Research and Analysis Journals 5(08): 36-57, 2022

e-ISSN: 2589-9228, p-ISSN: 2589-921x

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Reserch Article

Critical Review on Synthetic Routes and Catalytic Applications of Hollow Nanomaterials

Tayyaba Azam[1], Fawad Ahmad[1*], Zaheer Ahmad[1]

[1]Department of Chemistry University of Wah Quaid Avenue, Wah Cantt (47040) Punjab, Pakistan

Abstract:

The most significant trend for the improvement of material's performance is increasing of their surface area. So the pore volume and surface to volume ratio enhance as well. That leads huge attention from various fields and scientists. Hollow nanomaterials are unique materials to evolve because of special attributions like surface area as these materials have wide surfaces than others. Synthesis of hollow nanomaterials has been special not only for obtaining the size and shape of particles with chemical composition but also have command on hollowness that characterize such materials. Hard-template, self-template, soft template, simple and template free methods are commonly used synthetic strategies. The characterization has based on scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Hollow nanomaterials have wide range applications in catalysis, sensors, lithium ion batteries, water treatment, drug delivery, nanoreactors and dye sensitized solar cells etc. Herein we had summarized the strategies for preparation of HNMs and their application.

Keywords: Hollow nanomaterials, template based synthesis, catalysis, high surface area, polymer templates, carbon hollow shells, Emulsion Templates

Introduction:

Nanostructures having a hole or inside cavity refers as hollow nanostructures. These materials usually contain large fractions of void spaces.[1] Hollow nanomaterials are solid structures made of distinct shell and void spaces having nanoscale dimension.[2] These materials are classified on the basis of shapes (hollow tubes, boxes, fibers and spheres), number of outer shells (single, double and multi-shelled hollow nanomaterials), compositions of shell(polymer, ceramic, metal and composite) etc. Various categories may combine to obtain more precise and authentic classification of hollow nanomaterials.[3]When hollow structure bear spherical or cubic/tubular morphology, they form multi-shelled, rattle or yolk-shell hollow spheres and cube in box, multi-walled tubes or wire in tube structures, etc. The templates have designed from various conventional and nonconventional ways (air bubbles, liquid droplets).[4]They have been evolved from organic or inorganic nanostructures, polymer nano-spheres and classic colloidal particles of silica. More than silica and polymer many functional groups e.g. metals, chalcogenides, metal oxides, and complex compounds are used in the formation of shell structures.[5]

Hollow nanomaterials are quite better from their solid counterpart of similar size and composition because of great loading capacity, huge surface area and very low density.[6] These characteristics enhances their uses and applications in a variety of disciplines i.e. catalysis (support material, active catalyst), biomedicine (drug delivery carriers), energy storage (imaging contrast agents), sensors, lithium ion batteries (as anodes or cathodes) nanoreactors, water treatment and environmental remediation.[7]

Solid precursor within interior void used to synthesize hollow nanomaterials however to maintain uniformity, controlled morphology in cost effective and reproducible way is quite difficult.[8] Hard templating approach transcendentally the easiest and accessible one among soft templating and self templating approaches. Metal nanoparticles or ceramics, silica, polymer beads and carbon used to form hard templates.[9] Typical process includes coating of shell material on the outer surface of solid precursor, which leads to hollow material after selectively removing the template.[10] As coating process helps to measure shell thickness, size and shape of void associated with the shape and size of template. Some process supports complete removal of templates as they do not contribute in the final composition of product.[11]

Droplets, micelles/vesicle, gas bubbles and emulsions used in fluid form, as soft template may not remove in coating process. [12] Complicated, highly tune able external and internal structure with less uniformity in products obtained in soft template approach as compared to hard template strategy.[13] Hollow nanomaterial can be synthesized directly without any template in self-template approach.[14]Self-template approach has various advantages as reduction in production cost, flexible scaling process, ease in synthesis and has more practical applications than other approaches.[15]Although its applications are lemmatized due to specific composition of hollow nanostructures.[16]

These three approaches used together or separately according to the structure design and mechanism because the boundaries among them are flexible with the advancement of nanotechnology.[17] For example, etching process could be self templating because the template converted in to hollow nanomaterial and it turns to hard template as the removed core has shown sacrificial template nature.[18] By incorporating hard and soft templating strategies hollow nanostructures of mesoporous shells synthesized successfully.[19]

Fig 1: Hollow, multi-shelled and yolk-shelled nanostructures

In this review we discuss hard, soft and self-template approaches with detail mechanism, characteristics and controlled morphology of hollow nanomaterials.[20] Then we discuss their vast applications in various fields.

Hard template approach:

This is the most general or applicable technique for the generation of hollow nanomaterials.[21] In this method hollow nanomaterials obtained by selectively removing the core. [22]Surface functionality (polarity, surface charge) can be changed by surface modification process leads to successful coating on the outer surface of template.[23]

Hydrothermal or sol gel process are used to coat the template with shell material.[24] Similarly, dissolving in particular solvents, calcinations or thermal analysis and etching techniques used for selective removal of hard template.[25] Calcinations and reduction process are also used to obtain better characteristics of shells (final product).

Fig 2: Formation of shell and removal of template

A variety of hard templates use to manage the morphology of hollow nano structures will briefly discuss here.[26]

Polymer based hard templates:

Poly (methyl methacrylate) (PMMA), formaldehyde resin and polystyrene with derivatives used in this simple and popular method of synthesizing hollow nanomaterial.[27] Selective removal of template is easiest one among all techniques.

Polystyrene templates:

Polystyrene colloidal templates:

Caruso and coworkers in 1998, first time synthesized inorganic silica and polymer hybrid hollow spheres.[28] They used colloidal template on which polymer multilayer and silica nanoparticle were self-assembled inlayer by layer fashion.[29]

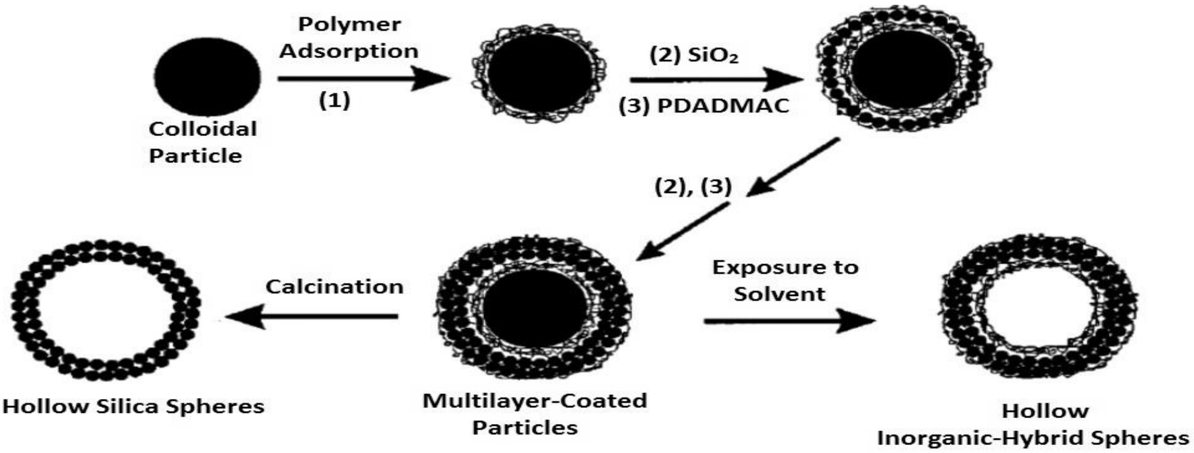

Fig3: Generation of inorganic and hybrid hollow spheres through templating against polystyrene. Reproduce with permission from ref 29. Copyright 1998. The American Association for the Advancement of Science

Templates were made of polystyrene negatively charged latex particle (d=640 nm) where poly(diallyl dimethyl ammonium chloride) (PDADMAC) three-layer cationic film was deposited.[30] SiO_2(d=25nm) particles adsorbed on positive surface. Then polystyrene templates removed with the help of THF dissolution and additional calcination.[31] Various strategies could have applied to adjust the thickness of shell (10-100 nm) such as tuning of SiO_2-PDADMAC layer deposition.[32] The coated particles help to remove the core of melamine-formaldehyde, when come in contact of (DMSO) dimethyl sulfoxide or acidic solution having p^H less than 1.6.[33]

White, tang and coworkers, synthesized hollow carbon nanospheres by the help of polystyrene templates.[34] A mixture of desired size polystyrene latex was heated at 180°C for 20 h comprises of carbon and d-glucose precursor.[35] Carbonaceous shell then graphitize by heating the composite mixture above 500°C.[36]Polystyrene and glucose ratio helps to adjust thickness of carbon shell (~12 nm here). [37] Polystyrene templates are extremely effective in the generation of various hollow shell materials e.g. mesoporous silica hollow nanostructure, double shelled hollow silica microspheres, mesopore free hollow silica particles, double-shelled TiO_2/SnO_2 composite hollow spheres.[38]

Yang et al. used polystyrene beads (amine functionalized) as template to synthesize titinia and silica nanoparticles.[39] Hydrolyzed tetra-methoxysilane (TMOS) and titanium tert-butoxide (TBOT) were precursor in the synthesis of titinia and silica shell respectively.[40] At last polystyrene core removed by high temperature calcination process or by dissolving in ethanol and dichloromethane mixture.[41]

