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Review Article

Review on Energy Storage and Sensor Applications of Microcube Structure Materials

S Suresh[1], Bhagyashree Kesherwani[2], S Brindha[3] and S Ravichandran[4]*

[1]Department of Chemistry, St. Martin's Engineering College, Secunderabad, Telangana, India

[2]Department of Agriculture, KPHEI Jhalwa Affiliated to Prof Rajendra Singh Rajju Bhaiya State University, Prayagraj, Uttar Pradesh, India

[3]Assistant Professor in Computer Applications, Vellalar College for Women, Thindal, Tamilnadu, India

[4]Professor in Chemistry, Lovely Professional University, Punjab, India

***Corresponding Author:** S Ravichandran, Professor in Chemistry, Lovely Professional University, Punjab, India.

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Abstract

Microcube structure materials (MSM) have currently gained attention due to its high surface area, high porosity and other unique surface properties that are certain requirements for materials used in energy storage devices and sensor technology. The hydrothermal/solvothermal approach proved to be effective to synthesize microcube structure materials (MSM) with good surface properties. This review discusses the various preparation methods of microcube structure materials (MSM) and its applications in energy storage devices and sensor applications.

Keywords: Microcube Structure Materials (MSM); Energy Storage; Gas Sensor

Figure 1

Introduction

Cubic nanostructures have gained interest due to their unique properties that arises from the exposing well defined crystal planes and their advantages in designing multifunctional devices [1-7]. The performance of materials with respect to its physical and chemical nature widely depends on their composition, crystal phase and surface properties that has relation to the particle shape and grain size. In novel cubic microstructures the cubic frame ensures the structural stability during repeated deintercalation of lithium ions. In designing hollow cubes some researchers utilized phase segregation combined with selective leaching strategy that has certain disadvantages during the fabrication process. There is significant interest in preparing hollow microspheres by various methods that has application in different fields. In designing the nanostructures, there exists a challenge in engineering unique hollow cubic structure as it is difficult to find

non-spherical templates that can be employed for its synthesis. There is significant interest in synthesizing SnO_2, In_2O_3, and Fe_2O_3 microcubes as promising candidates due to low cost, ecofriendly, and high performance in sensor applications [8-15]. Currently porous SnO_2 microcube materials were widely employed in sensor application due to its high specific surface area, good stability and low density that favors rapid gas diffusion and higher material transportation that resulted in enhanced sensitivity of the sensor. The porous nature and unique morphology of hierarchically porous SnO_2 microcubes has attracted scientists due to their significantly enhanced properties as anode in Li-ion battery and sensor applications. There are various In_2O_3 nanostructures like nanorods, nanocubes, nanoparticles, nanospheres etc. that has potential application in various fields, hollow nanostructure is unique as it shows low material density, large surface area and mesoporous nature. The presence of abundant nanopores was evident on the surface of In_2O_3 microcubes by simple annealing of the precursor prepared by hydrothermal treatment. In microcube materials carbon (or) graphene oxide (GO) based materials were observed to have good specific capacity in energy storage applications.

Synthesis of microcube structure materials (MSM) for energy storage and sensor applications

Hydrothermal method followed by calcination (or) annealing was widely employed in synthesizing microcube materials. Precipitation method was another approach that proved effective to yield novel microcube structure materials with porous nature and high surface area for energy storage and sensor applications.

