Energy Conversion Based on Superhydrophobic Surfaces

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Contribute Equally

Different fabrication methods of SHS:

Laser method

Laser method has been widely used for manufacturing multi-modal surfaces with micro/nano structure on different substrates because of its high precision processing, extensive materials processing, and strong controllability.[1-3] Multiscale grooves with sizes ranging from hundreds of nanometers to tens of microns on the metal substrate were fabricated by laser ablation technology, such as stainless steel and aluminum-magnesium alloy, and the micromorphology of the surface could be adjusted by changing different laser scanning parameters, as shown in Figure S1(a) and (b).[4, 5] Similarly, the protuberances and pores with the size of about several microns could also be constructed by ultrashort pulse laser ablation on non-metal substrates, such as polymer[6] and glass[7], and the processed rough sample was then further modified by low surface energy substance to obtain the superhydrophobicity, as shown in Figure S1(c) and (d).

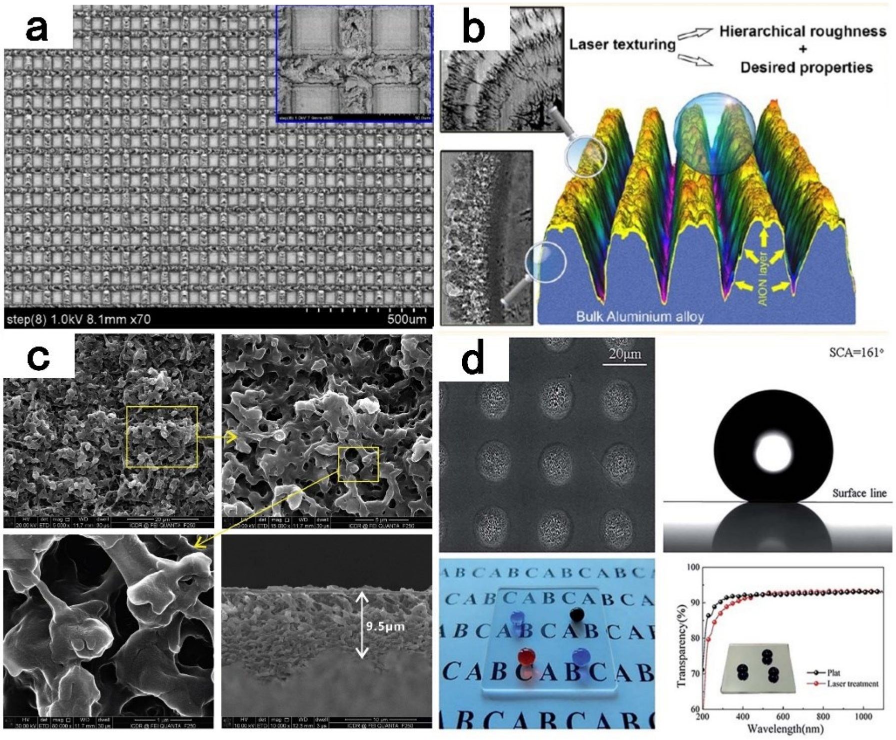

Figure S1. Different surfaces ablated by laser. a) Stainless steel. Reproduced with permission from ref. [4], copyright 2014, Elsevier. b) Aluminium alloy. Reproduced with permission from ref. [5], copyright 2017, American Chemical Society. c) Polyamide-6 (One kind of Nylon). Reproduced with permission from ref. [6], copyright 2017, Wiley-VCH. d) Glass. Reproduced with permission from ref. [7], copyright 2018, Royal Society of Chemistry.

Chemical method

Chemical method refers to chemical etching and chemical deposition, which has the characteristics of simple steps, low cost, and high efficiency.[8, 9] Chemical etching constructs rough structures through preferential corrosion of grain boundaries and dislocations of metal materials. Fu et al. employed chemical etching method by immersing the aluminum plate in a mixed solution of nitric acid and silver nitrate, and found that a large amount of micro/nano-scale network porous structures were formed on the surface, thereby obtaining SHS after being modified with decyltriethoxysilane ethanol solution (Figure S2(a)).[10] Likewise, micron scale rough structure could also be fabricated on stainless steel mesh by chemical etching, as shown in Figure S2(b).[11] On the other hand, chemical deposition includes chemical vapor deposition (CVD)[12, 13] and chemical liquid deposition[9, 14]. Li et al. fabricated translucent and superhydrophobic glass surfaces by aerosol-assisted chemical vapor deposition, and obtained surface gave excellent superhydrophobic properties with a high water contact angle and low sliding angle, as shown in Figure S2(c).[12] The chemical deposition method could also be applied for preparing micro/nano structures on cooper mesh, and the processed surface possessed good superhydrophobicity after modifying by materials with low surface energy, as shown in Figure S2(d).[14]

