ROLE OF POROUS NANOMATERIAL'S IN WATER PURIFICATION, ELECTRONICS, DRUG DELIVERY AND STORAGE: A COMPREHENSIVE REVIEW

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Nanoporous materials and their study gained tremendous significance in view of their potential applications such as drug delivery, water purification, biosensing, electronics and storage etc. Based on their synthesis with required shape and size make them application oriented. Nanoporous materials are materials with pore size of hundred nanometres or less. They have inorganic or organic framework supporting regular porous structure. The pores in these materials are occupied with fluid. These materials represent a transition from atom to solid in which pores of uniform shape and diameter need to be obtained for them to be used in some applications. Nanoporous materials possess specific electric, optical and magnetic properties that make them highly potential in applications related to signal transmission, energy, biological applications, catalysis, gas storage and medicine. In spite of existing nanoporous by nature tailored materials can be produced with combination of polymers with different melting points. A nanoporous material with accurate pore sizes allow certain matter to pass through, while blocking others. In view of their tailored properties they find extensive applications at present and in near future. Keeping this in mind, an attempt was made to review the potential applications of these materials with more emphasis on water treatment and drug delivery reported in the last five years in a nut shell.

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1. Introduction:

Porous materials gained significant attention due to the presence of empty spaces whose dimensions can be controlled at nanometric, molecular and atomic scales. These materials are categorized into micropores with diameter less than two nm, mesopores with diameter in the range two nm- fifty nm and macropores whose diameter is greater than fifity mm. In this paper nanoporous materials (NPM) with pore diameter less than hundred nm will be reviewed. These materials exhibit high potential in many areas related to Li-ion batteries, fuel and solar cells, super capacitors,gas purification, drug delivery, water purification, sensor applications, magnetic, optical and electronic devices. Zeolites, activated carbon, silicates ceramic materials etc. represent synthetic and natural nanoporous materials. Usage of these materials mainly depend on the required design at molecular and atomic level that control their surface area and porosity. NPM's are developed in labs with templates of organic/ inorganic type. The porosity of the developed product depends on the inorganic templates existing pore size or organic templates structure. The nanosized pores can be used to soak nanoparticles so as to satisfy various functions of practical interest. Majority of the nanoporous materials are categorized into bulk materials (zeolites and activated carbon) or membranes(cell membranes). As already mentioned unnatural materials can be produced by combining polymers of different melting points. A NPM of consistent sized pores will allow only definite matter to pass through while stopping the other[1].For the last few years,

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lot of effort has been put in development and designing of npm's with some hindrances such as basic knowledge of structure-property relation and tailoring these structures for particular applications. Research in this area was pivoted towards emerging applications that include energy storage, biosensors, fuel cells, drug delivery, gas separation, catalysis and photonics. Water treatment was one of the major application related to these materials where graphene based structures play vital role. Purification of water with nanoporous crystals surrounded by graphene membranes were reported [2].They used reduced graphene oxide nanosheets and constructed two dimensional channels for process of filtering driven by pressure. They included three dimensional nanoporous crystals into two dimensional graphene laminates leading to enhanced performance in water purification with more permeability by 15 times when compared to reduced grapheme oxide membrane with near dye retention rate.

Investigation of nanoporous materials and their applications provide an opportunity to identify novel materials and new applications. Recent advances in synthesis of nanoporous materials was reported by [3].Schwanke and Pergher [4] reviewed nanoporous materials with Mobil twenty two topology(MWW) and reported the development of MWW precursor and three dimensional zeolite along with their physical and chemical properties. They also discussed the usage of directing agents in obtaining various materials of MWW type already reported. Silva et al. 2018 [5] studied materials in graded order. They created mesopores in microporous zeolite structure and evaluated the properties of modified zeolites. Vinaches et al.2018 [6] reported another method of introducing Al into zeolitic framework in which synthesis of zeolite in pure form of silica was done and Al was added with in situ produced seeds. These substances were used as catalysts on dehydration of ethanol. Their selective nature towards ethylene and diethyl ether confirmed the existence of acidic sites. Similarly Pereira et al.,2018[7] reported zeolite synthesis from that of derived from white and red kaolin. The obtained zeolite was used as an adsorbent. Likewise Zhang et al.2018 [8] reported comparison between two glycerol zeolite systems with difference in residual gas and indicated the existence of microproous and mesoporous material formed by lamellar material pillarization apart from zeolite. In continuation to this Jalilet.al.,2018 [9] reported the development and evaluation of three clays pillared with silica as adsorbents of tetracycline and ciprofloxacin from aqueous media of alkaline nature using a different raw material for separation process.