Hydrothermal/solvothermal synthesis

Microcube structure materials (MSM) were synthesized via different methods with hydrothermal method followed by calcination or annealing being the most common method. The microcube SnO precursor powder was prepared through a hydrothermal method. The SnO powder along with the home-made hydrogel was calcined at 600˚C in inert atmosphere through a disproportionation reaction to obtain Sn/SnO_2@NC microcube. Hollow MnO microcubes were prepared through a facile hydrothermal treatment and subsequent annealing at 500˚C for 6h in N2/H2 (5vol% H_2) to obtain MnO hollow microcubes. The microcube varied from hollow structure to solid structure with different pore size on adjusting the amount of urea. In synthesizing microscale core shell cubic MnO@C (CCM) microcubes, the agaric based solution was prepared first by simple hydrothermal treatment (120˚C/10h) followed by complexation with $KMnO_4$ and secondary hydrothermal treatment at 180˚C/12h to prepare the cubic precursor $MnCO_3$/C. The microscale core shell cubic MnO@C (CCM)microcubes were formed by the subsequent calcinations process. The $ZnSn(OH)_6$ hollow microcubes were synthesized and calcined in argon atmosphere followed by carbon modification via hydrothermal approach to yield $ZnSnO_3$-C hollow microcubes. Hierarchical porous carbon microcubes(PCM) was prepared by in built template method. The Agaric based solution obtained by hydrothermal method (120˚C/10h) was treated with manganese source followed by hydrothermal treatment (180˚C/12h) calcinations and etching yield hierarchical porous carbon microcubes. Surface porosity-rich In_2O_3 microcubes were synthesized through hydrothermal and subsequent simple annealing method with good sensing ability that was attributed to the enhanced surface availability by porosity-creating. $ZnSnO_4$/SnO_2 microcubes were synthesized using a facile single step hydrothermal route at 130˚C followed by calcination that provided more specific surface area with unique microcube structure. A facile one-step hydrothermal method to synthesize a novel nanoarray SnO2 hollow microcube using neither templates nor substrates with a side length of 2-3μm. Uniform Zn_2SnO_4 solid and hollow microcubes were synthesized by a facile hydrothermal route without using any surfactant or capping agent exhibit excellent sensor properties due to its unique structure. Hollow Fe_2O_4/Co_3O_4 microcubes were fabricated using MOF of Prussian blue as soft template through a hydrothermal process at 120˚C/6h followed by calcinations to obtain uniform microbes with rough surface and a side length of around 400nm and an outer shell thickness of 20-40nm. Thermal decomposition of the manganese tin hydroxide yields an intimate mixture of Mn_3O_4/SnO_2 hybrid, this was followed by hydrothermal acid washing process to obtain SnO_2 microcubes. The precursors $ZnAc_2$, Fe^{3+} and $NH_3.H_2O$ were mixed in a facile hydrothermal process to synthesize Zn doped α-Fe_2O_3 microcubes. The mechanism reveal that the complex $[Fe(OH)_6]^{3-}$ reacted with $[Zn(NH_3)_4]^{2+}$ to obtain $m[Fe(OH)_6]^{3-}$ and $n[Zn(NH_3)_4]^{2+}$. The subsequent decomposition of the precursors of $m[Fe(OH)_6]^{3-}$ and $n[Zn(NH_3)_4]^{2+}$ in the hydrothermal process resulted in Zn-doped α – Fe_2O_3. To synthesize hollow indium oxide (In_2O_3) microcubes (HIMC), the precursors $InCl_2$ and L-alanine were utilized in the hydrothermal process to prepare $In(OH)_3$ microcubes (IHMC), The IHMC was annealed at 450˚C for 3h to synthesize HIMC. The $CaSn(OH)_6$ precursor after hydrothermal treatment at 140˚C for 1h

was calcined at 500˚C for 5h in Ar atmosphere to prepare $CaSnO_3$ microcubes with pure perovskite phase and edge length of ~1µm. 3.0 wt % of hierarchical Cu-doped α – Fe_2O_3 microcubes were synthesized through a simple one step hydrothermal reaction and investigated in sensor application. The incroporatio of Cu into the lattice of α-Fe_2O_3 without affecting the original crystal structure was evident from XRD studies. Cu_2O cubes were prepared using simple hydrothermal method followed by the synthesis of CuO@ ZnO core shell heterostructure using different ZnO precurson concentration. In a low-cost hydrothermal process α-MnO_2 interlocked mesoporous microcubes were prepared and tested for its selectivity to NO_2 gas. Carbon doped $MnCo_2S_4$ microcubes (edge length, 10µm) on nickel foam was synthesized by a simple solvothermal approach using low cost chemicals and employed as novel electrochemical energy storage materials as these ternary metal sulfides outperform their oxide counter synthesized copper benzene-1,3,5-tricarboxylate polyhedron ($[Cu_3(btc)_2]_n$) by solvothermal method followed by thermal decomposition to yield hollow porous CuO/C composite microcubes by using MOF templates. In_2O_3 microcubes (X Zhou., *et al*. 2017) was prepared by hydrothermal treatment at 150˚C followed by heating at 400˚C for 3 minutes in O_2 to get microcube structure with high specific surface area (30.3634m^2/g). 5at% Al doped In_2O_3 was synthesized through a simple solvothermal route with high specific surface area (19.91m^2/g) and excellent sensitivity.