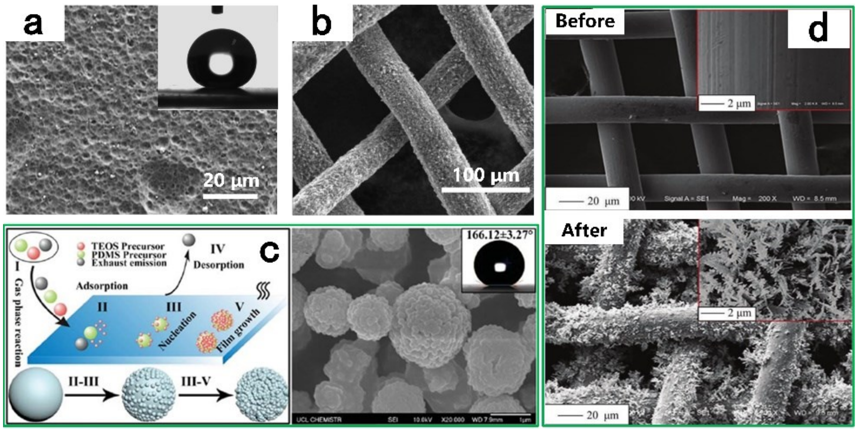

Figure S2. Different surfaces obtained by chemical method. a) Micro-nano-scale network porous structure by nitric acid and silver nitrate etching. Reproduced with permission from ref. [10], copyright 2008, Elsevier. b) Stainless steel mesh before and after hydrochloric acid etching. Reproduced with permission from ref. [11], copyright 2016, American Chemical Society. c) The schematic diagram of CVD and the SEM image of the as-prepared SHS. Reproduced with permission from ref. [12], copyright 2018, Royal Society of Chemistry. d) Surface morphology of the copper mesh before and after reacting in an aqueous solution of $AgNO_3$. Reproduced with permission from ref. [14], copyright 2017, Elsevier.

Electrochemical method

The electrochemical method refers to a technology in which current flows through the migration of positive and negative ions in the electrolyte solution under the action of an external electric field. Generally, the electrochemical method is divided into anode reaction composed of electrochemical etching reaction and anodic oxidation reaction, and cathode reaction commonly known as electrochemical deposition. Due to the advantages of facile, low cost, high efficient and good reproducibility, the electrochemical method has been extensively used for fabricating large-area SHS with different shapes, such as cauliflower-shaped multiscale morphology,[15] dandelion-like microstructures,[16] and nanoneedles structures,[17] as shown in Figure S3(a)-(c). Additionally, the gallium arsenide disk (Figure S3(d)) with sizes of about several microns could also fabricated by cavity-enhanced photoelectrochemical etching, with good selectivity and high precision.[18]