2. Nanoporous membranes for water purification

Life without water can't be imagined. Even though earth's surface has water covered about 75% only 0.03 % of freshwater could be used by mankind that include river water and ground water. Urbanisation and industrial development lead to water pollution misbalancing the freshwater resources and ecological environment [10]. Water pollution may lead to severe health issues in human body and hence water need to be purified. Hence developing efficient water purification methods are of prime concern. At present many technologies have been widely used in purifying wastewater. In spite of being operated at room temperature, consumption of low energy, high efficiency, low cost and simple operation technique of membrane filtration gain more attention for purification of water when compared to other technologies. In this context microporous membranes having a pore size of 0.1μm–5 μm could be used to filter particles with 1 μm –10 μm limiting their role in water purification. However, nanoporous membranes could filter majority of the pollutants (1nm–10 nm) exhibiting high performance for water purification [11,12].

Design of nanoporous membranes with high performance using organic, inorganic and hybrid materials were reported [13,14]. Desalination of water through usage of nanoporous materials like single-layer graphene, nanoporous membrane of sub-10 nm diameter cellulose nanofibers etc. was demonstrated by many researchers[15][16]. Zhuqing Wang et al.,2018 reported the latest studies on the role of np membranes in water purification. They reviewed the fabrication techniques, design and their mechanism of purifying various water pollutants. This may help in development of novel npm's for fast, economical and highly efficient water purification[17].Water purification np membranes are categorized organic, inorganic, and organic-inorganic hybrid membranes depending on composition of materials. Organic membranes are generally fabricated with polymeric materials[18] while ceramics are used to make inorganic membranes[19], graphene [20], carbon nanotubes (CNTs) [21] and organic-inorganic hybrid membranes are made by polymeric matrix system after inducting inorganic materials[22].

Fabrication of nanoporous membranes used in RO(Reverse Osomosis),UF(Ultra Filtration) and NF(Nano Filtration) for wastewater purification include phase inversion: a classification process of converting a pure solution to solid[23],interfacial polymerization: a method already used for fabrication of NF and RO membranes[24] based on reaction (polycondensation) between two monomers[25],track-etching: method thatprecisely controls membranes pore size distribution in which pore size can be altered between few nm to tens of µm and pore density between 1 cm^{-2} to 10^{10} cm^{-2} [26][27] and electro spinning: an old method of fabricating nanofibrous membrane materials[28] whose size distribution of pore, porosity and morphology may be controlled through adjustment of electric field applied, conditions of environment and solution flow [29]. The performance efficiency of any nanoporous membrane depends on it characteristics. Figure 1. Below show some of its key characteristics.

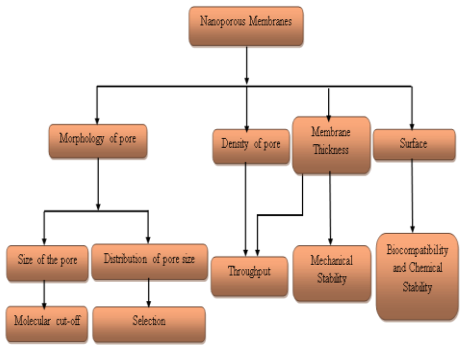

Fig. 1.Charcteristics of nanoporours membranes.