Song et al. reported hybrid hollow spheres of SiO_2/TiO_2.[42]This nitrogen doped hollow structure prepared by using trimethylamine (nitrogen source).[43]One step calcination process leads removal of polystyrene core, crystallization of $TiO_2$and doping process simultaneously. [45]

Polystyrene crystalline array as hard template:

According to Xia and coworkers polystyrene beads via crystalline array used as a template in the generation of mesoscale hollow spheres of TiO_2 and SnO_2.[46] Preparation of polymer beads require fabrication of two glasses substrate along aqueous solution, which then evaporated at room temperature leads to polymer beads shrank by ~20%.[47] Polystyrene beads were separated by infiltration of packing cell through capillary action utilizing a solution of sol-gel precursor solution.[48]Polystyrene beads have dense coating around them which is a precipitated gel. When precursors exposed to the moisture, they hydrolyzed into metal oxide sol and gel.[49] Polystyrene templates removed when substrates in toluene and packing cell immersed together.[50] Further sonication of sample in water bath leads hollow ceramic sphere. Shell thickness and size of void (hollow sphere) could be easily commanded by the measurement of diameter necessary for polystyrene template and the congregation of sol gel precursor solution.[51] With functionalized interior surfaces, ceramic mesoscopic hollow spheres obtained through polystyrene crystalline array in a simple way.[52]

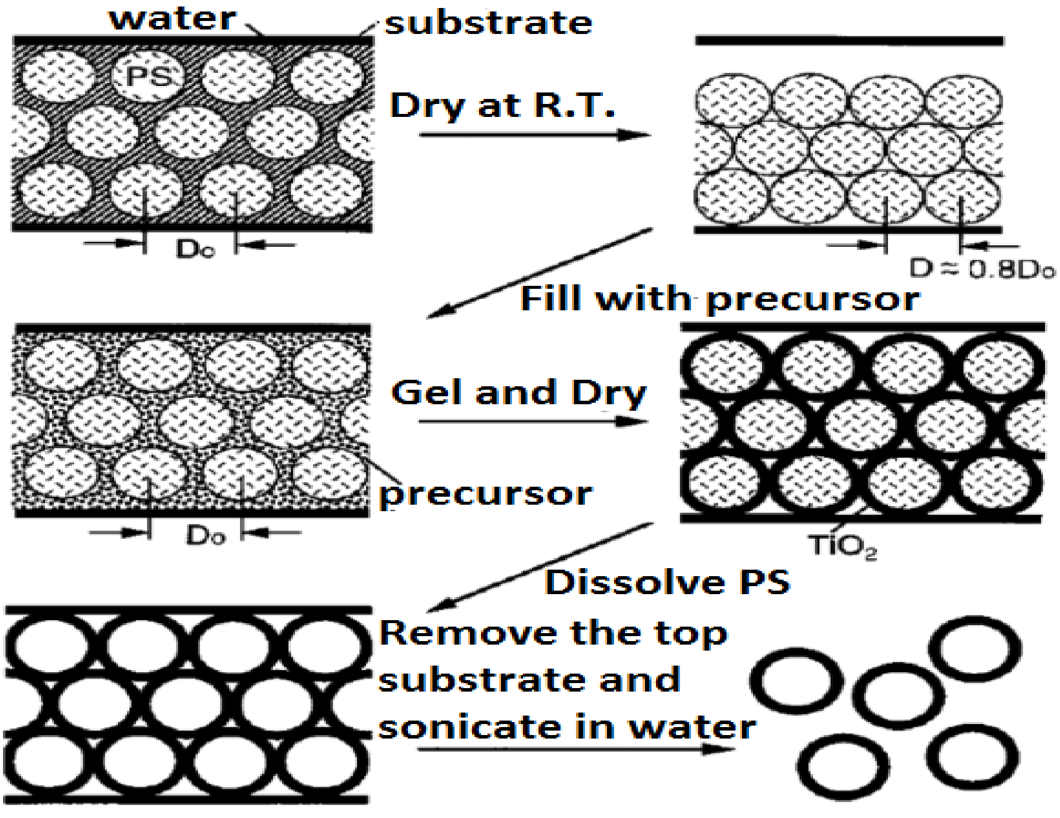

Fig 4: Cross sectional area of cell with outline of procedure. Reproduce with permission from ref 48. Copyright 2000 John Wiley and Sons

Chen et al. reported Single or multiple layer polystyrene crystals use as templates for the generation of hollow silver spheres.[53]

Actually these synthesized hollow spheres of silver are two and three dimensional ordered structure.[54] Polystyrene crystalline array also acts as template for the generation of a number of zinc oxide hollow nanostructures i.e. ZnO hollow hemisphere, urchin like ZnO thin films and also for carbon hollow nanospheres.[55]

Synthesis of shell layer on polystyrene surface results due to the assembly on substrate followed by oblique angle deposition and electro deposition process.[56] Organic dissolution or calcination used to remove polystyrene templates to obtain successful structure array.[57]

Formaldehyde resin templates:

Melamine formaldehyde template:

Melamine formaldehyde (MF) colloidal particles exercised in terms of hard template for the generation of hollow nanomaterials.[58] However, these weakly crossed- linked particles decomposes in aqueous medium having p^H value below 1.6.[59] Melamine formaldehyde particles slowly dissolved in ammonia solution. Choi et al. synthesized yolk shell structured hollow nanoparticles by core-dissolution method.MF@SiO_2 core–shell nanomaterials results when melamine formaldehyde particles coated with silica through sol-gel method.[60] These melamine formaldehyde nanomaterials then immersed in to ammonia solution and dissolved gradually. Melamine formaldehyde core size could easily tune as it depends on exposure time and dissolution is a slow process in this case.[61]Core shell nanostructures undergoes 9 h treatment to form a complete hollow shell silica structure.[62] Hollow goethite shell (α-FeOOH) and rattle-type MF@α-FeOOH structures may also synthesized through this approach.[63]

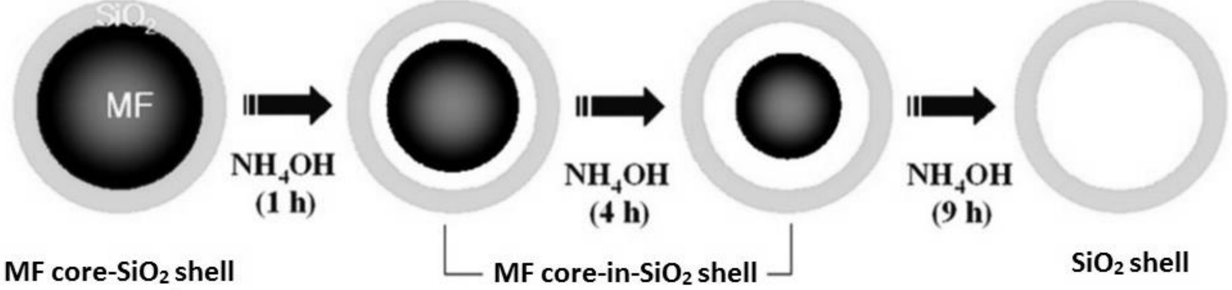

Fig 5: MF@SiO_2core shell particles. Reproduced with permission from ref 60.Copyright © 2008, American Chemical Society

Resorcinol formaldehyde templates:

Stober method as hard template used to synthesize resorcinol formaldehyde (RF) which is a cross- inked colloidal sphere similar to melamine formaldehyde.[64] This is a phenolic resin, which could be removing quiet easily from various atmospheres through calcination. Resorcinol formaldehyde (RF) based hollow TiO_2 nanostructure synthesized by Yin and coworker.[65] These nanoparticles obtained by using silica or resorcinol formaldehyde as hard template with controllable phase and crystallinity. Silica or RF secondary coating protect these colloidal sphere (already coated with TiO_2) during calcination process.[66]Hollow TiO_2nanoshell obtained when all the protection layers and templates remove after calcination process. NaOH etching is necessary if silica act as protecting layer.[67] Resorcinol formaldehyde act as both the template and external layer to synthesize metal hollow nanostructure. i.e. metal@RF core–shell nanomaterials (M= Ag, Pd, Pt, Au etc.) synthesized by Zhang and coworkers. When the mixture of air and ammonia gas come in contact with Ag@RF core–shell nanostructures silver shell formed and deposited on resorcinol formaldehyde.[68] Encapsulated silver transformed into Ag shell which results the void @RF@Ag multi- layered shell nanostructures.[69]

Different Polymer Templates:

Various template from different kinds of polymers utilized for the synthesis of hollow nanomaterials.[70] Hollow nanospheres consist of alternating grapheme nano-sheets and titania. Layer by layer (LBL) adsorption technique and PMMA beads as templates used to obtain these nanostructures. [Tu et al.] [71]Titania and graphene loading obtained by the successive modification with positively charged polyethylamine and negatively charged $Ti_{0.91}O_2$ nanosheets. Which leads to second layer of polyethylamine (+ive charged) with graphene oxide (GO) suspension (-ive charged).[72] To obtain enough titania and graphene loading above process repeated several times. Graphene oxide irradiated in Ar-environment with carbon powder reduced in to graphene.[73] PMMA sphere act as a sacrificial template and after the removal of polyethylamine these spheres converted into exhaust gases. Tetrahydrofuran used for the complete removal of PMMA residue.[74]