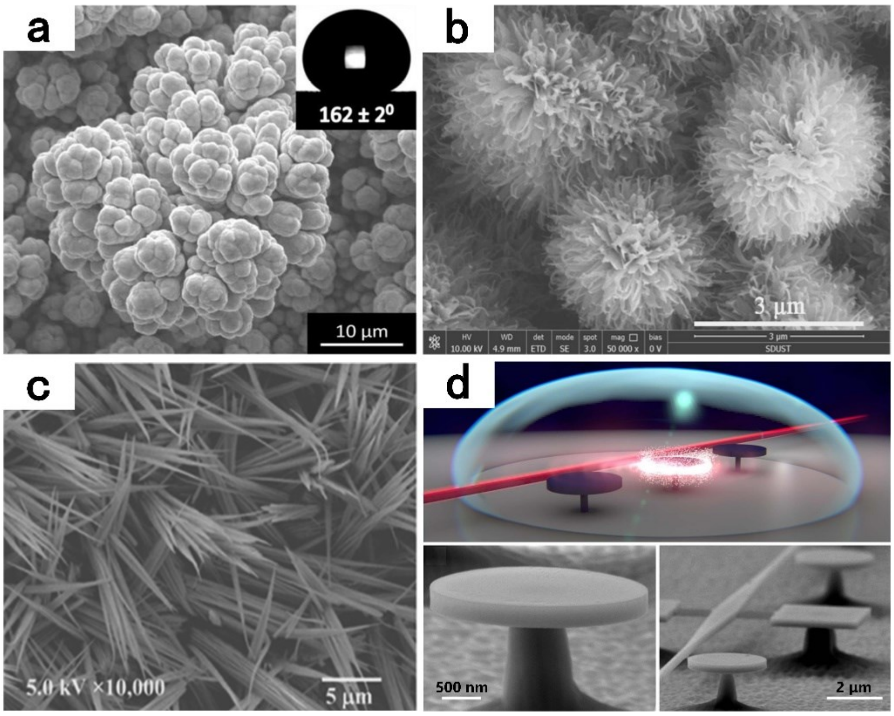

Figure S3. Different surfaces fabricated by electrochemical method. a) Cauliflower-shaped multiscale morphology obtained on copper substrate by two-step electrodeposition process. Reproduced with permission from ref. [15], copyright 2018, American Chemical Society. b) Dandelion-like microstructures fabricated on steel sample. Reproduced with permission from ref. [16], copyright 2016, Elsevier. c) Nanoneedles structures deposited on copper substrate by electrochemical anodization in an aqueous KOH solution. Reproduced with permission from ref. [17], copyright 2015, Royal Society of Chemistry. d) Gallium arsenide disk by photoelectrochemical etching.[18]

Wire Electrical Discharge Machining (WEDM)

With high precision, good shape adaptability and excellent controllability, WEDM has also been applied for fabricating surface microstructures.[19-21] Bae et al. used WEDM method to prepare SHS on aluminum alloy substrate and obtained multi-scale microstructures by wire-feeding and surface etching reaction synchronously. The contact angle and rolling angle of water droplets on the fabricated SHS were 156° and 3° respectively, as shown in Figure S4(a) and (b).[19] Subsequently, Liu et al. combined WEDM and chemical etching to fabricate a copper surface patterned with a square lattice of tapered posts decorated with nanostructures, and the surface exhibited superhydrophobicity with an apparent contact angle of over 165°, as shown in Figure S4(c) and (d).[20]

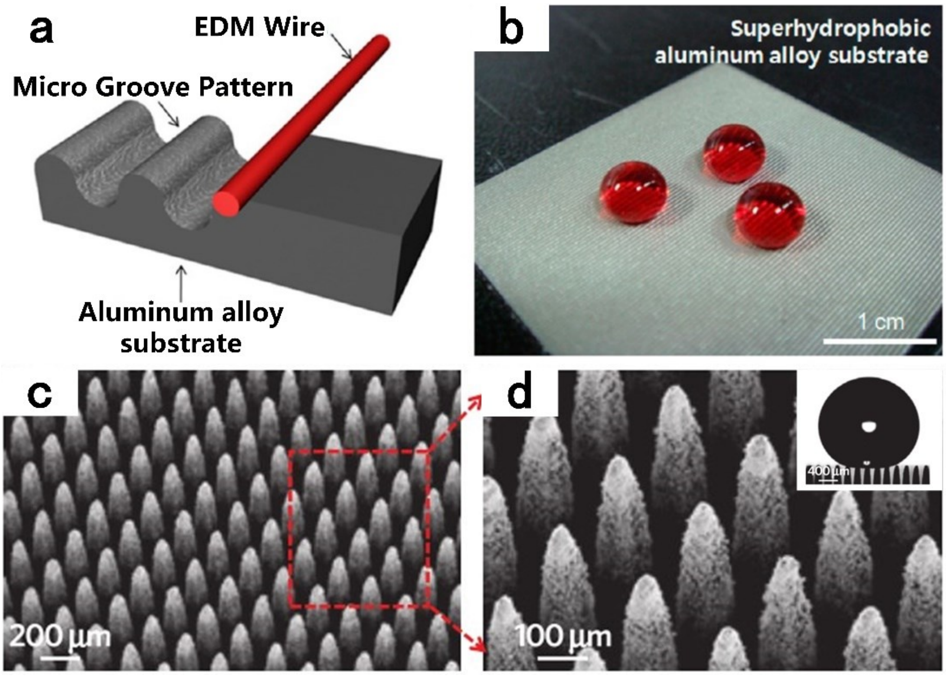

Figure S4. a) Schematic illustration to fabricate dual-scale structures on the Al alloy surface by WEDM. Reproduced with permission from ref. [19], copyright 2012, American Chemical Society. b) The fabricated surface had excellent water repellency. c) d) Copper surface patterned with a square lattice of tapered posts decorated with nanostructures by WEDM and chemical etching. Reproduced with permission from ref. [20], copyright 2014, Springer Nature.