Precipitation methods

Precipitation method is another efficient approach to synthesize microcube structure materials. Ni-doped cobalt hexacyanoferrate(NiCoHCF) microcubes were prepared by co-precipitation method in room temperature. The doping of nickel ions on the CoHCF microcubes resulted in reduced grain size of the CoHCF microcubes and this was evident from SEM and XRD studies. The $Co_3[Co(CN)_6]_2$ synthesized by modified co-precipitation method was utilized to prepared Co_3P_3 microcubes and were coated with PPy to synthesize CoP_3@PPy microcube. The H-$ZnSnO_3$ microcubes were synthesized through a co-precipitation method followed by calcination process. The as synthesized H-$ZnSnO_3$ microcubes were carbon coated via. a glucose-assisted hydrothermal process to obtain H-$ZnSnO_3$@C microcubes (Ma., *et al*. 2019). The $ZnSn(OH)_6$ microcubes were prepared by a facile co-precipitation method and mixed with graphene oxide prepared by modified hummers method in a facile ingenious two-step strategy to synthesize the N/S dual-doped reduced graphene oxide (rGO) encapsulating hollow $ZnSnS_3$ microcubes (N/S-rGO@$ZnSnS_3$ microcubes). The $ZnSnO_3$ hollow microspheres obtained by in-situ precipitation method followed by hydrothermal treatment using different doping amount of SnO_2 to obtain $ZnSnO_3$/SnO_2 concave microcubes. The Co-PBA microcubes were synthesized by a simple precipitation method followed by the growth of $Ni(OH)_2$ on Co-PBA microcubes through a facile hydrothermal process. The Co_3O_4@NiO microcubes obtained were functionalized with Pt through a modified impregnation method to synthesize Co_3O_4@ NiO@Pt microcubes. The cube like hollow zinc hydroxystannate ($ZnSn(OH)_6$) HCs decorated with $Pd(OH)_2$ was prepared through self templating precipitation method the subsequent annealing and acid etching process yields PdO-SnO_2 hollow microcubes with enhanced surface area (103m^2/g) and more active chemical sites. The $CoSn(OH)_6$ precursor formed by co-precipitation undergoes thermal decomposition at 700˚C for 3h to yield Co_3O_4/SnO_4 hybrid microcubes. This was followed by dissolution of the Co_3O_4 phase to yield porous SnO_2 microcubes. Other methods were also used in the synthesis of porous microcube structure materials. The Prussian blue (PB) precursor prepared by liquid phase synthesis, was utilized as template and mixed with $Mn(Ac)_2$ in ethanol followed by heat treatment in air to yield MnO/$MnFe_2O_4$ microcubes. Graphene oxide (GO) synthesized by modified hummers method and GeO_2 particles are interconnected with graphene sheets by adding sodium borohydride solution. The obtained precursor was calcined in Argon atmosphere to synthesize GG-RGO composite microcube. In a low temperature phosphorization process employing Prussian blue as reaction template a well designed porous core-shell structured Co@FeP microcubes were interconnected with reduced graphene oxide (RGO) to obtain RGO interconnected core shell structured RGO@CoP@FeP porous microcubes. The $PbBr_2$ and CsBr precursors were dispersed in DMF and poured on ITO glass substrate and subsequently toluene was added to grow ligand free microcubes in a process that is extremely fast, easy and oxygen free environment to prepared well crystalline $CsPbBr_3$ microcubes. The $ZnSn(OH)_6$ microcubes were synthesized through a facile chemical solution method followed by calcinations in argon atmosphere to obtain $ZnSnO_3$ double shell hollow microcubes. The SiO_2 hollow microcube was synthesized using $MnCO_3$ microcube as hard template and mixed with $CoCl_2$. $6H_2O$ and calcined in Ar atmosphere at 700˚C to get amorphous Co_2SiO_4 hollow microcube. The Prussian blue (PB) precursor was kept at 550˚C for 6h under air atmosphere