Su et al. synthesized hollow nanospheres of Polypyrrole. Pyrrole monomer may polymerize in-situ by utilizing PMMA surface. PMMA core removed with the help of acetone washing.[75] Zeng et al. used porous polystyrene-divinylbenzene (PS-DVB) as template for the generation of multishelled titania hollow spheres.[76] Multishelled and sphere-in-sphere hollow structures of titania results after different heat treatment for the seeded polymerization of polystyrene-divinylbenzene and infiltration process of titania sol within polymer beads.[77] According to Gao and coworkers CdTe nanotubes may also prepared employing 1-D Cd-thioglycolic acid nanowire in the form of hard template.[78]As NaHTe added in the aquous solution of Cd-Thioglycolic acid snanowires, turns into dark brown CdTe.[79]During the formation of hollow tubular structure, morphologies and initial size of templates remain same.[80]

Silica based hard templates:

Silica in sol-gel, mesoporous shell form make use of hard template to synthesize variety of hollow nanostructures.[81]Low cost, tunable size and high uniformity are some of the unique features which makes silica a widely used hard template.[82] Here are some examples of silica used as hard template.[83]

Solid silica templates:

Stober method used to synthesize colloidal silica particles of size ranges 50 nm to 2 μm. [84] Mechanism involved hydrolyzation of alkyl silicates with alcohol-water mixture. Ammonia solution facilitates this reaction. [85]

Metal/Metalloid Hollow Shells Structures:

Heyon and coworkers in 2002 synthesized palladium (Pd) hollow nanostructures against silica as hard template.[86] Mercapto propyl trimethoxysilane ($HS(CH_2)_3{-}Si(OCH_3)_3$)in toluene used to functionalize silica surface.[87]Palladium acetylacetonate ($Pd(acac)_2$) (precursor) absorbed on the surface. Metallic palladium obtained after heating the sample for 3 h at 250 °C.[88]Finally, Pd hollow sphere formed after the removal of template with 10M HF as etchant.[89]

Amino functionalized silica spheres employ as a template to synthesize Pt spheres.[90] These spheres contain nano-sponge like shell and hollow interior generated by mixing precursor solution of platinum with silica spheres.[91]0.1 M ascorbic acid added for the complete synthesis of platinum nanoparticles.[92] Nucleation sites results when amino groups interact with Pt nanoparticles and attached to silica surface.[93] These nucleation sites promote growth of platinum. Surfactants assist the attribution of nanosponge shell followed by 3-days etching process with 10% aqueous HF at room temperature.[94]

Synthesis of ceramic hollow shells:

Colloidal silica via hard sacrificial template exercised for the synthesis of ceramic hollow nanomaterial i.e. ZrO_2, TiO_2, SiO_2 etc.[95]Preparation of template, coating of targeted layer and template removal are major steps in this process.[96]Park et al. used coordinated polymer of silica template to synthesize hollow spheres of (M_2O_3) metal oxide (M= Y^{3+}, Gd^{3+}, Eu^{3+}).[97] These polymer contains isophthalic acid and precursors of metal (embedded) which formed metal oxide on calcination. By using HF etchant may obtained only metal oxide hollow sphere with the removal of silica template.[98] Coordinated polymer shell which has embedded metal precursor directly control the composition and thickness of hollow shells. Modifying the thickness polymer shell and changing the composition of precursor desired results may obtain.[99]

MoO_3 and MoS_2hollow nanospheres prepared by using silica powder as template. Suslick et al. synthesized $SiO_2@MoS_2$ core−shell nanostructures via sonochemical method. Silica spheres of nanometer-sized in isodurene and mixture of Mo $(CO)_6$, S_8treated in Argon atmosphere with ultrasonic irradiation.$SiO_2@MoO_3$may obtain following similar procedure.[100]

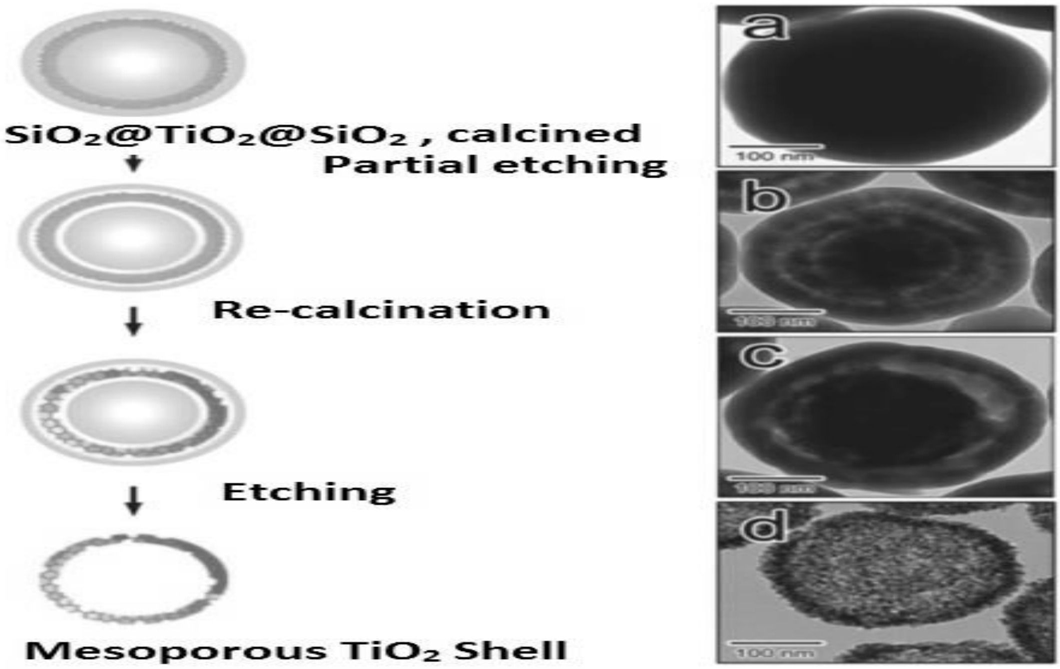

Fig 6: $SiO_2@TiO_2@SiO_2$ particles via TEM. Reproduced with permission from ref 95. Copyright 2011 Royal Society of Chemistry.

Formation of hollow nanomaterials by templating against silica particles is more applicable than other methods.[101] Silica used both protecting layer as well as template to synthesize nano iron oxide particles. Hyeon and co-workers coated β-FeOOH (spindle shaped) nanoparticles with silica then heated under air at 500 °C. Hollow hematite nanostructures obtained after 5 h heating. 0.1 M NaOH solution used to remove silica template, which results hollow hematite capsules. [102]Hollow magnetite nanoparticles formed if reduction occurs before the removal of silica layer. Shrinking cause spherical nanoparticles during reduction or calcination.[103]

Polymer hollow shells by solid silica template:

Another way to synthesize variety of hollow polymer structure is colloidal silica nanoparticles. Silica sphere promotes in situ polymerization via polymer layer which is use as hard template. After the removal of template surface modification, take place. Surface modification promotes the coating process.

Hollow nanocapsules usually fused together to form nanotubes. Kondo et al. first polymerized poly(D-lactic acid) and poly(L-lactic acid) on the surface of silica. After the removal of silica core through HF, nanocapsule's of poly (lactic acid)s obtained.[105] By using a substrate i.e. poly-ethylene terephthalate water could evaporate at ambient temperature from hollow nanocapsules to form tubular assemblies.[106]

Formation of carbon hollow shell structure:

Colloidal nanoparticles of silica widely operated as template to synthesize hollow carbon sphere. Benzene through chemical vapor deposition leads to hollow carbon sphere.[107] HF treatment removed silica template**.**[Wang et al.]

Gierszal et al. used carbonization of polymer to synthesize large volume carbon shells. Phenolic resin film carbonized around colloidal silica template to obtain carbon shell.[108]Zang et al. obtained multishell structure carbon hollow sphere with foam like cores against silica template which were already coated with RF in addition to second layer of silica (SiO_2@RF@SiO_2).[109] This carbonized outcome obtained in the presence of nitrogen gas. Multi shell structures could obtain through repeat coating and templating.[110]

Mesoporous silica templates:

Mesoporous silica (MS) materials obtained from sol-gel method. They have 2-50 nm pore size and enlarge surface area. These materials plays vital function for the synthesis of hollow spheres or shells.[111] Nanoporous materials with size less than 2 nm reported by Caruso and co-workers. They deposited oppositely charged polyelectrolytes within mesoporous silica surface.[112]Mesoporous silica (pore size= 10-40 nm) surface heated for 2 h at 160 °C before each deposition process. Exposure to HF facilitate the removal of template leads to polyelectrolyte hollow sphere.[113]

Yang et al. synthesized complicated nanographene constructed hollow carbon sphere by combining mesoporous and sol-gel silica.[114] Mesoporous silica has straight channels and space between core and shell which is tunable. So mesoporous silica used as template.[115] High temperature calcination required after filling of carbon precursor in the channel. NaOH required to remove the template by etching of solution.[116] In lithium ion batteries these synthesized hollow carbon shells used as anode.

