Viruses for Plasmonics:
Virus-based Fabrication of Plasmonic Metamaterials

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Materials chemistry yearns to push beyond the known limits of nature in hopes of creating the next generation of functional materials. Within the past few decades, an opportunity to test these boundaries has presented itself in the form of virus-based designing of plasmonic metamaterials. Metamaterials are composite materials with artificially designed geometry, shape and arrangement of sub-wavelength unit structures[1,2]. The structural units of a metamaterial are known as meta-molecules and are smaller than the wavelength of operation[3]. Metamaterials have attracted the attention among the research community as they exhibit exotic electromagnetic properties such as negative refractive index, artificial magnetism and invisibility cloaking[4–6] (Figure 1).

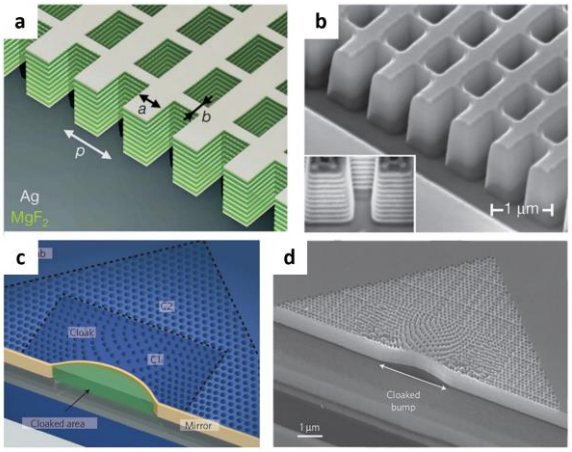

Figure 1: Metamaterials and the structure of meta-molecules. (a) Schematic and (b) SEM image of a negative refractive index metamaterial with alternating silver and magnesium fluoride multilayers (adapted from reference 5). (c) Schematic and (d) SEM image of an invisible cloaking metamaterial fabricated on a silicon-on-insulator wafer (adapted from reference 6).

The fields of metamaterials and plasmonics evolved separately until the interlacing of the two areas proved promising in novel applications of biosensing, sub-wavelength imaging, optoelectronics[7–9]. Plasmonic metamaterials consist of nanoscale meta-molecules which use the energy from oscillating free electrons to express material properties in the mesoscale[3,10,11]. As the material properties of plasmonic metamaterials depend on the size, shape and interparticle distance of the nanoscale structures, the fabrication of these meta-molecules demands a synthetic technology with 1–100 nm scale spatial control, especially when designing subwavelength scale features for metamaterials operating in the near infrared and visible regimes[12]. Conventional plasmonic metamaterial fabrication employs top-down lithography with high spatial

resolution and the ability to construct three-dimensional structures using a layer-by-layer procedure[12,13]. However, top-down lithography methods require expensive, complex tools and are not cost effective for mass production[11].

Recently, nature-inspired bottom-up approaches have emerged as an alternative method to fabricating plasmonic metamaterials[7,11,14]. While research in this area is still in its initial stages, using natural building blocks such as DNA and proteins, are proving to be simple and powerful routes in pursuing controlled self-assembly of nanostructures into mesoscale multidimensional materials[15,16]. In this light, viruses offer an opportunity as precise and controllable building blocks in plasmonic metamaterial synthesis.