Fig.1shows the characteristics of nanoorous membranes that improve their performance. Fabrication of membranes with required pore size and narrow distribution make them highly suitable for controlled molecular transport. Many applications desire less flow resistance that can be obtained by high porosity and low membrane thickness. Finally sufficient mechanical strength, chemical and thermal stability for various biological environments is required on long term basis.

3. Nanoporous structures in organic electronics

Electronic devices has been playing a key role in today's life. In this regard the material used for fabrication of these devices is of prime importance. Generally these materials should satisfy certain conditions such as durability, efficiency, space, cost effectiveness etc. Organic Electronics is an emerging field in material science that deal with designing and synthetization of organic molecules that exhibit sensible electronic properties like conductivity. Unlike traditional inorganic materials like semiconductors materials used for organic electronics are of low cost making them highly potential in commercial aspect. The advantage of these materials include variation in conductivity with dopant concentration, high thermal stability and mechanical flexibility. In this context electronic device made with organic materials gain significant interest in spite of their low cost due to roll to roll processing and solution based replacement to traditional devices of inorganic nature. They show huge potential in biomedical and stretchable electronics, foldable displays, IC's and storage of energy[30-34].Organic electronic devices embedded with np composition enhance their performance in different applications. Recent advances in this regard was reviewed by Deyang Ji.etal.,2020[35] who summarized latest research related to usage of np structures in organic devices. Nanofabricated components used in organic electronic devices will perform better and make them highly potential in the field of engineering and material science[36.]. As on today different building blocks such as nanowires, nanotubes are fabricated using various techniques which play significant role in developing optoelectronic devices. It is reported that photocurrent in organic photovoltaic device increases due to usage of metallic nanodots with localized Surface plasmon resonance through enhanced light absorption[37][38][39].It is also reported that organic memory devices performance and charge trapping effect are modulated[40]. Likewise producing organic nanopillars in photovoltaic devices enhance their performance [41]. Joanna Cabaj and Jadwiga Soloducho, 2018[42]has nicely reviewed the role of nanoporous conductive polymers in biocompatible sensors. Figure. 2 shows organic electronic based sensing platform for body metabolites. Figure 2.A shows the monitoring of metabolite level in human blood. It was an antibody mediated platform on top of a gold electrochemical sensor that can avoid interfering signals and measure creatinine in blood at fast rate and accurately. Fig. 2B shows an organic electrochemical transistor that can measure metabolic profiles of humans. Similarly sensing of metabolite from whole cells of a human body has been demonstrated. Fig. 3demonstrates the monitoring of metabolites on continuous basis using wearable devices which uses nanoporous conductive polymers as key elements. In addition to above nanostructures discussed nanoporous structures and their role in organic electronic devices was gaining severe importance because of their specific advantages in semiconductor films, sensors, solar cells etc. [43].

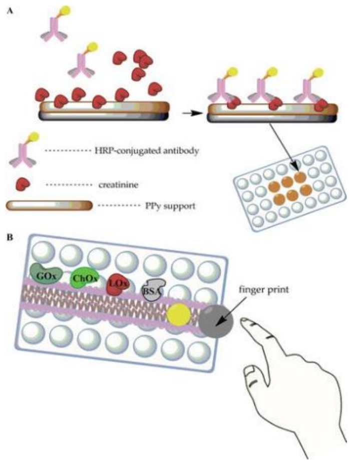

Fig.2. Organic electronics based care system; A. Measurement of creatinine from serum using polymer sensor; B. Measurement of human glucose using organic electrochemical transistor [Courtesy: Ref.42].

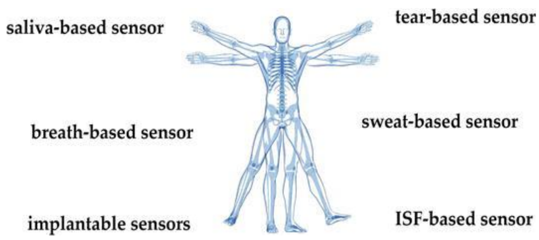

Fig. 3. Wearable Biosensors Courtesy; Ref 42.