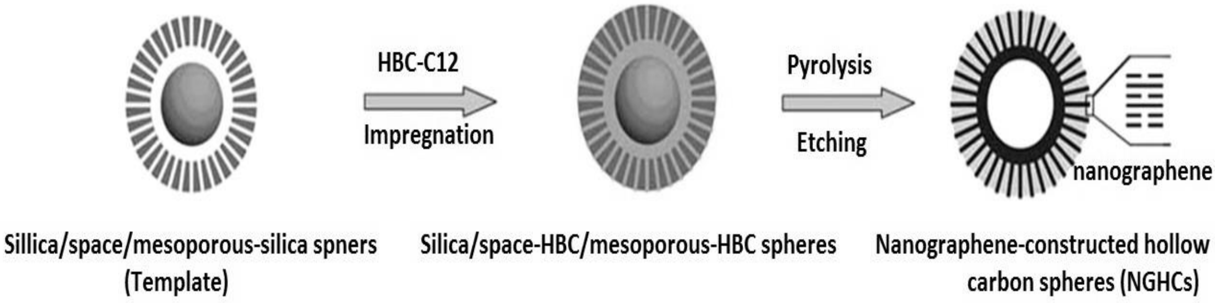

Fig 7: Formation of Nanographene-constructed hollow carbon sphere. Reproduced with permission from ref 114. Copyright 2009 John Wiley and Sons.

Silica shells as hard templates:

Hollow silica shell with additional coating and cavities which promotes growth on one side both sides and oneside used as template like other mesoporous or solid silica nanoparticles. Au @polymer core–shell structure synthesize by Xia and coworkers in 2003. These nanostructures have moveable cores. Gold nanoparticles coated with silica particles in the first step then new layer of poly(benzyl methacrylate) generate through polymerization (in situ). Finally, gold particles with moveable cores obtained after etching by HF.[117]Lou et al. followed same strategy to synthesize Au@SnO_2 hollow nanostructure. Lee et al. synthesized Au@TiO_2 yolk–shell structure by templating against composite nanoparticles (Au@SiO_2). Deposition of TiO_2 layer and template removal are other steps involved in synthesis.Silica nanoreactors used in the preparation of manganese oxide hollow nanoparticles. [Li and Wang et al.]

Other hard templates:

Preparation of hollow nanostructures may possible using metal- organic framework, metal nanoparticles, inorganic salt, ceramics and carbon sphrere as hard template which could remove after the formation of nanoshell materials.[118] Polymer beads and silica did not use as hard template.

Carbon-Based Templates:

Porous and low loose surface of carbon spheres promote them as widely used hard template and facilitate the process of shell formation. [119]

Mesoporous Templates of Carbon:

Carbon spheres are economical and removable that is why exercised as hard template to synthesize a variety of hollow nanomaterial. Some carbon spheres absorb many precursors to form shell structure due to their porous and loose surface. Mesoporous hollow nanostructures also synthesized by ordered mesoporous carbon structure as hard template. Mesoporous carbon structures have pores which are inverse replica of carbon template followed a nanostructured route. Hollow spheres of metal oxides (MgO, $Al2O_3$, TiO_2, ZrO_2) prepared in pore carriers of carbon templates. Alkoxide employed as precursor to synthesize hollow metal oxide spheres.[120]

Solid Carbon Templates:

One-pot synthesis use during hydrothermal preparation of carbon spheres. Titirici et al. synthesized hollow metal oxide sphere by employing carbon template. In the first step carbon precursors dissolved in water. Following 24 h of heating at 180°C in an autoclave, D-glucose monohydrate and metal salts act as precursors here. Metal ions incorporate themselves within hydrophilic shells. Calcination process required for the removal of carbon templates.[121]Fe_2O_3, NiO, Co_3O_4, CeO_2, MgO, and CuO are example of hollow metal oxide nanosoheres. Multi-shelled, rattle type or baall-in-ball hollow structure could prepare by using solid carbon template.

Metal-Based Templates:

Metal nanoparticles exercised hard template to interweave hollow nanostructures. Two main strategies utilized in this process. First, one involved metal@shell core formation. Then obtain the hollow shell structure after the removal of metal core through etching. Galvanic replacement reactions used as second strategy to obtain hollow nanostructures with partial or complete removal of metal NPs (sacrificial scaffold).[122]Chen et al. prepared RuNPs from Ni @Rucore @shell nanomaterials. Nickel nanoparticles acted as hard template so with the removal of nickle through HNO_3 etching. Ru shells have∼2 nm, ∼14 nm thickness and diameter respectively which were obtained from $Ru_3(CO)_{12}$.[123]

Ceramic Templates:

Yi et al. used iron oxide as hard template for the synthesis of rattle-type nanoball structure. Reverse microemulsion technique has played major role in the preparation of Fe_2O_3@SiO_2 composite which surface covered with silica later.Fe_2O_3removed through HCL with etching process. Concentration and time of etchant indicates partial and complete removal of Fe_2O_3core.
Mushroom like hollow derivatives of Fe_xO_y@PS-SiO_2nanostructure were reported Feyen et al. by templating against iron oxide. Hollow nanoboxes could synthesize by templating against copper oxide nanocubes.[124]

Inorganic and complex salts by hard template strategy:

In some situation, hard templateact as sacrificial template particularly when they are carbonates, complex salts and inorganic salt. e.g. controlled shape and size ability of calcium carbonate (nanosized) make it recommendable sacrificial template.
Chen et al. used calcium carbonate as hard template to interweave silica NPs. $Na_2SiO_3\cdot 9H_2O$ used as silica precursor. Silica layer formed on calcium carbonate surface that was removed through HCl etching. Various metallic organic framework uses as template to generate hollow nanomaterials. e.g. Hollow porous titaniacould be synthesized through zeolitic imidazolate frameworks and Cu−Ni bimetallic organic frameworks as template employed to form hollow CuO@NiO spheres.[125]

Natural Materials as Hard Templates:

Hollow nanostructures could synthesize by templating against natural materials. Nanomaterials are economical (low cost), present in large quantity and environment friendly. Hollow nano-structured TiO_2 fibers synthesized by Ghadiri et al. Natural cellulose is most abundant, inexpensive, ecological and economical polymer used as a template in this process. In the first step, TiO_2 layer covered with cellulose that was removing through calcination at next. Finally, TiO_2 fibers obtained after 3h heating at 500°C.[126]
Removal of core may possible by dissolving its crystal in water while NaCl facilitate this process. Sodium chloride is an ionic compound and has face-centered cubic crystal structure.

Soft Templating Synthesis:

Hollow nanostructures consist of metal oxides, carbons, $SiO_2$and composites may synthesize by soft templating synthetic strategies.[127] Soft templating strategies not only facilitate the tuning of internal and external structures but also the size and morphologies. Soft templating follows various synthesizing techniques such as

1. vesicle/micelle strategy
2. Emulsion template strategy and
3. Gas bubbles strategy. Now a day's electrospray method has used to synthesize hollow nanostructures. Here is the detail of these processes

Emulsion-based technique:

An immiscible mixture of two liquids or more than two liquids having 10 nm to 100 μm size droplets forms emulsion. They may be nano or microemulsion <100 nm and macroemulsion >100 nm. They may be direct and reverse emulsion based on polarity (dispersed and continuous phase). When water as continuous phase dissolves in oil which is a dispersed phase, water based or oil in water emulsion may attain. Opposite to this phenomenon where oil as continuous phase dissolves in water as dispersed phase known as water in oil or oil based emulsion.[128]

Direct Emulsion Templates:

Synthesis of Polymer Hollow Spheres:

Hollow polymer spheres could have synthesized by direct emulsion template. Emulsion polymer used to synthesize nanoparticle of PMMA. MMA and ethylene glycol dimethacrylate(EGDMA) in the presence of heptane solvent used as reactants. Heptane and PMMA have huge hydrophilicity difference which promotes formation of particles at the centre. Evaporation of heptane results hollow nanoparticles. [129]Hollow PS nanospheres synthesize by following same route.