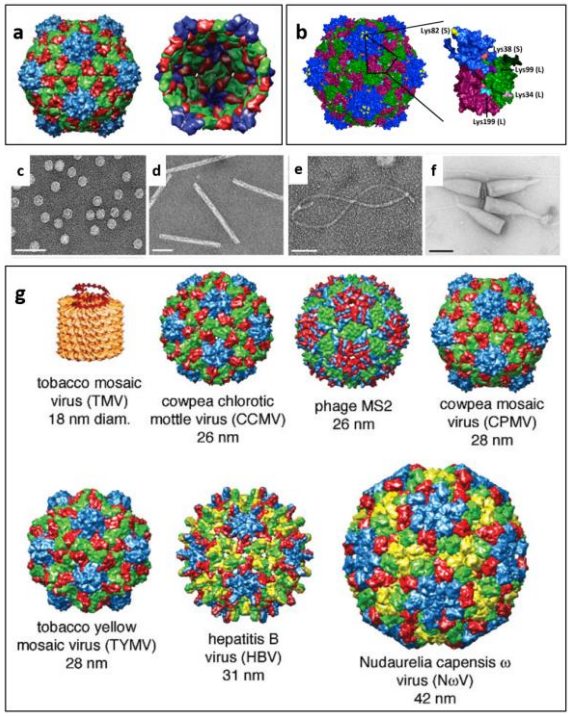

Figure 2: Structures of virus capsids. (a) Cowpea mosaic virus capsid surface and cross section with the hollow core (adapted from reference 17). (b) Protein subunit of cowpea mosaic virus (adapted from reference 18). TEM images of (c) icosahedral cowpea mosaic virus, (d) helical tobacco mosaic virus (e) tubular grapevine virus and (f) bottle-shaped *Acidianus* virus (scale bars: 100 nm) (c–f adapted from reference 19). (g) Schematic showing various sizes of viruses (sourced from VIPER database http://viperdb.scripps.edu).

Viruses used in metamaterial research are non-enveloped viruses, containing a simple basic structure with a protein coat enclosing viral genetic material[17]. The virus coat, or capsid is composed of protein subunits self-assembled to form symmetric monodisperse viruses of sizes ranging from 10–100 nm and shapes such as icosahedrons, tubes and helices[18,19] (Figure 2). As a result of these structural features, viruses can be viewed as polyvalent particles capable of assembling into three-

dimensional nanoscale structures[18]. Furthermore, genetic modifications or bioconjugation can also drive virus capsids to self-assemble into multidimensional higher-ordered structures[20]. These properties, along with the ease of production by culturing in plants or cells and stability in a range of pH, temperature and solvent conditions, propel viruses to be a contender as a nanoscale template and a mesoscale scaffold to precisely control the position and symmetry of plasmonic particles[7]. Thus, virus-based fabrication of metamaterials have the advantages of rapid synthesis of virus capsids in mass-scale, along with versatility of capsid chemistries including genetic engineering and bioconjugation[21].

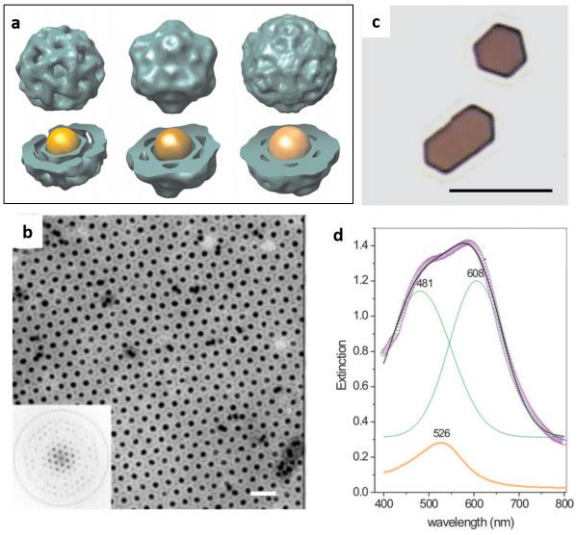

Figure 3: The first virus-based plasmonic metamaterial. (a) 3D reconstruction of three different brome mosaic virus capsid shell structures enclosing 6, 9 and 12 nm gold nanoparticle cores. (b) Negative stain TEM image of the 2D lattice formed by self-assembly of 12 nm gold nanoparticle core-shell structure (scale bar: 50 nm). (c) Transmission optical image of the 3D crystal formed with the 12 nm gold core-shell structure, (scale bar: 50 μm). (d) Optical spectra for 3D crystal (purple circles) with a double hump compared with nanogold core-capsid shell structures in solution (orange line) is shown. Gaussian fit (black line) and the peaks superimposing to form the double hump (green) are also given (a–d adapted from reference 22).

The first virus-based plasmonic metamaterial was demonstrated using a core-shell structure formed via self-assembly of protein subunits around plasmonic nanoparticle cargo. Brome mosaic virus capsid proteins were used as a scaffold to synthesize nanogold core-capsid shell structures followed by assembly into two- and three-dimensional crystals[22] (Figure 3b, c). Gold nanoparticles of 6, 9 and 12 nm diameters resulted in three capsid shell structures, indicating that the morphology of the self-assembled capsid depends on the size of the core (Figure 3a). Optical spectrum for the three-dimensional crystals grown from nanogold core-capsid shell structures showed multipolar plasmonic coupling between adjacent gold cores[22] (Figure 3d).