3D Printing method

Modern additive manufacturing (e.g. 3D printing) can also be used to fabricate SHS. As shown in Figure S5, SHS with different shapes were prepared by 3D printing, such as pine needles,[22] eggbeater arrays,[23] lattice, hollow ball,[24] and porous structure.[25] Besides, a variety of materials from metal to non-metal (e.g. polymer) could be employed to fabricate SHS by 3D printing method, which had shown good applicability. Yang et al. fabricated superhydrophobic micro-scale artificial hairs with eggbeater heads by 3D printing process, and the prepared structure had excellent performance of water droplet manipulation, micro reactor and oil/water separation, as shown in Figure S5(b).[23] Likewise, superhydrophobic membranes with an ordered porous structure were also fabricated by 3D printing approach, which could separate of oil and water mixture with high efficiency (Figure S5(d)).[25]

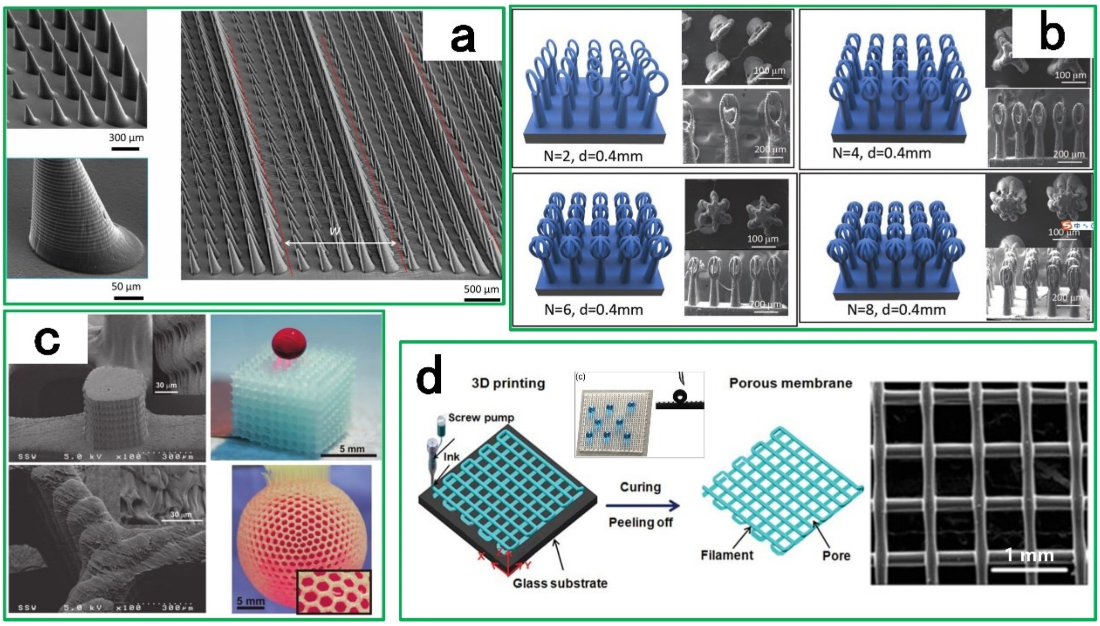

Figure S5. Different morphology fabricated by 3D printing. a) Tilted conical pillars.[22] b) Eggbeater arrays. Reproduced with permission from ref. [23], copyright 2017, Wiley-VCH. c) Lattice and hollow ball. Reproduced with permission from ref. [24], copyright 2013, Royal Society of Chemistry. d) Superhydrophobic membranes and meshes with porous structure. Reproduced with permission from ref. [25], copyright 2017, Royal Society of Chemistry.