to prepare porous microcubes. PDA acted as reducing agent and carbon source, Tollen's reagent was used as Ag precursor in a novel hydrothermal annealing procedure to prepare Ag-introduced iron oxide microcubes (Fe_2O_3-C-Ag). The binary $Co_{0.33}Mn_{0.67}CO_3$ template formation with microcube structure was induced by ammonia evaporation followed by Li and Ni permeation through calcinations at 800˚C for 16h to obtain $Li_{1.2}Mn_{0.5}Co_{0.25}Ni_{0.05}O_2$. α–$Fe_2O_3$ microcubes with 2~3μm size was synthesized using a facile thermal treatment of iron oxalate dihydrate microcubes obtained by hydrothermal reaction. The α–Fe_2O_3 microcubes posess a surface area and pore volume of $36m^2/g$ and $0.15cm^3/g$ respectively. Porous Cu_2O microcubes were prepared through a simple sonochemical route with promising microstructure and employed in biosensor applications. $NiC_4H_6O_4$ was mixed with $ZnSn(OH)_6$ in ethanol and calcined to obtain pure Ni^{2+} sensitized monodisperse amorphous zinc tin oxide (a-ZTO) microcubes. The Fe-based MOF precursor, $Fe_4[Fe(CN)_6)_3$, and $NiC_4H_6O_4.4H_2O$, $CoC_4H_6O_4.4H_2O$ as co-templated precursors were utilized to synthesize hierarchical Ni-doped $CoFe_2O_4$. The Ni/Co substitution in the microcubes can be controlled systematically to pepare hierarchical $Ni_xCo_{1-x}FeO_4$($0 \leq x \leq 0.5$) microcubes. The precursor ($MnSn(OH)_6$) on thermal decomposition yields Mn_3O_4 and porous tetragonal SiO_2. This was followed by simple acid-washing of hollow cube like Mn_3O_4/SnO_2 hybrid to obtain hollow porous SnO_2 microcubes. To synthesize Ni-doped SnO_2 microcubes, the precursors were subjected to thermal decomposition and this was followed by simple acid washing of the NiO/SnO_2 hybrids to leach out the cubic phase NiO and yield the porous microcubes. Indium oxide microcubes (In_2O_3 MCs) were prepared by a facile low-temperature wet chemical synthesis method. The body-center cubic crystal structure of In_2O_3 MCs was evident from XRD, Raman and XPS studies.

Energy storage applications of microcube structure materials

Nitrogen-doped carbon (NC) coating encapsulating heterostructural Sn/SnO_2 microcube powder (Sn/SnO_2@NC) as promising anode material for lithium ion batteries. The Sn/SnO_2@ NC electrode presents a high intitial discharge specific capacity of 1058 $mAhg^{-1}$ at 100 mAg^{-1} The NC coating can effectively relieve the volume effect to improve the cycling performance and the uniquely heterostructured microcube can accelerate the transfer rate of lithium ions by shortening the transmission path. The synthesized $MnO/MnFe_2O_4$ microcubes as anode material for Li-ion batteries. The discharge specific capacity was reported to reach 898 $mAhg^{-1}$ with 100 cycles of 100 mAg^{-1} current density. The Synergistic effect of the bimetal and porous cubic structure provides excellent electrochemical performance for the $MnO/MnFe_2O_4$ microcubes. The porous structure of $Mn/MnFe_2O_4$ microcube provides more insertion sites for lithium and increased structural stability. The prepared $CsPbBr_3$ microcube as anode for energy storage application. The CsPbBr3 microcube based anodes was reported to have high specific capacity of 549 $mAhg^{-1}$. The presence of more interfacial area between the $CsPbBr_3$ microcube and the electrolyte, with more active sites on the exposed microcube facets favour the Li-ion intercalation. The porous CoP_3@PPy microcubes were utilized as anode material for lithium-ion batteries that exhibits high specific capacity of 1310 $mAhg^{-1}$ at 100mAg^{-1}. The hollow MnO microcubes with high surface area and stable hollow structure and tested it as potential anode material for lithium-ion batteries. The hollow MnO microcube exhibits a high reversible capability of 914.6 $mAhg^{-1}$ at 0.5C even after 200 cucles. The hollow MnO_2 microcube was prepared through a facile hydrothermal treatment. The porous MnO hollow microcube (S3) was prepared by adjusting the amount of urea (15mmol) shows excellent cycling stability and a specific capacity of 923 $mAhg^{-1}$ at 378m Ag^{-1} after 200 cycles. The synthesized core-shell MnO@C microcubes (CCM) through simple hydrothermal treatment and calcinations process. The CCM sample posess a high specific capacity of 1147 $mAhg^{-1}$ at 0.1 Ag^{-1} with a reversible capacity retention of 802 $mAhg^{-1}$ after 950cycles at 1 Ag^{-1}. Luo., *et al*. (2019) synthesized porous carbon microcubes (PCM) with high specific surface area ($1052m^2/g$) for energy storage application. The PCM electrode in lithium ion battery anode reaches a high specific capacity of 849 $mAhg^{-1}$ at $1Ag^{-1}$. The PCM electrode as a supercapacitor (SC) electrode posess high gravimetric specific capacitance of 338Fg^{-1} at 0.5 Ag^{-1}. The amorphous $ZnSnO_3$-C hollow microcubes and used as anode material for lithium ion batteries. The $ZnSnO_3$-C hollow microcubes posess an approximate shell thickness of 145nm and average edge length of 1.0 μm. The amorphous $ZnSnO_3$-C hollow microcubes exhibit a high reversible capacity of 703 $mAhg^{-1}$ at 100 mAg^{-1} after 50 cycles.