The first step in fabricating plasmonic metamaterials is the synthesis of the plasmonic meta-molecule. Nanoparticles can be arranged on the virus capsid surface to form metamolecules with collective plasmonic responses[7]. This virus-templated synthesis, which uses the symmetry of the capsid, is facilitated via bioconjugation or electrostatic interactions between the plasmonic nanoparticle and the virus capsid, achieved by either genetic modification of capsid protein amino acid sequence or surface modification of the metal nanoparticle[21]. Precise ordering of gold nanospheres on cysteine-mutated cowpea mosaic virus presents an example of viral templating of plasmonic meta-molecules[7,8] (Figure 4a, b). The mutated icosahedral virus contained exposed thiol groups at the 12 vertices to position gold nanospheres with defined spacing and symmetry, experimentally forming three-dimensional nanoclusters with 6–12 nanospheres per capsid. The engineered nanocluster showed resonance at visible frequencies due to interactions between adjacent nanospheres. Furthermore, three-dimensional finite-element simulations for nanoclusters with 12 nanospheres with 30 nm diameter indicated ten-fold enhancement of local electromagnetic fields, occurring as a result of near-field coupling from small interparticle distances[7]. The fabrication of silver nanoparticle-based plasmonic meta-molecules has been demonstrated using tobacco mosaic virus (TMV) discs[23]. Wild-type TMV discs were decorated with 5 to 6 silver nanoparticles by photo-reducing silver ions in the presence of the carboxylate groups in the discs (Figure 4c, d). When compared to the surface plasmon resonance of colloidal silver nanoparticles at 394 nm, the peak for the TMV-silver nanoring broadened with an additional mode at 500 nm due to in-plane coupling of adjacent nanoparticles[23]. Furthermore, TMV was mutated to include exposed cysteine groups, which provided additional binding sites for plasmonic nanoparticles[23]. The cysteine-mutated TMV discs formed continuous silver rings after photo-reduction (Figure 4e). The plasmon resonance for the continuous silver nanoring was red-shifted compared to colloidal silver nanoparticles, and displayed a weak mode at 730 nm as a result of the magnetic coupling of rings with electromagnetic radiation[23]. Another synthesis route of TMV-based meta-molecule fabrication uses the rod-shaped virus to produce chiral nanogold metamaterial building blocks[24] (Figure 4f, g). Gold nanoparticles were attached to wild-type and peptide modified TMV rods, where enhanced circular dichroism in both ultra-violet and visible regions are observed[24].

Virus-based multidimensional material with plasmonic components have been presented which could, in theory, impart metamaterial properties. Virus nanocages can be used to direct the self-assembly of encapsulated plasmonic nanoparticles into multicomponent superlattices with diverse functionalities[25]. An example for such a material is the hierarchical assembly of binary nanoparticle superlattices, which was achieved using electrostatic interactions between cowpea chlorotic mottle virus (CCMV) and gold nanoparticles[25]. CCMV has an overall negative surface charge, with charge density localized in patches symmetrically distributed on the capsid surface. Interaction between the capsid with negative patches and gold nanoparticles with positive surface charge was used to drive the formation of binary nanoparticle superlattices. The self-assembled CCMV-gold nanoparticle superlattice formed a face-centered cubic crystal structure, with lattice constants shorter than visible wavelengths[25].

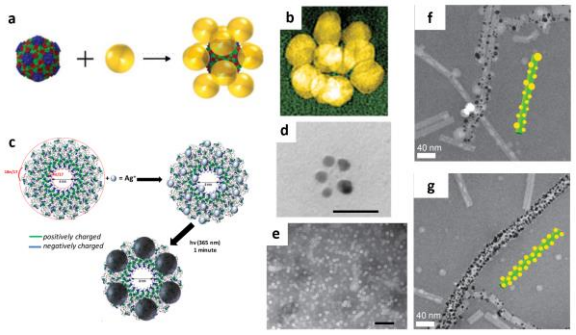

Figure 4: Fabricating meta-molecules using virus-templates. (a) Schematic showing gold nanoparticles attaching onto the cysteine-mutated cowpea mosaic virus capsid. (b) False-colored TEM image of the nanocluster (scale bar not given) (a, b adapted from reference 7). (c) Schematic of tobacco mosaic virus-templated synthesis of silver nanorings. (d) TEM image of the discontinuous nanoring showing five silver nanoparticles (scale bar: 50 nm). (e) Continuous silver nanoring fabricated using tobacco mosaic virus discs (scale bar: 100 nm) (c–e adapted from reference 23). TEM images and schematics of the (f) wild-type and (g) peptide modified tobacco mosaic virus-based chiral nanogold meta-molecule (f, g adapted from reference 24).