Template method

Template replication technology has the characteristic of high efficiency, low cost, and easy operation, which can maintain high replication accuracy and excellent shape adaptability in the fabrication of the microstructures of SHS. On the basis of the template replication technology, regular micro/nano structures with dissimilar shapes and sizes can be fabricated, including conical arrays, circular truncated cone, and syringe needle shape. Li et al. fabricated the conical PDMS smooth needle microstructures with the single needle size of about tens of microns by template replication technology, which could be used for the collection of micro-sized oil droplets, as shown in Figure S6(a).[26] Gustav et al. also fabricated the SHS successfully. The PDMS circular truncated cone arrays about bottom diameter of 200 µm were fabricated by template replication and the nanostructures were fabricated by spraying the PTFE coating (Figure S6(b)).[27] Song et al. used demolding method to replicate rough syringe needle shape and straight conical pillar shape microstructures of the aluminum plate surface on PDMS, the rough microstructures facilitate the fabrication of superhydrophobicity, as shown in Figure S6(c).[28]

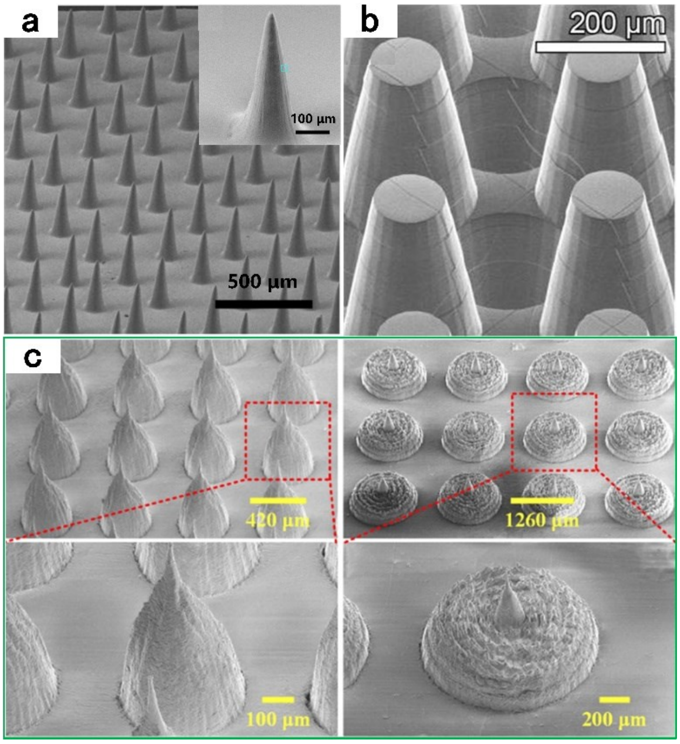

Figure S6. Different morphology fabricated by template replication. a) Conical PDMS needle structures.[26] b) PDMS circular truncated cone. Reproduced with permission from ref. [27], copyright 2018, American Chemical Society. c) PDMS arrays. Reproduced with permission from ref. [28], copyright 2019, American Chemical Society.

Coating method

Coating method refers to the application of a superhydrophobic coating directly on the substrate, which is universal for most materials ranging from hard materials such as metals and ceramics to soft materials such as sponges and fabrics. Lu et al. fabricated the SHS with high strength by coating ethanolic suspension of perfluorosilane-coated nanoscale titanium dioxide nanoparticles on the surfaces of glass, steel, cotton and paper, and the SHS maintained excellent water repellency after finger wipe, knife-scratch, and even tens of abrasion cycles with sandpaper (Figure S7(a)).[29] The coating can also be formed by other methods, such as sol-gel method,[30, 31] self-assembly technology,[32] and electro-spray deposition[33]. Lin et al. activated the cotton fabric by plasma and then immersed it in an ethanol suspension containing tetraethoxysilane, hydroxyl-terminated polydimethylsiloxane and ammonium polyphosphate. After the addition of ammonia, the in situ sol-gel reaction was initiated to generate polydimethylsiloxane-silica hybrid, and the micro-nano structured composite coating on cotton fabric was successfully fabricated, as shown in Figure S7(b).[31] Chen et al. fabricated the surface with nanoscale SiO_2 particles on the meshes through electro-spray, then modified the microstructure mesh with low surface energy material to obtain superhydrophobicity, as shown in Figure S7(c). With the advantages of simple fabrication process and excellent performance, coating method has been widely applied to fabricate SHS.