Synthesis of Inorganic Hollow Spheres through Direct Emulsion Templates:

Hydrothermal or sol-gel process as direct emulsion template used to synthesize inorganic hollow nanostructures. Hydrogen bonds and other slightly weak forces (electrostatic) facilitate the coating of inorganic matter on emulsion droplets. Silica spheres (monodipersed) prepared from direct emulsion template method explained by Zoldesi and Imhof.[130] Oil in water emulsion was generated by dissolving DMDES in water. Metal hollow spheres can be generated by applying direct emulsion template method as a result 0.6 to 2 μm size droplet formed. Wang et al. used an emulsion of beeswax in water to prepare hollow silver (Ag) spheres. Sonication used to form the mixture of beeswax, KBr, CTAB and water. Electrostatic attraction starts between the surface of template and silver bromide seeds after the addition of silver nitrate solution. Beeswax particles of Ag reduced in to Ag^+ which was removing by washing with ethanol. Beeswax could remove by raising temperature results silver nanoshells of 200 nm size.[131]

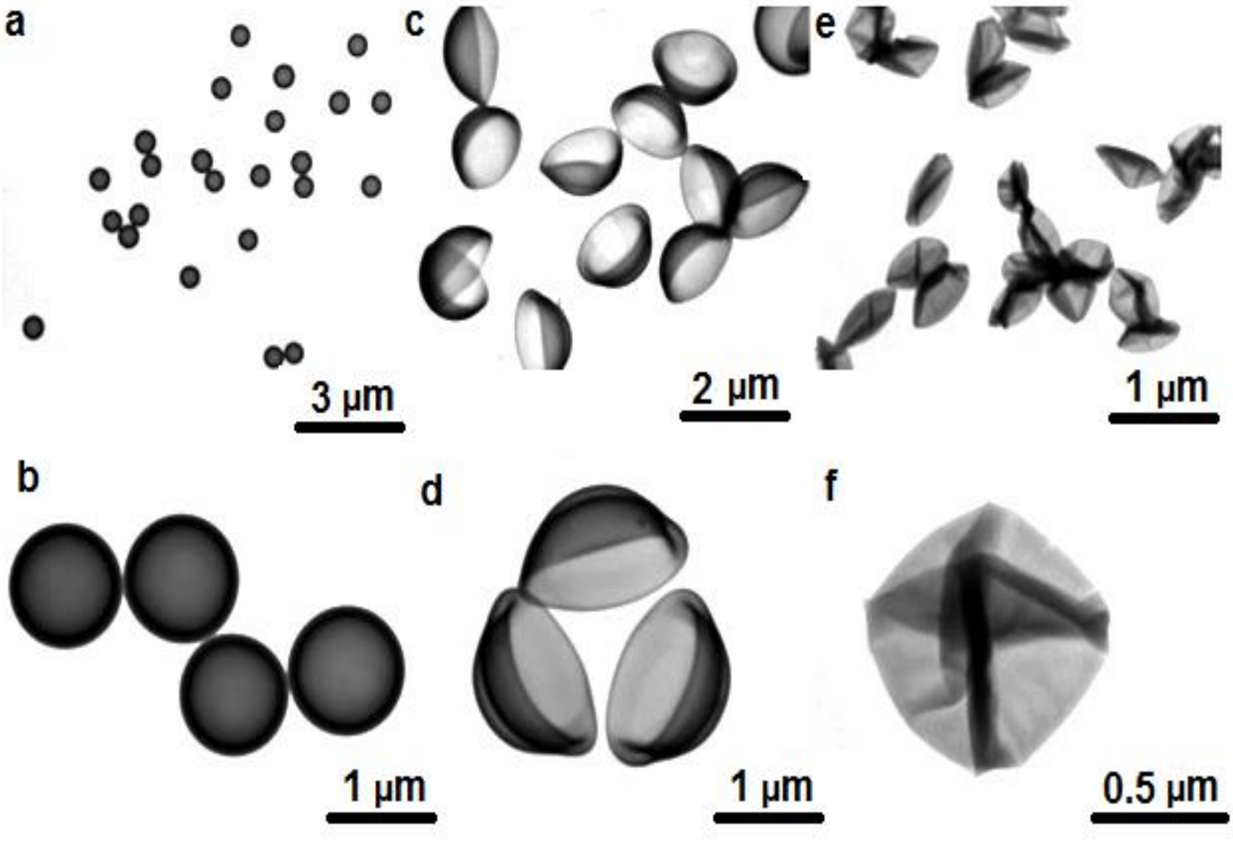

Fig 8: Images of hollow silica, silica microcapsule and silica microballons. Reproduced with permission from ref 131.Copyright 2011 John Wiley and Sons.

Reverse Emulsion Templates.

Metal oxides and sulfides hollow nanostructures may synthesize through reverse emulsion template. Yu et al. used carbon disulfide in water emulsion for the direct synthesis of hollow copper sulphide structure. CuS nuclei formed at droplets interface. Carbon disulfide released S^{2-}which combined with diffused out $Cu^{2+}$to form shell structure. ~200 nm diameter carbon disulfide nanoparticles with ~30 nm thickness of shell obtained. Bourret and Lennox used interface formed by the mixing of water and dichloromethane (CH_2Cl_2). $Cu(OH)_2$ self-assembled itself by coordinating with alkylamines. Cu^{2+}ions from oil phase reacted with amines to form soluble metal salts. Water play vital role not only in the formation of reverse emulsion but also in the generation of interface.[132]Copper amine complex could tune in size and morphology by adding n-butanol. Hollow nanomaterials of about 100 nm may obtain with reverse emulsion procedure.

Double Emulsion Templates:

Dispersion of reverse emulsion in an aqueous solution referred as double emulsions techniques e.g. water/oil/water (W/O/W). Ultrasound irradiations are quite helpful to generate this system. Wu et al. synthesized hollow nanomaterials of silica via double emulsion templating. They formed double emulsion system with the help of strong shearing. TEOS hydrolysis converted oil in water macro emulsion to W/O/W double emulsion with sub-100 nm of particle size.[133]

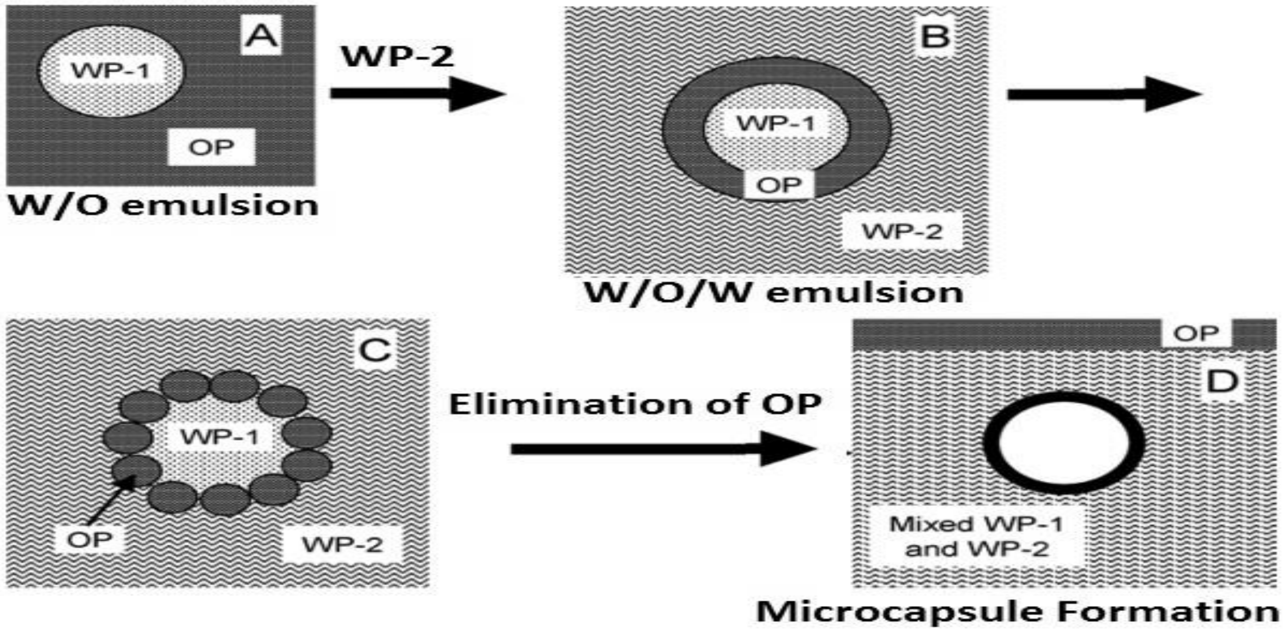

Fig 9: W/O/W emulsion templating scheme of hollow silica nanostructures. Reproduced with permission from ref 133.Copyright © 2004, American Chemical Society

Gas Bubble-Based Soft Templates:

Gas bubbles as soft template may exercise to form nano hollow structure. Gas bubbles formed in the first step then use to absorb particles on their surface. Particles growth or aggregation facilitates the shell formation. Size, hydrophilicity and charges on particles surface show the presence of gas bubbles as template. Various techniques used to generate gas bubble emulsion e.g. sonication, chemical reaction and sprinkling gas bubbles in reaction system. SO_2 gas released by deterioration of $[Pb(S_2O_3)_2]^{2-}$ ions. That is use as template to synthesize lead sulfide nanomaterial. Sasaki and Yang utilized hydrogen peroxide to obtain O_2 gas bubbles which are employed for the synthesis of hollow CoOOH spheres. CuS, SnO, Fe_3O_4 and La_2O_3 etc. are other nanostructures synthesize from this method. These synthesized spheres ($CoFe_2O_4$, $MnFe_2O_4$ and MoS_2) also used in lithium ion batteries. NH_3bubbles also used as template for the synthesis of MoS_2 nanocages. [134]Ammonia bubbles released from $(NH_4)_2MoS_4$ and size of particle was 100 nm.