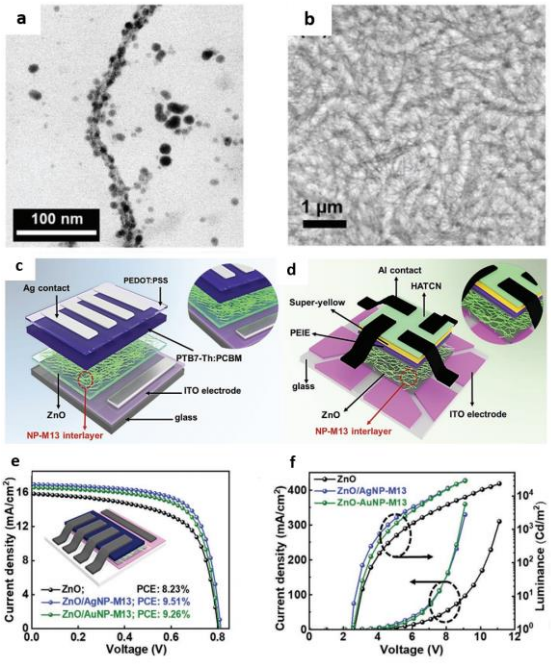

Figure 5: Application of virus-based plasmonic metamaterials in optoelectronics. (a) TEM image of M13B virus decorated with silver nanoparticles. (b) FESEM image of the M13B virus-silver nanonetwork of the metamaterial. (c) Architecture of the organic solar cell (SC) with the virus-based plasmonic metamaterial labelled in red. (d) Architecture of the organic light-emitting diode (LED) with the virus-based plasmonic metamaterial labelled in red. (e) J-V characteristics of the organic SC and (f) J-V-L characteristics of the organic LED fabricated using silver (blue) and gold (green) plasmonic meta-structures compared to devices with ZnO layer only (a–f adapted from reference 9).

Virus-based plasmonic metamaterials have potential applications in the fields optoelectronics[9]. Recent work presented plasmonic gold or silver nanoparticle decorated M13 bacteriophage (M13B) bio-nanostructures incorporated into organic solar cells (SC) and light-emitting diodes (LED)[9]. The plasmonic metamaterial demonstrated enhanced plasmon-coupled resonance and gap-plasmon effect. When introduced into organic SC and LED devices, the nanoparticle-M13B metamaterial improved the power conversion efficiency by 15.5% and quantum efficiency by 22.6% respectively[9] (Figure 5).

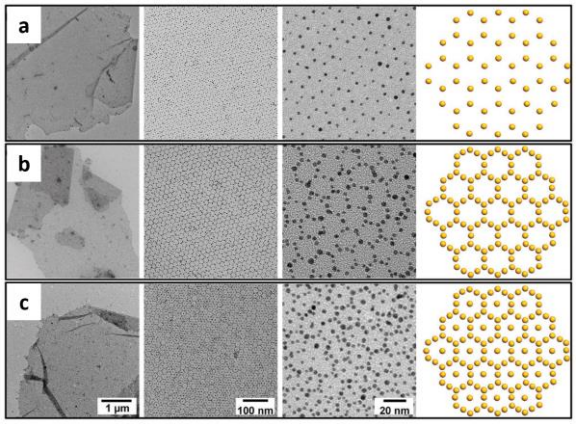

Figure 6: Controlled self-assembly to form virus-based plasmonic metamaterials. TEM images and schematics of (a) honeycomb, (b) ring and (c) ring-central nanoparticle 2D lattices (a–c adapted from reference 26).

Despite the successful developments in fabricating virus-based meta-molecules, one of the main challenges from the perspective of metamaterials lies in the difficulty of assembling virus-based meta-molecules into mesoscale metamaterials. Unlike nondecorated viruses which have the tendency to undergo controlled self-assembly[20], inducing self-assembly of virus-based plasmonic meta-molecules requires integrating capsid protein-protein interactions with protein-nanoparticle interactions[26]. For example, recent work shows TMV disks with inner-ring cysteine and outer-ring histidine mutations, self-assembling into a 2D monolayer via Cu^{2+}-histidine chelation, followed by periodic binding of gold nanoparticles to give three different 2D lattices which have not been observed before[26] (Figure 6). Such work paves the way to actualizing the aspiration of creating metamaterials by controlled assembly of virus-based plasmonic meta-molecules.

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