4. Porous silicon nanoparticles and their role in nano-medicine

Porous silicon (pSi) a special configuration silicon element has been exploited before 25 years through electrochemical etching of silicon substrate[44,45]. Since then nanostructures of pSi are being used in clinics, biosensors as well as drug delivery[46]. They are highly biocompatible in interaction with body[47] and get degraded to silicic acid of non-toxic type in aqueous fluids [48]. These particles created new prospects in applications related to drug delivery due to scale reduction enhancing the passage of drug loading[49].It is reported that nanosized pSi materials are highly potential in overcoming the hurdles faced by regular therapeutic administration[50].

pSi is suitable for varying adsorption capacities as well as liberation kinetics for therapeutic agents. Its adjustable and narrow pore size, uniform porous structure, big porosity, big ratio of surface area versus and easy functionalization of surface makes it vital in drug release vehicles[51]. The open networks in this particle allow loading of huge range of drugs. The payload is protected from degradation due to load being concealed within these porous networks[52,53]. Generally pSi nanoparticles are fabricated from pSi films either by electrochemical etching or stain etching. Tuning of shape and size of pore through altering density of current, concentration of electrolyte can be done through this etching[54]. Higher area in surface due to high porosity enhances adsorption capacity[55]. pSi NPs having more pore size favor loading of bio molecules with more molecular weight[56]. Large pore size can be obtained with increasing current density or decreasing concentration of HF electrolyte[57]. Rate of degradation was dictated by tuning in pore size and porosity[58]. Stain etching is considered to be less reproducible than electrochemical etching which is not able to produce multilayered pSi materials. However it used to create pores within Si particles and powders [59]thus giving path for not creating pSi films first. Fabrication of pSi NP of huge surface area by porosifying low cost Si powders was done through stain etching [60-62].

4.1. Designing pSi NPs for drug delivery

Effectiveness of drug delivery is purely based on its control. Drug concentration beyond a certain range cause adverse effects on human body. In this context different ways of drug delivery mechanisms and their targeted systems are reviewed in the direction of minimizing drug loss and maximizing drug accumation in specifc area required so as to enhance the drug bioavailability. Also measures are to be taken to prevent any harmful side-effects in human body. In this context role of nanoparticles is of prime importance. To check the feasibility for drug delivery nanoparticles must be biocompatible and suit for particular purpose. They should act as non-toxic and inert carriers in biological environment. As silicon element is non-toxic change of its physical properties at nano scale may give rise to adverse responses[63]. Utilizing pSi nanoparticle therapeutic delivery testing of anti-tumor therapy and gene delivery were reported.

4.1.1. Anti-tumortherapy

Specific targeting of cells help in therapeutic delivery to a tumor site by reducing side effects due to chemotherapy. In this context three main strategies are implemented to direct pSi nanoparticle based drug carriers into tumors given by designing nanoparticle of size and shape that allow accumulation within the tumor, that avoid immune clearance and temporary union of ligands to the NP surface in the microenvironment of tumor. Once intravenous injection is given pSi nanoparticles are fastly removed from circulation, get accumulated in liver and later reduced into silicic by products and get cleared through kidneys[64]. Since small particles penetrate into tumors more uniformly and quickly than large particles, they might carry the therapeutic agents in a betterway [65]. Once infused shape of the particle is vital in directing the circulation of nanoparticle: smaller particles collection liver and spleen, while bigger particles get deposited in lungs[64]. These particles can decrease the side effects of chemotherapy [66]. It is reported that designing of specific targetted particles that stick to tumor microenvironment can increase drug penetration into tumor sites hugely[65]. Hence, temporary union of antibodies to pSi nanoparticles will bind associated receptors on cells surface facilitating targeted therapeutic delivery [67]. The main challenge for targeted drug delivery for tumor microenvironments is to access the tumor across the binding site barriers and large intravascular distances amid dense tissue matrices and non-cancer cells. It is of prime concern, how targeted nanoparticles can be incorporated into cancer cells that are out of reach from blood vessels[65].