Electrospray Method:

Most of the nanospheres and nano-fibers generated through electrospray method. This is the most accessible appoach to synthesize hollow nanomaterials in present days. A capillary tube (stainless steel) filled with liquid. Then the liquid distorted in to sharp cone by applying strong electric field, which help to formed charged liquid droplets. Sometimes additional ripening or evaporation of solvent required to obtain hollow nanostructures. After the evaporation of enclosed solvent NPs deposited on substrate. The flow rate, voltage, concentration of precursor and substrate, concentration of precursor and temperature play major role to maintain the morphology of product. Suhendi et al. used collection electrode to obtain hollow colloid some of silica. Colloid some with polystyrene core could obtain by adding PS and silica in charged droplets solution.[135]These core removed by heating them at high temperature. Hollow silica nanoparticles obtained through electrospray method.

Self-Templating Synthesis

Hollow nanomaterials could synthesize without additional template so have minimum production cost, ease of scaling process and other significance. Various techniques follow the principle of self templating in order to generate hollow nanomaterials such as galvanic replacement, kirkendall effect, etching (surface protected), Ostwald ripening etc. the two widely used steps are

(1) The generation of nanomaterial template.

(2) Formation of hollow nanostructure from template.

Composition of outer shell and inner shells maintain by the same template unlike previous used strategies. Soft templating methods have great control on particle uniformity, thickness, synthetic process, high reproducibility and low production cost made them more beneficial than other procedures. Self-templating conveniently use for scaling up large quantity production.

Surface protected etching:

Polymeric ligands etching agent used to coat solid oxide particles and interior materials results surface protected etching. [Yin and co-workers in 2008].

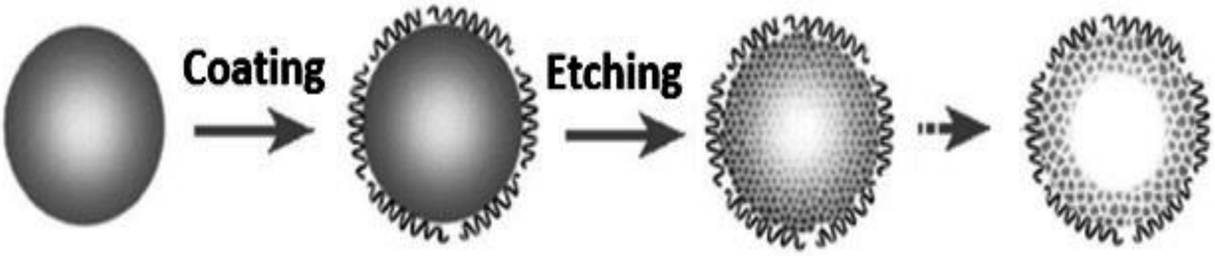

Fig 10: Process of surface protected etching. . Reproduced with permission from ref 136. Copyright © 2008, American Chemical Society

Lou and co-workers synthesized nanoboxes from nanocubes through etching. $CoSn(OH)_6$nanocubes rapidly converted to nanoboxes in alkaline medium. The advantage of using cobalt specie is that instead of PVP (polymeric ligand) a stabilizer surround liquid-solid interface in the form of CoO(OH).[136] Yamauchi and co-workers prepared hollow nanocubes (shell in shell) of Prussian blue PB@PB. These hollow structures obtained due to acid etching of hydrothermal process. Higher etching rate of core part due to more defects in outside shell results hollow shell-in shell structures.[137]

Ostwald's ripening:

Ostwald's ripening defined by IUPAC in 2007 as over time change in an inhomogeneous structure immersed in liquid sols or solid solution. It is also termed as matter relocation because disintegrated species deposited at the surface in large crystals. Solubility of small particles enhanced by highly energetic large particles called ripening process. This mechanism has studied under self-template synthesis for the generation of complex nanostructured materials. Zhang et al. synthesized hollow nanostructure copper oxide. Morphology and number of shell for theses multilayered hollow nanostructures controlled through ripening process. [138]

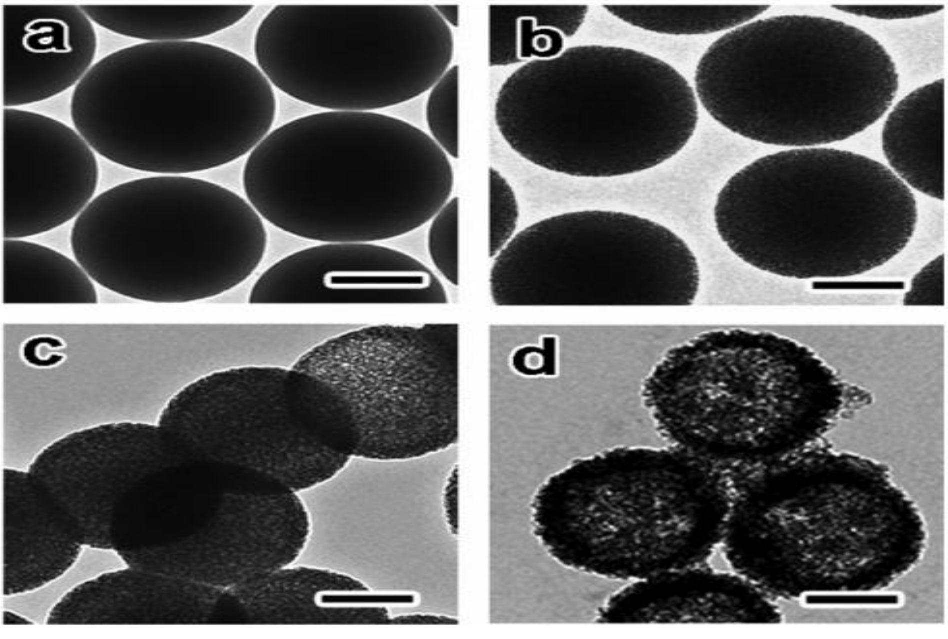

Figure 11:TEM images of PVP treated Cu_2Oimages.Reproduced with permission from ref 139.Copyright © 2008, American Chemical Society

Steps involved in Ostwald ripening mechanism define triple-layer and quadruple-layer type hollow structure. Deposition of crystallites in the reaction mixture by adding additional reactants generated single layer Cu_2Onanoshells.Multi-shelled ZnO spheres synthesized by Wu et al. following same strategy.[139]

The Kirkindall effect:

Discrepancy in diffusion rate of metal atom facilitates motion of boundary layer between them termed as Kirkindall effect. This is a vacancy-mediated mechanism used in metallurgy. Flow of faster diffusing specie neutralize by opposing flow of vacancies that concentrates into voids. However experimental data during inter diffusion has shown unequal flow of matter for vacancy mediated mechanism in crystalline materials.[140]Coalescence of vacancies into voids occur due to high value of saturation. This process causes some severe side effects in metallurgical processes. Kirkindall voids in solders and alloys damage the manufacturing process of metallurgy. Now days it is use to manufacture hollow nanomaterials. In 2004 first time kirkindell effect used to exploited the nanoscale materials.[141]

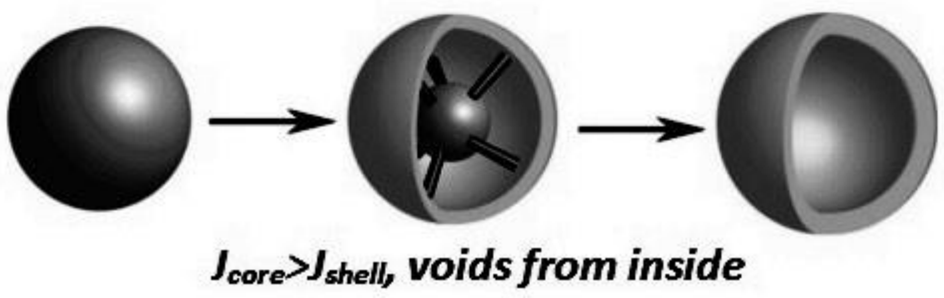

Fig 12: Formation hollow nanocrystal through Kirkendall effect. Reproduced with permission from ref 142. Copyright © 2013, American Chemical Society

Galvanic replacement

Hollow nanostructures with desirable characteristics like porous walls, tunable composition, controlled shape and size could possible through galvanic replacement method. This is an effective self-templating technique to synthesize nanostructures with noble metals. The working mechanism depends on potential difference between anode and cathode establish between one metal and salt of other. These electrodes act as oxidizing (cathode) and reducing agent (anode), which were synthesized and oxidized first.[143]Metal ions have higher value of reduction potential which facilitate the oxidation and dissolution of anode nanomaterials in solution. On the other hand, outer surface of template employ to align and reduce the metal ions. There is also a close resemblance between initially used anode metal and finally synthesized hollow nanostructure. Xia and co-workers reported hollow gold nanomaterial by using pre synthesized silver nanostructures. Au^{3+}salt used in galvanic replacement procedure to obtain well defined void spaces andcrystallinewalls.$HAuCl_4$used to oxidize suspended nanostructures of silver as Ag+/Ag (0.80 V) have less positive electrode potential than AuCl4 /Au (0.99 V)

$3Ag_{(s)} + AuCl_4^{-}{}_{(aq)} \qquad Au_{(s)} + 3Ag^{+}{}_{(aq)} + 4Cl^{-}{}_{(aq)} \longrightarrow$

Gold nanostructures obtained in this strategy possess crystalline morphology. Various framed or hollow nanostructures could synthesize through this procedure with control shape, size and morphology by templating against silver nanocubes.[144]

Properties and applications:

Nanostructures having a hole or inside cavity refers as hollow nanostructures. These materials usually contain large fractions of void spaces. Hollow nanomaterials are quite better solid counterpart of similar size and composition because of great loading capacity, huge surface area and very low density. These characteristics enhances their uses and mad various them applicable for a variety of disciplines including catalysis (support material, active catalyst), biomedicine (drug delivery carriers), energy storage (imaging contrast agents), sensors, lithium ion batteries (as anodes or cathodes) nano-reactors, water treatment and environmental remediation.[144]

Nanostructures and reactors:

Chemical reaction takes place in a confined atmosphere known as reactor. Microenvironment formed due to void spaces present in the shell. Hollow nanostructures have wide range of applications as nanoreactors to host reactions or carry chemicals.[143]They are usually in the form of inorganic hollow tubes/shells, polyelectrolyte spheres and polymeric vesicles. e.g. silica nanotubes could be used as nanoreactors to generate rod like structure. Gao et al. synthesized nanorods of Au, Ag, Pt, and Pd following seed growth within silica nanotubes.[145] Nanorods of nickel hydrazine facilitate the synthesis of silica nanotubes. 3-aminopropyltriethoxysilane(APS) used for the first coating on the surface of nickel hydrazine nanorods which in turn promotes silica gel coating on template. Gold seed loading at selective areas results the addition of amino groups inside the silica shell via APS. Highly attributed gold nanorods were synthesized by seed growth and template (silica) removal. Nanorods with a variety of composition may achieved by using various metals as precursors.

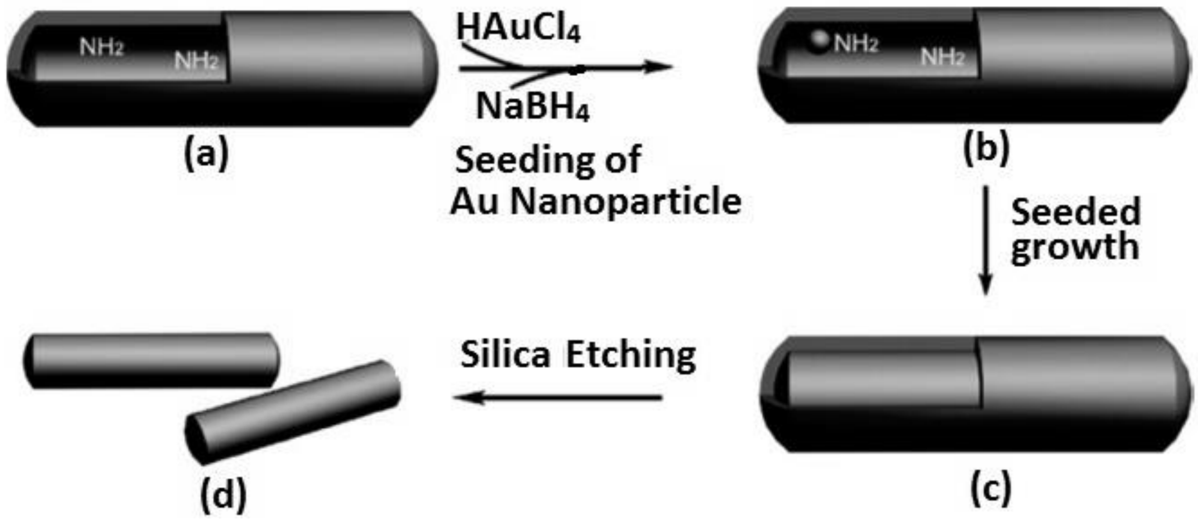

Fig 13: General synthetic process of metal nanorods. Reproduced with permission from ref 146. Copyright 2011 American Chemical Society

Optical properties and applications:

When incident light falls on metal nanostructures following resonance condition oscillations arise leads to the localized surface plasmon resonance (LSPR). Shape, size and dielectric environment are the factors responsible for the peak position obtain in localized surface plasmon resonance. Nanoshells and nano cages generated wide range spectrum of tunable wavelength with localized surface plasmon resonance mode. [Neeves and Birnboim]. Silica nanoparticles coated with gold layer also give localized surface plasmon resonance peaks which can be seen in the region of near infrared. [147]

Use in lithium ion batteries and super capacitors:

Environment friendly, long service life, high power density and no memory effect are salient features of Lithium-ion batteries (LIBs) which make them most dominating in electronic devices and have terrific future in electric vehicles. An electrolyte-permeable separator with electrolyte separates the cathode and anode in lithium ion cell. Lithium metal oxide and graphite having theoretical capacities less than 200 mAh/g and ∼372 mAh/g respectively used as cathode and anode in lithium ion batteries. Carbonaceous materials could replace with better and suitable anode material, which has certain advantages on traditional ones.[148] High surface area and less diffusion ways of hollow nanomaterials help to overcome low cycling proficiency, pulverization and capacity loss. Electrochemical performance enhanced by combining transition metal oxide with hollow nanomaterials e.g. $CoSnO_3$, $ZnMn_2O_4$etc. Zhou et al. synthesized yolk shell nanocomposite via heating vulcanization with better capacity of cycling. They were composed of polyaniline sulfur core shell with a capacity of 765 mAh/g at 0.2Cafter 200 cycles.[149]

Energy storage phenomenon categorized Super capacitors, or electrochemical capacitors into two classes one of them is electrical double layer capacitor (EDLC), and other is redox super capacitor or pseudo-capacitor. EDLCs used electrode of high surface area and electric conductivity while capacitance due to charges collected from interface of electrode and electrolyte.[150] Electrode materials with maximum conductivity and surface area generated high capacitance in electrical double layer capacitor. Using charge storage or near surface reactions redox super capacitor could establish. Lou and co-workers synthesized core-in-double shell complex of uniform hollow nanospheres. $NiCo_2O_4$shell consist of small nanocrystals of high porosity. Redox reactions occur as electrolyte entrap in to the shell.[151]

Al-shareef and co-workers synthesized hollow $NiCo_2S_4$ spheres. They used 2D-self-assembled nanosheets, which have marvelous rate progress and high value of specific capacitance (1263 F/g at 2 A/g).

Catalysis (electrocatalysis and photocatalysis):

Large surface areas, less density and controllable hollow spaces make yolk-shell structures a remarkable reactor for various catalytic reactions. Inside composition of hollow shells also responsible for their use in various catalytic reactions such as electrolysis and organic transformation.[152]

Catalytic use in organic modifications:

Modern organic chemistry comprises of various coupling reactions such as Sonogashira cross coupling synthesis, Suzuki-Miyaura coupling reactions and Heck-Ullmann reactions. Hollow nanomaterials of noble and transition metals used as catalyst for the synthesis of particular reactions. [153]Hyeon and co-workers synthesize hollow nanospheres of palladium metal. Pd hollow nanostructure obtained by templating against silica spheres and widely used in Suzuki coupling reactions.∼10 nm Pd nanoparticles used for 15 nm core shell, which is use for the synthesis of 300 nm diameter palladium nanospheres. As organo borane complexes are main constituent of Suzuki coupling reaction so iodo thiophene reacted with boronic acid to obtain this reactant.[154]

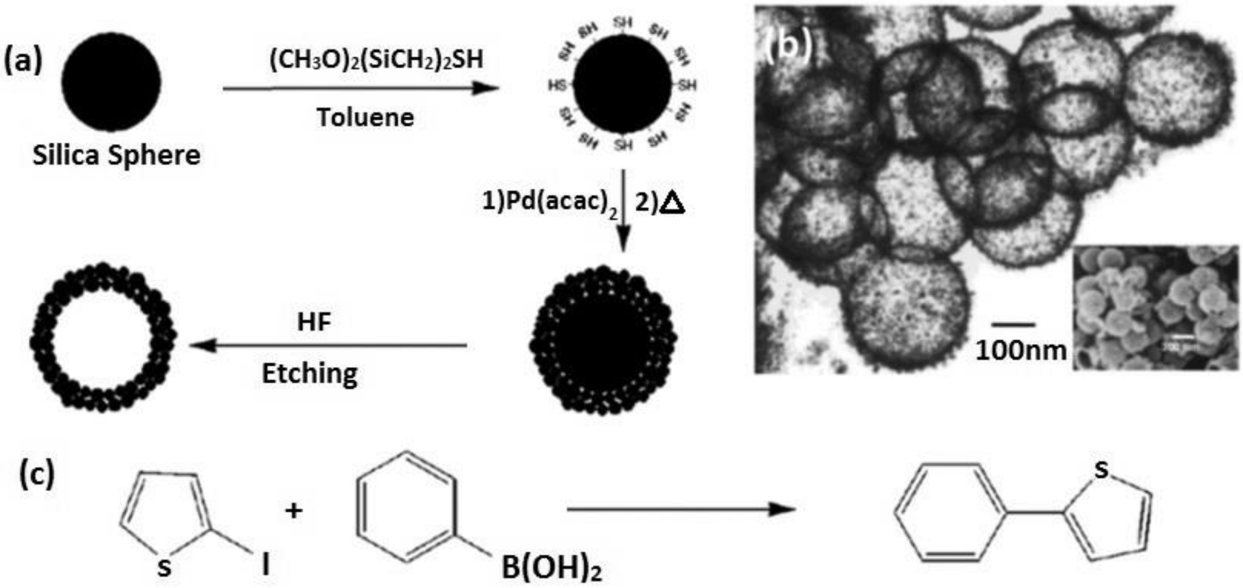

Fig 14: (a) synthesis of hollow Pd spheres. (b) SEM and TEM images. (c) Pd catalyst in Suzuki cross coupling reactions. Reproduce with permission from ref 155. Copyright © 2002, American Chemical Society

Catalyst may have reused and recycle as maintain its activity after reaction.