The CuO/C composite microcubes by using metal-organic framework templates having excellent cyclic performance and rate capability for lithium-ion batteris. The CuO/C composte microcubes possess high reversible capacity of 510.5 $mAhg^{-1}$ at 100mAg^{-1} after 200 cyles. When used as anode material for lithium ion battery the CuO/C composite microcubes having nanosized

subunits in the shell with special structure, exhibit excellent cycling stability and rate capacbility for Li-ion insertion/extraction. The synthesized amorphous $ZnSnO_3$ double-shell hollow microcubes through a facile chemical solution method in argon and used it as a promising electrode material in lithium ion batteries. The D-$SnSnO_3$ microcube maintain a high reversible capacity of 741 $mAhg^{-1}$ at 100 $mAhg^{-1}$ after 50 cyles. The discharge capacity of D-$ZnSnO_3$ was 1198 $mAhg^{-1}$ at 100 mAg^{-1}. The prepared heterostructured hollow $ZnSnO_3$@C microcube (H-$ZnSnO_3$@C) composite and tested the electrochemical performance. The H-$ZnSnO_3$@C microcube exhibits high specific capacity of 817 $mAhg^{-1}$ at 0.1 Ag^{-1} after 100cycles. The surface carbon coating shell of $ZnSnO_3$@C microcube can improve the electrical conductivity with unique structural benefits that results in high rate capability and good cyclic stability. A facile hydrothermal method and calcining process and tested as anode material in lithium ion battery. The porous and amorphous structure of hollow Ca_2SiO_4 microcube improved the surface area and resulted in good electrochemical property. The hollow Ca_2SiO_4 microcube was reported to have higher specific capacity and longer cycling life of 610 $mAhg^{-1}$ at 500 Ag^{-1} after 380 cycles. The Ge/GeO_2 graphene oxide microcube (GG-RGO) exhibit good electrochemical properties. The GG-RGO composite microcube can retain a high reversible specific capacity of 933 $mAhg^{-1}$ at 100 mAg^{-1} after 50 cycles. The GG-RGO composite microcube was reported with the specific discharge capacities of 1375, 1360, 1309, 1179 and 927 $mAhg^{-1}$ at the current densities of 0.1, 0.2, 0.5, 1.0 and 2.0 mAg^{-1}. The prepared silver incorporated Fe_2O_3-C(Fe_2O_3-C-Ag) porous microcubes with improved conductivity and tested as anode materials for Lithium ion batteries (LiBs). The introduction of noble metal (Ag) and carbon to transition metal oxide in the porous Fe_2O_3-C-Ag microcube can efficiently increase the conductivity of the material. The reversible specific capacity of Fe_2O_3-C-Ag microcube with 10%(wt%) Ag content was 858 $mAhg^{-1}$ at 100 mAg^{-1} after 200 cyles. The presence of Ag nanoparticles on the porous microcube structure can significantly improve the conductivity of the material. The $MnCO_3$ microcube@MnO_2 heterostructure exhibits high capacities of 363Fg^{-1} and 290Fg^{-1} at 1 Ag^{-1}. The novel $Li_{1.2}Mn_{0.5}Co_{0.25}Ni_{0.05}O_2$ microcube exhibits high initial discharge capacity of 272.9 $mAhg^{-1}$ at 20 mAg^{-1}.