4.1.2. Gene delivery using pSi NPs

A process of introducing new or rectified genes into a cell or tissue is known as gene therapy[68]. Clinical trials report wide range of diseases that include several cancers for which this process is suitable. Gene delivery may be carried out with viral or non-viral vectors[69]. Viral vectors use reproduction cycle as a tool to commute genetic matter into cells[70]. In view of advanced safety compared to reproduction vectors, non-reproduction vectors are investigated in gene therapy but they exibit unexpected side effects [71]. Keeping this in view non-viral vectors with several advantages are explored. They are easy to synthesize, can target cell/tissue, have low immune response and can be produced on lrge scale easily. Different non-viral carriers are being developed for providing good performance in targeted delivery for various organs[72].

5. Role of nanporous silica nanoparticles in drug delivery regulation

Nanoporous silica nanoparticles are treated to be good drug delivery agents in view of their superior properties. Recent progresses of these particles was reviewed by Ruoshi Zhang et al.,2021 by relating their mechanism of formation, structure and drug delivery regulation. They reported that these particles are highly benefited due to combination of molecular units as switches which improves the drug delivery regulation exhibiting better efficacy of anticancer[73]. Fig.4. shows nanoporous engineering drug delivery through anodization. Nanoporous Anodic Alumina (NAA) is one of the most popular self-ordered periodic, porous templates which was obtained through two step anodization process. It exhibit excellent properties such as electrical insulation, optical transparency and chemical stability which can be used in drug delivery, biomedical devices for dental and bone implants and carriers for cells transplantation.

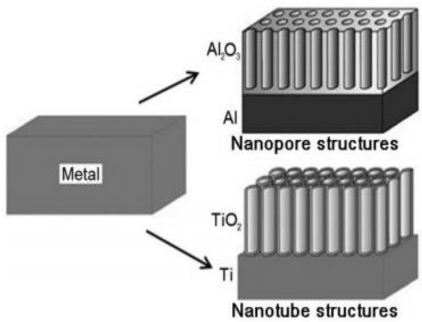

Fig.4. Nanoporous and Nanotube Metal Oxides(Al_2O_3 and TiO_2 formed through self ordered anodization for drug delivery; Courtesy: Ref.102.

Fig.5 shows magnetic drug delivery regulation where cancer can be treated through targeted delivery of anticancer drugs which can be realized through drug delivery vehicle with strong magnetic moment.

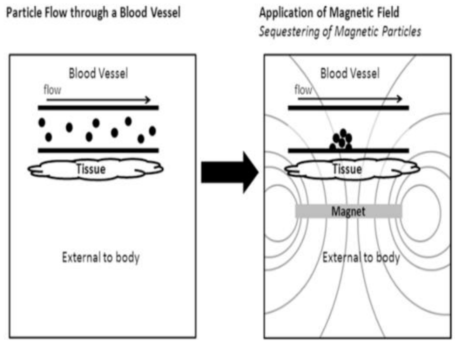

Fig.5. Magnetic Sensitive Drug Delivery; Courtesy: Ref.102.

Fig.6 shows the schematic diagram of ultrasound drug delivery in which ultrasound has been used to treat many diseases such as diabetes. Ultrasound was used for targeted disruption of drug carrier vessels by releasing their therapeutic payload for uptake by the target cells.

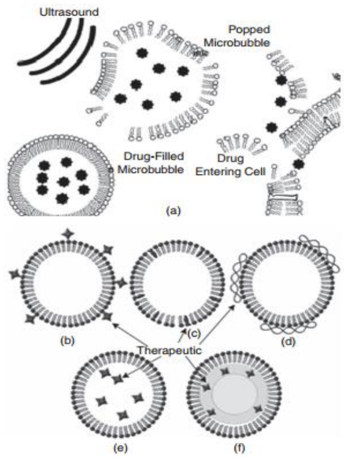

Fig.6. Ultrasound Senstive Drug Delivery; a. Drug delivery through targeted microbubble destruction using ultrasound; b., c., d., e., f.Different styles of therapeutic agent loading; (b.Attaching to membrane); (c.embedding in the membrane); (d.noncovalent bonding to microbubble surface); (e.packing in to interior of microbubble)(f.formation of an oily film surrounding the microbubble); Courtesy:Ref.102.

