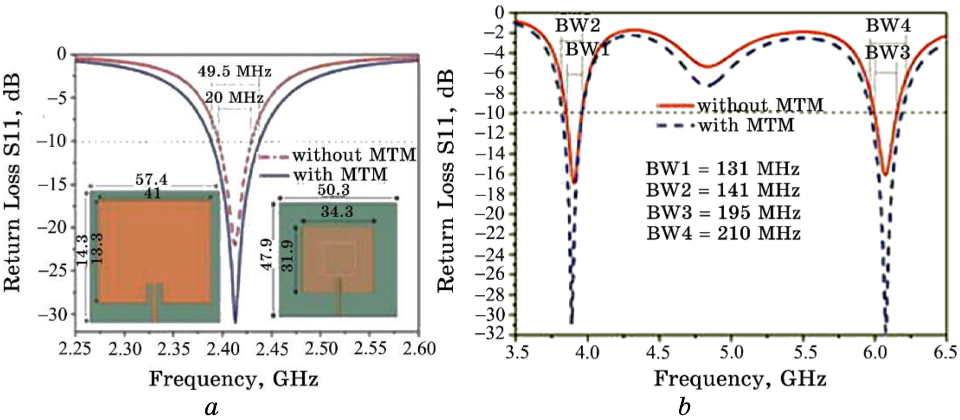

Fig. 3. (*a*) S-parameters of an antenna without and (*b*) with metamaterial [3].

9. CLOAKING

Cloaking is a technique of masking objects with the help of metamaterials. An object really doesn't vanish but appears as though vanished through illusion. This can be achieved by metamaterials by diverting specific frequencies [108]. Either light reflection or refraction regulates the process of illusion. The concept of cloaking gained importance with production of novel metamaterials. Electromagnetic cloak and Stealth cloak are two important cloaking devices.

10. ELECTROMAGNETIC AND STEALTH CLOAKS

A device that masks an object for electromagnetic radiation of specified frequency range is an electromagnetic cloak. For an object to be masked, waves should not be reflected back to the source [109]. This can be achieved by reduction of scattering cross section, which can be obtained with materials of relative permittivity less than unity [110]. It is reported that cloaking through scattering cancellation technique limits bandwidth even though simple [111, 112]. Cloaking devices with anisotropic metamaterials create zero electromagnetic field in the device. It is also reported that limited values of permittivity and permeability lead to narrow bandwidth at desired cloaking effect [113] and reduce cloaking performance [114]. Stealth is technique of designing an aircraft not to be detected by radar/sonar. This technique can only minimise radars' reflecting power. This can be achieved if and only if the aircraft is covered with an absorbing layer so that the scattering field in the direction of illumination will be minimized. This technique hides the aircraft from front view, and it can be seen from side or back.

11. SENSORS AND SOLAR CELLS

Sensors are important in our daily life. Sensors developed with various materials play vital role in all sectors; however, metamaterial sensors have various advantages. Sensors designed with metamaterial capable of detecting liquid chemicals were reported [115]. Similarly, metamaterial-based optical sensor with E-beam lithography technique for detection of sucrose was reported; its sensitivity was higher than an ordinary sensor. This sensor has a central wavelength of 967 nm as compared to gold sensor of 933 nm ensuring more bandwidth and better sensitivity [116]. In continuation, semiconductor metamaterial sensors in THz range [117], sensors, which sense alcohols' permittivity [118], and high-Q gas sensors for environmental monitoring [119] were reported.

Metamaterials can be used in solar cells to enhance the absorption capacity. They can be fabricated with wide band angle matching solar spectrum to receive light in different angles increasing incident and reducing reflected lights. This has certain disadvantage—narrow band only supports perfect absorption. Hence, absorbers, which utilize solar energy in perfect way, need to be designed. In this context, solar cells with metamaterials are reported with 77% and 84% absorptions of solar and visible regions [120]. Solar cells made with Si having back reflectors made with metamaterial exhibiting maximum reflection are reported. If ordinary metallic mirrors are used, reflected light has phase reversal, which leads to reduced intensity. This can be overcome by using metamaterial mirrors leading to increased absorption in solar cells [121].

13. CONCLUSIONS

This paper mainly reviewed some of the important applications reported over last five years related to nanoporous and metamaterials. The role of nanoporous materials in water purification (membranes), storage of energy, organic electronics (sensors, semiconductor films) and nanomedicine (cancer, therapy) was mainly reviewed. The role of porous silicon in drug delivery and its regulation was of importance. Apart from nanoporous materials, review of metamaterials was also done. Even though both are connected directly or indirectly through some common applications, review of metamaterials in the area of antenna design is note worthy. The role of metamaterials in antenna design, cloaking, sensors and solar cells was reviewed in brief. Tailoring of metamaterials for novel characteristics is an unending process. However, research in the direction of investigating novel nanoporous metamaterials may lead to new application in the field of photonics and optics in addition to the existing applications in the fields of electronics and medicine.

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