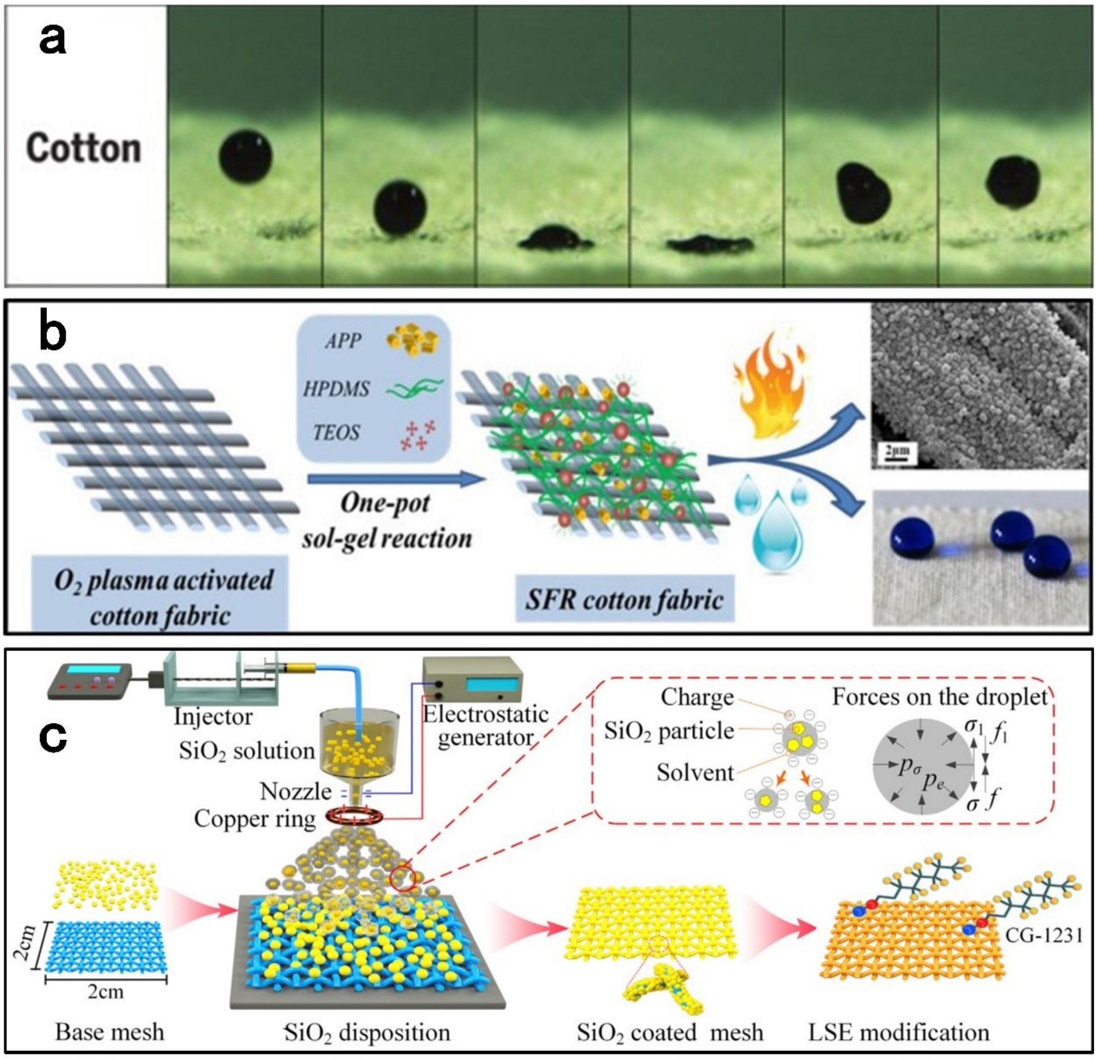

Figure S7. SHS fabricated by coating method. a) Droplet bouncing on the surface of cotton coated with nanoparticles. Reproduced with permission from ref. [29], copyright 2015, American Association for the Advancement of Science. b) SHS fabricated by col-gel method. Reproduced with permission from ref. [31], copyright 2018, Elsevier. c) SHS fabricated by electro-spray method. Reproduced with permission from ref. [33], copyright 2020, Elsevier.

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