6. Nanoporous materials in energy storage

Production of energy from non-renewable resources is a continuous process to meet growing demand in energy which project environmental issues of serious concern. Hence it is necessary to move towards renewable energy resources. In this context the role of heterogeneous catalysts in converting renewable sources into fuels and chemicals is of significance. Since the efficiency of heterogeneous catalysts depends on their surface area, nanoporous heterogeneous catalysts are of importance due to their big inner surface area and huge number of active sites produced by curved inner surfaces. It is reported that the total performance of nanoporous dissimilar catalysts is much greater than that of planar catalysts counterparts [74]. Jintao Fua et al.,2018 reviewed the usage of three dimensional np metals along with their composites in electrocatalytic conversion of renewable sources into fuels and chemicals. They focused on dealloy metal based material fabrication since they can be directly used as high performance electrocatalysts. One of the popular method for fabrication of nanoporous metal catalysts is traditional dealloying in aqueous media. In this process, generally the highest electro chemically active element is removed from parent alloy using an acidic or alkaline aqueous corroding medium. In some cases an external voltage may be applied to drft the dealloying process provided the involved reactions are not spontaneous [75]. Electro catalytic processes is one of the process that can be used for fuel production. This process include water oxidation, methanol and carbon dioxide reductions.

Water oxidation reaction is an appealing process for production of fuel on sustainable basis. In addition to huge quantities of water being available for energy applications on large scale, water oxidation generates electrons that reduceCO_2 and protons into H_2 and carbonaceous fuels[76]. Direct methanol fuel cells are simple to operate with high density of energy density making them highly potential in portable electronics and automobiles[77].Protection of environment and sustainability can be attained through electrochemical reduction of CO_2 into carbon fuels that are reusable that includeCH_4 and CO[78]. At the same time nanoporous heterogeneous electrocatalysts are said to have some drawbacks such as costly materials (noble metals) and stability due to hardening during electro catalytic processes on long term basis.

Nanoporous structures synthesized by leaching may be directly used as high-performance electro catalysts, as three dimensional current collectors in combination with electrocatalyst materials of poor conductionin directly. These two cases achieve increased catalytic performance. Regular two dimensional thin film water oxidation electrocatalysts function well, but low quality limit their use practically. In this context bulk nanoporous materials may be an alternative since they mix the quality of materials with electrocatalytic properties of nanostructures. Current literature indicated that dealloyed bulk nanoporous NiFe based systems of high performance act as water oxidation electrocatalysts. Similarly nanoporous metals can be used as catalyst and template simultaneously. Lu Liqiang et.al.,2018 reported synthesis of three dimensional nanoporous graphene by using nanoporous nickel templates using solid state growth approach[79]at low temperature range 600°C –800°C without varying the novelty. Also the pore size can be adjusted through the method of low temperature solid state growth. Apart from storage of energy, porous grapheme is tested for application in batteries [80]. Also by altering the nanoporous nickel templates the size of tubular pores could be altered on nanoscale of wide range that lead to manufacture of nanoporous graphene on large scale and give scope for designing of electrochemical energy storage devices.