S. No	Microcube materials	Specific capacity	Current density
1	Co@PPy microcube	1310 $mAhg^{-1}$	100 mAg^{-1}
2	D-$ZnSnO_3$ microcube	1198 $mAhg^{-1}$	100 mAg^{-1}
3	Sn@SnO_2@NC microcube powder	1058$mAhg^{-1}$	100mAg^{-1}
4	MnO@C microcubes	1147 $mAhg^{-1}$	0.1Ag^{-1}
5	Hollow CuS@MoS_2 microcubes	998 $mAhg^{-1}$	-
6	GG-RGO composite microcube	933 $mAhg^{-1}$	100 $mAhg^{-1}$
7	MnO/$MnFe_2O_4$ microcube	898 $mAhg^{-1}$	100 mAg^{-1}
8	$CsPbBr_3$ microcube	549 $mAhg^{-1}$	-
9	MnO microcubes	923 $mAhg^{-1}$	378 mAg^{-1}
10	Porous carbon microcubes (PCM)	849 $mAhg^{-1}$	1 Ag^{-1}
11	$ZnSnO_3$-C hollow microcubes	703 $mAhg^{-1}$	100 mAg^{-1}
12	CuO/C composite microcubes	510.5 $mAhg^{-1}$	100mAg^{-1}
13	H-$ZnSnO_3$@C microcube	817 $mAhg^{-1}$	0.1 Ag^{-1}
14	Co_2SiO_4 microcube	610 $mAhg^{-1}$	500 mAg^{-1}
15	Porous (Fe_2O_3-C-Ag) microcubes	858 $mAhg^{-1}$	100 $mAhg^{-1}$
16	N/S-rGO@$ZnSnS_3$ nano microcube	501.7 $mAhg^{-1}$	0.1 Ag^{-1}
17	$MnCO_3$microcube@ MnO_2	-	-
18	Carbon doped $MnCoS_4$ microcube	525.7 $mAhg^{-1}$	5 Ag^{-1}
19	$Li_{1.2}Mn_{0.5}Co_{0.25}Ni_{0.05}O_2$ microcube	272.9 $mAhg^{-1}$	20 mAg^{-1}
20	CoP@FeP microcubes interconnected by rGO	456.2$mAhg^{-1}$	100 mAg^{-1}

Table 1: Microcube materials used in energy storage applications.

Sensor Applications of Novel Microcube Materials

The $ZnSnO_3$/SnO_2 concave microcubes prepared by a simple hydrothermal method. The presence of SnO_2 nanoparticles on the rough surface of the concave microcubes resulted in high surface area and more active sites for gas adsorption-desorption. The $ZnSnO_3$/10wt% SnO_2 concave microcube displayed a high gas sensing response (19.1) towards 50 ppm acetone at an