Coupling reactions of alkyl halide by Ullmann, Heck- and Sonogashira have utilized hollow nanospheres of Pd-Fe as catalyst in aqueous medium. [Li et al.]. This was a vesicle-assisted chemical reduction.[156] Reduction reactions may attain with the aid of metal@shell yolk-shell or metal's hollow structure. $NaBH_4$ as catalyst facilitate the reduction of *p*-nitrophenol to *p*-aminophenol. Au@SiO_2 and Ag@PMAA are very helpful in this reduction process. Porous wall containing nanocages of Pt-Pd alloy were generated by Hong et al. He had enumerated their enhanced catalytic (oxygen reduction) activities.

Electrolysis:

In electro catalysis hollow nanomaterials play vital role due to their minimum diffusion length for charge and mass transport, less density and maximum surface area, which also make them better than solid NPs. High energy conversion, low operating temperature and absence of pollutants or environment friendly properties of methanol fuel cells have made them attractive from past few years. Nanoporous PtCu and PtAg, hollow ligament carrying alloys to enhance electrolysis were synthesized and reported by Xu et al. various nonprecious metals like Mo which tend to manifest catalytic properties like platinum. [157]MoS_2 showed high stability and activity at certain reaction conditions however, its active sites bounded to edges. Yu and co-workers synthesized hollow microspheres of $MoS_2$for hydrogen evolution reaction (HER). Moreover, they were capped with hollow MoS_2. High performance for HER could possible through nickel phosphide Ni_2P synthesized by Popczun et al. Ni_2P paryicles exposed (001) facets due to large and accessible surface area showed highest HER activity than other materials.[158]

Photo-catalysis Process:

Photo-catalysis process on semiconductor has drawn the attention of various research fields as they facilitate light-driven chemical reaction. Fujishima and Honda described the water splitting on TiO_2electrode. Light irradiation used to separate electrons and holes (h+). Their conductivity lies between insulator and metals. Yang and co-workers synthesized CdS−Au−TiO_2 hollow nanotube for catalytic decadence. TiO_2 deposited on zinc oxide nanorod template results hollow TiO_2 nanotube. Acid used for etching of zinc oxide.[159]

Wide band gap ZnS semiconductors have an immense photochemical and optical properties which grabs huge attention from all field of science in recent times. Hexagonal wurtzite phase has 3.77eV band gap value while cubic phase lie at rough3.72eV. According to Yu et al. hollow spheres of ZnS NPs with rough inner sides, huge surface area and tiny grain size showed highest photocatalytic activity than ZnS powder which is used commercially for decadence of RhB. The peculiar characteristics of hollow ZnS nanospheres have ideal adsorption sites for reactants.[160]

As Drug Carrier:

Various drugs such as doxorubicin (DOX), ibuprofen and cefradine etc could load more conveniently through yolk@SiO_2 shell, Mesoporous nano silica spheres and hollow SiO_2 nanospheres. Similarly stacking and releasing of compact drugs, enzymes, proteins or DNA could possible through polymer capsule, hollow shell of carbon and hollow magnetite shells. Hyperthermia cancer therapy and drug delivery are some important applications of gold NPs with hollow iron oxide nanoparticles. [Sun et al.]

As Multifunctional Biomedicine materials:

These materials promote optical/MRI imaging with drug delivery at the same time. Various groups have been investigated hollow nanostructures based imaging-guided therapy and drug delivery. An important example of multifunctional materials used as photo-thermal material and drug delivery carriers is AuNC@SiO2. These double walled nanocages of Au in association of hollow silica shells results when two excavated hollow techniques galvanic replacement and surface protected etching use simultaneously.

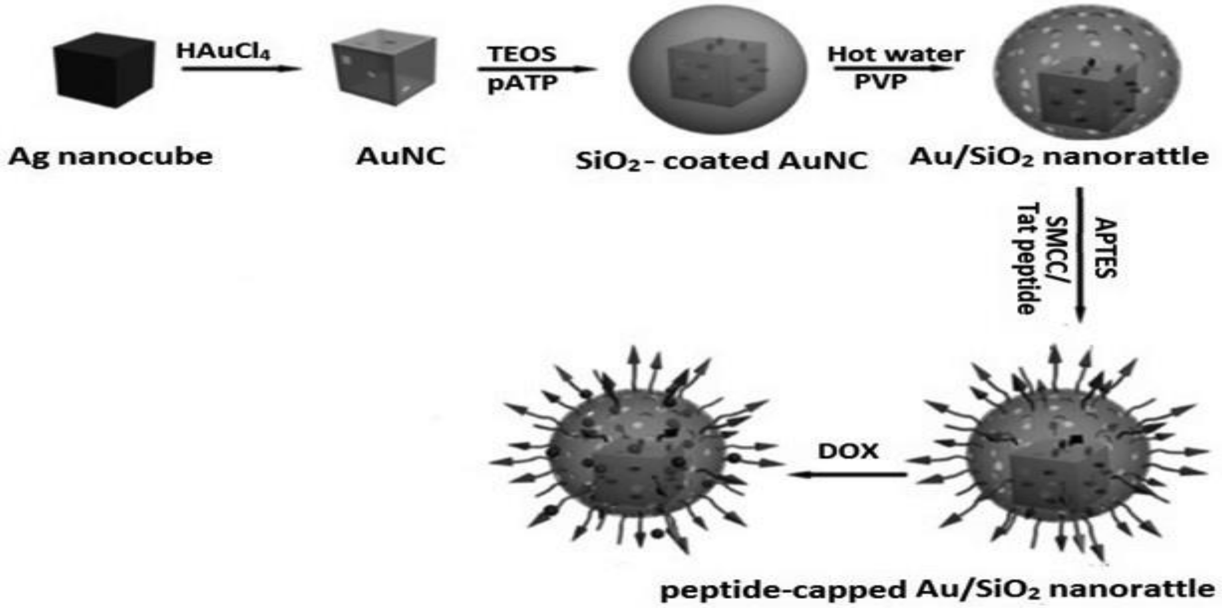

Fig 15: Synthetic scheme of Au/SiO_2 nanorattles. Reproduced with permission from ref 161. Copyright 2015 John Wiley and Sons.

Conclusion and Recommendations:

There have been tremendous advancements regarding the synthesis of hollow nanomaterials in near few years. Various impactful procedures and strategies have promoted to generate hollow nanostructures. Hard-template, self-template, soft template, template free and simple mechanism are commonly exercised synthetic strategies. Other than these Kirkendall effect, Ostwald’s ripening and galvanic replacement also use commonly. Each approach has its own merits and demerits. Coating of desired shell material on presynthesized particle with the removal of template core is the simplest way to synthesize hollow nanostructures. Come across hard template strategy. This is the most popular, simplest and widely used strategy to produce any kind of nanomaterial. However, heterogeneous coating process, low reproducibility and toxic etchant or solvent used for the removal of template core usually limits its applications. Formulation of emulsion, gas bubbles (soft template) is much easier and cost effective than hard template strategy. Highly polydispersed and micrometric range material may generate. The structure uniformity and size restricts practical applications of soft template method. Self- template synthesis comprising all advancements and improvements has a distinct edge on traditionally used techniques. With the advantages like heterogeneous coating and easy scalp up processes has widely used at large scale for variety of applications but very specific in action. Certain surfactant, solvents, and reaction temperature require for specific case not used generally for all work assemblies. Besides all advancements, improvements and applications still various challenges need to be address. For example, various organic applications emphasize on chiral nanostructures to make hollow shells, which are difficult to obtain due to lack of chiral template. Modifications in combining different functionalities like positive/negative charges and hydrophilic /hydrophobic system still a great challenge. Activity and selectivity of certain chemical reactions by improvising certain intermediates inside the cavity may enhance but difficult to achieve.

Future research needs to overcome these challenges of production cost, synthetic scale and safety measure. Practical applications need production cost at kilograms and tons level instead of gram and milligram. Reagents with high purity and reproducibility may increase production cost, which overcome with low cost alternatives for shell and template synthesis. Sometimes less uniform structured hollow shell fulfills the requirements of large-scale material production which interns reduce the cost. Biomaterial based templates exist naturally in large quantity and easily (cheap) assessable may help to overcome above challenges. Previously called “useless” inorganic solid substances contain inexpensive minerals, calcium carbonates and magnesium oxide compound are getting the attention from nanomaterial community. Low cost, ubiquity, environment friendly and easy removal is some promising advantages of theses material as template. Materials with complex structures and desirable characteristics are dream to obtain right now should be focus in future research. Design and fabrication of novel functional materials and devices incorporating hollow nanomaterials as building blocks needs development of full synthetic strategies may possible in future.

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