7. Nanoporous materials in gas storage

Consumption of fossil fuels and related harmful gases leadto disaster in energy supply along with environmental pollution. Hence it is mandatory to implement technology of renewable energy that include usage of hydrogen gas as another possible energy for fuel cell vehicles considering safe, convenient and commercial storage media[81]. Different materials have been tested for hydrogen adsorption including porous carbon[82-85]. Natural gas (CNG) is a good alternative that mainly contain methane and can be stored in compressed fluid form at room temperature. Less emission of pollution and large global stock methane makes it act as clean fuel for vehicles [86.]. At the same time in view of certain disadvantages with CNG, ANG (adsorbed natural gas) with porous materials was suggested[87]. During this period usage of fossil fuels extensively and emission of harmful gases like CO_2 led to development of adsorbents that capture and store carbon gained significance in reducing emissions [88]. Out of many sorbent materials activated carbons are reported to be efficient adsorbents in storing hydrogen, carbon dioxide and methane due to less cost, high porosity large surface area, desired chemical stability and extensive availability [89][90][91][92].Practically, activated carbon must be synthesized to form membranes, electrons and thin films from carbon powder [93].D. Lozano-Castelló et.al.,2002 reported an efficient gas adsorbent by using activated carbon cloth which can be easily handled compared to powder [94]. In addition, fast adsorption was exhibited by activated carbon cloth due to large surface area on comparison with powder and activated carbon with granules. Development of adaptable nanoporous activated carbon cloths exhibiting multiple functions and excellent properties textural wise allowing high storage capacity of hydrogen, methane and carbondioxide was reported [95]. These type of cloths were assembled by deposition of polymer nanoparticles on viscose rayon cloth and then carbonized and activated physically or chemically. To check the potential of this method in meeting energy density target of American Department of Energy high pressure hydrogen, carbon dioxide and methane adsorption measurements were performed[96,97].

Gas storage in solids is technologically important in view of potential applications such as energy, environment, medicine etc. Porous materials that include zeolites, carbon etc. exhibit various composition and architectures suitable for adsorption and can store many gases such as H2, CH4, NO and CO2. At the same time designing of materials with required capacity of adsorption, control on delivery rate etc. is a challenge. The properties of the porous materials need to match with the chemistry of different gases for a given application[98]. New tools are required to develop nanoporous materials for storage of energy gas. Nour F. Attia et al.,2020 developed a high porosity flexible nanoporous activated carbon cloth with surface area of ~2000m2 g−1, total pore volume of 0.85 cm3 g−1 and high nitrogen content. This cloth exhibited excellent hydrogen and methane storage capacities as well as carbon dioxide capturing property when compared to previously reported carbon cloth and values were comparable or higher than already reported for powder activated carbons. Therefor it is reported that this cloth is effective for greenhouse gas such as carbon dioxide during post combustion and precombustion conditions[99] D.P. Broom et.al.,2019 highlighted the idea of hydrogen storage in a much better way in nanoporous materials. They explained various approaches in increasing gravimetric, volumetric H2 storage capacities of np materials and capacity enhancement of a material between upper storage and delivery pressures. They used machine learning and data science technology in searching new materials for hydrogen storage. They reported that various component combinations and substitutions in different porous materials ideally suit to machine learning approach[100].Nandini Das and Jugal Kishore Das, 2020 explained the role of zeolites in storage of hydrogen gas[101 Zeolites are used for separation and storage of hydrogen gas. Since hydrogen gas in heterogeneous form mixed with CO_2 it is to be removed for obtaining pure hydrogen gas. In this context membrane based separation comes into picture with zeolite as key component for developing defect free membrane as well as for storage of hydrogen gas. They have reviewed microporous zeolite for gas storage applications. They highlighted three types of zeolites given by DDR,SAPO34 and Bikitaite out of which the third one show high storage ability of hydrogen gas.

8. Conclusions

This comprehensive review mainly dealt with some of the potential applications of nanoporous materials with emphasis on developments in the last five years. Their applications related to water purification, organic electronics, nano medicine, drug delivery, and gas storage were reviewed. Microprous membranes in water purification were reviewed. The role of nanoporous structures in organic electronic devices was reviewed in view of their significance in biosensors that sense metabolitic properties of human body.

The role of porous silicon nanoparticles in nano-medicine was reviewed along with their applications in drug delivery and its regulation. Finally their role in gas storage was reviewed. Even though remarkable progress is being made in usage of nanoporous materials in for storage of hydrogen the present status and future aspects like volume of adsorbed phase and density that influences storage capacity need to be further analyzed while developing new materials. Similarly usage of porous nanomaterials for drug delivery is always advantageous but concerns related to toxity need to be addressed in future.

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