operating temperature of 260˚C. The highest gas sensing response was with 3wt% pt doping for the sensor based on Co_3O_4@NiO@ Pt microcube at 200˚C. The novel hollow Co_3O_4@NiO-2.0@ Pt3.0 microstructure exhibits high specific surface area and high resistance with a response value of 250.0 towards 100 ppm H_2S at an optimum working temperature of 200˚C. Yang., *et al*. (2020) prepared surface porosity rich In_2O_3 microcube using a combined hydrothermal and annealing method and studied the NO_2 sensing. The sensor response of In_2O_3 microcube was 17.3 towards 1 ppm NO_2 at a temperature of 100˚C. Zn_2SO_4/SnO_2 microcubes (ZTO/ SnO_2) synthesized through a facile single step hydrothermal route at 130˚C and tested the gas sensing property. The Y doped ZTO/ SnO_2 microcubes exhibit higher response (46.07) for 100 ppm formaldehyde(HCHO) at a lowered optimal working temperature of 210˚C. The high gas sensing performance of Y doped ZTO/SnO_2 microcubes was attributed to the smaller size and the unique microcube structure that provided more specific surface area resulting in superior sensing property in detecting formaldehyde. The nano arrays SnO_2 hollow microcubes synthesized through a simple "one pot" template free hydrothermal method and studied the gas sensing properties. The response of the gas sensor to 100 ppm of ether was reported to rise gradually with the increase in heating voltage and reached a maximum response value of 32.079 at an optimum heating voltage of 4.5V. The mesoporous hematite cubic framework (α-Fe_2O_3 microcube) synthesized and used as formaldehyde (HCHO) gas sensor. The α-Fe_2O_3 microcube possessed a uniform and cubic geometry with a high specific surface area of 36m^2/g and ordered framework structure. The gas detection ability of α-Fe_2O_3 microcube was excellent even at low HCHO concentration (~50ppb) with a high response value of 5.2 at 1 ppm. The structure of the nanoflower built hollow microcube was unique with large surface area and increased gas diffusion channels that resulted in good gas sensing property. The In_2O_3 microcubes (In_2O_3 MC) synthesized *via* a simple hydrothermal method and investigated its gas sensing properties. The In_2O_3 microcubes exhibit good gas sensing performance with high sensitivity and selectivity towards ethanol vapour. The high gas sensing performance of In_2O_3 MCs was attributed to its large specific surface area and its well exposed facets. The In_2O_3MCs reached the highest response value (23) for 100 ppm ethanol at 210˚C. The hollow Fe_2O_3/Co_3O_4 microcubes that exhibits higher gas detection of aceton compared to that of pure Fe_2O_3 and Co_3O_4. The response value was 21.2 towards 20 ppm acetone at a shorter time of 5 sec and working temperature of 200˚C. The porous SnO_2 microcubes posess large number of active sites for enhanced sensitivity, fast response and short recovery time for formaldehyde and ethanol vapours. The SnO_2 microcubes exhibit good response even at low concentration (1 ppm) of formaldehyde and ethanol with a value of 7.7 and 4.8 respectively. The Sensor response value increased with increase in concentration (100 ppm) of formaldehyde and ethanol with a value of 57.4 and 45.8 respectively. The synthesized Pd-doped SnO_2 hollow microcubes (PdO-SnO_2 HCs) through a self-templating precipitation process, followed by annealing and acid etching process. The response of PdO-SnO_2 HCs doping of Pd with 1% molar ratio was excellent towards ethanol (200 ppm) at 300˚C with a value of 90. The high gas sensing performance of PdO-SnO_2 HCs was due to the special hollow interior void architecture that provided high surface area and more active chemical sites. The Zn doped α-Fe_2O_3 microcubes synthesized *via* a facile hydrothermal method and tested the gas sensing properties. The sensor response value was 4.7 for 10 ppm acetone and reached 44.3 for 300 ppm acetone at 240˚C. The acetone gas molecules are chemisorbed at the active sites on the surface of Zn-doped -Fe_2O_3 microcubes.

The synthesized Ni^{2+} sensitized monodisperse amorphous zinc tin oxide (a-ZTO) microcubes and tested the formaldehyde sensing performance. XPS studies show the presence of more chemisorbed oxygen and oxygen vacancies on the surface of a-ZTO microcubes due to Ni^{2+} sensitization. The hollow In_2O_3 microcubes (HIMC) synthesized by hydrothermal method followed by air annealing and tested the gas sensing performance. The HIMC exhibits huge sensing response (1401) to 100 ppm NO_2 gas with a very short response (Rs=16s) and recovery (Rc=1655) time at 100˚C. The HIMS was highly selective and sensitive for NO_2 gas with the response and recovery time being very short. The microcube material exhibits selective response for acetone in comparison with gases such as ethanol, methane, NH3 and trimethylamine at 240˚C. the $Ni_xCo_{1-x}Fe_2O_4$ composite microcube exhibits good acetone sensing properties with the strongest response value of 1.67 at 240˚C. The porous SnO_2 microcubes prepared and investigated the gas sensing properties of formaldehyde and toluene as target gases. The high selectivity for formaldehyde and toluene was attributed to the hollow structure and high porosity of the microcubes. The hollow porous SnO_2 microcube exhibits good response value of 42.4 and 16.1 for 100 ppm of formaldehyde and toluene at 280˚C. The porous SnO_2 microcubes exhibit response value of 10.7 and

5.8 respectively for 100 ppm of toluene and benzene. the surface area of the SnO_2 microcube was 42.7m^2/g and the porous nature of the microcube results in high sensitivity, fast response and short recovery time for toluene and benzene vapours. The Al-doped In_2O_3 microcubes synthesized by a facile hydrothermal process and investigated its ethyl acetate sensing properties. The Al-doped In_2O_3 exhibits superior ethyl acetate sensing ability with a response value of 56.3 to 100 ppm ethyl acetate at 184˚C. The high ethyl acetate sensing ability of Al-doped In_2O_3 gas sensor was attributed to larger chemical potential gradient, more electron transfer and the changes in grain size. The $CaSnO_3$ microcubes synthesized *via* facile hydrothermal method with subsequent calcinations at 500˚C for 5h. The $CaSnO_3$ microcubes exhibit high sensitivity (1.45) and selectivity to ethanol as compared to ammonia (1.3) and acetone (1.15). The sensitivity of the $CaSnO_3$ microcube towards 600 ppm ethanol, ammonia and acetone at 250˚C was studied. The Cu-doped α-Fe_2O_3 higherarchical microcubes through hydrothermal method and tested the gas sensing properties. The 3.0wt%Cu-doped α-Fe_2O_3 microcubes posess high response value (19) for 100 ppm ethanol at 225˚C. XRD results indicate that Cu ions entered the crystal lattice of α-Fe_2O_3 nanoparticles with the lattice constants of the doped samples being slightly smaller than the pure α-Fe_2O_3. The high gas sensing performance of CuO@ZnO microcubes was attributed to the coating of ZnO shell and the improvement of the effective electrical contact between CuO-ZnO heterojunction. The CuO@ZnO microcube exhibits 2.6 times higher response than the pristine CuO sensor for ethanol vapours at 240˚C. It has been synthesized porous Ni-doped SnO_2 microcubes and studied the gas sensing properties [10]. The high porosity and Ni-doping resulted in high sensitivity, rapid response and short recovery time for formaldehyde and ethanol vapours. The response value of porous Ni-doped SnO_2 microcubes for 50 ppm formaldehyde and 100 ppm ethanol was 33.9 and 33 respectively. The α-MnO_2 microcubes displayed good response (33) for 100 ppm NO_2 gas at 150˚C.

S. No	Micro cube gas sensing materials	Gas Concentration	Operating temperature	Response
1	In_2O_3 MCs	30 ppm NO_2 gas	60˚C	1884
2	Hollow In_2O_3 microcubes	100 ppm NO_2 gas	100˚C	1401
3	Co_3O_4@NiO microcubes functionalized with Pt	100 ppm H_2S	200˚C	250
4	$ZnSnO_4$ hollow microcubes	200 ppm acetone	260˚C	141.7
5	PdO-SnO_2 HCs	200 ppm ethanol	300˚C	90
6	Al-doped In_2O_3 microcubes	100 ppm ethylacetate	184˚C	56.3
7	0.75% Ni^{2+} sensitized a-ZTO microcubes	100 ppm HCHO	200˚C	53.22
8	Porous SnO_2 microcubes	100 ppm HCHO	280˚C	57.4
		100 ppm ethanol		45.8
9	Zn doped α – Fe2O3 microcubes	300 ppm acetone	240˚C	44.3
10	Y doped ZTO/SnO_2 microcubes	100 ppm HCHO	210˚C	46.07
11	$ZnSnO_3$/SnO_2 concave microcube	50 ppm acetone	260˚C	19.1
12	In_2O_3 microcube	1 ppm NO_2	100˚C	17.3
13	SnO2 hollow microcubes	100 ppm ether	4.5V	32.079
14	α – Fe_2O_3 microcube	1 ppm HCHO	300˚C	5.2
15	In_2O_3 microcube	100 ppm ethanol	210˚C	23
16	Hollow Fe_2O_3/Co_3O_4	20 ppm acetone	200˚C	21.2
17	$Ni_{0.1}Co_{0.9}Fe_2O_4$ composite microcube	200 ppm acetone	240˚C	1.67
18	Hollow porous SnO_2 microcube	100 ppm HCHO	280˚C	42.4
		100 ppmToluene		16.1
19	Porous SnO_2 microcubes	100 ppm Toluene	240˚C	10.7
		100 ppm Benzene		5.8

20	$CaSnO_3$ microcube	600 ppm ethanol	250˚C	1.45
		600 ppm ammonia		1.3
		600 ppm acetone		1.15
21	3.0 wt% Cu doped α-Fe_2O_3 microcubes	100 ppm ethanol	225˚C	19
22	CuO@ZnO microcubes	-		-
23	Ni doped SnO_2 microcubes	50 ppm HCHO	260˚C	33.9
		100 ppm ethanol		33
24	α - MnO_2 mesoporous microcubes	100 ppm NO_2 gas	150˚C	33

Table 2: Microcube materials in Gas Sensor applications.

Conclusion

The literature work on various preparation methods of microcube structure materials and its applications in energy storage devices and sensor applications are significant interest for researchers to to synthesize microcube structure materials with good surface properties. Microcube structure materials have currently gained attention due to its high surface area, high porosity and other unique surface properties that are certain requirements for materials used in energy storage devices and sensor technology. Definitely this review work will bring fruitful results in future.

Figure 2

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