ZnO tetrapod materials for functional applications

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In the last 15 years, more than 50,000 papers with zinc oxide (ZnO) in the title are listed within ISI database. The outstanding popularity of ZnO has many reasons; the most important one appears to be its multi-functionality, resulting in applications in physics, chemistry, electrical engineering, material science, energy, textile, rubber, additive manufacturing, cosmetics, and pharmaceutical or medicine, as well as the ease to grow all kinds of nano- and microstructures. A key structure is the tetrapod-shaped ZnO (T-ZnO), which we want to focus on in this mini-review to demonstrate the remarkable properties and multifunctionality of ZnO and motivate why even much more research and applications are likely to come in near future. As T-ZnO came into focus again mainly during the last 10 years, the big data problem in T-ZnO is not as severe as in ZnO; nevertheless, a complete overview is impossible. However, this brief T-ZnO overview attempts to cover the scopes toward advanced technologies; nanoelectronics/ optoelectronics sensing devices; multifunctional composites/coatings; novel biomedical engineering materials; versatile energy harvesting candidates; and unique structures for applications in chemistry, cosmetics, pharmaceuticals, food, agriculture, engineering technologies, and many others. The 3D nanotechnology is a current mainstream in materials science/nanotechnology research, and T-ZnO contributes to this field by its simple synthesis of porous networks as sacrificial templates for any desired new cellular materials.

Introduction

ZnO belongs to the direct and wide bandgap (~3.37 eV) metal oxide semiconductor family and is a very extraordinary material in terms of nano- and microstructuring and applications [1–13]. It exhibits a typical hexagonal-wurtzite crystal structure that offers very easy growth of different one-dimensional (1D) nano- and microstructures [5]. Because of high surface to volume (S/V) ratio, 1D ZnO nanostructures find interesting potentials for nanoelectronics and sensing applications. Their non-centrosymmetric crystal structure with Zn^{2+} and O^{2-} polar surfaces equips them with unique piezoelectric properties that make them rather more attractive for smart technologies, for example,

self-powered devices, energy harvesting, piezotronics, piezophototronics, piezophotocatalysis, etc. [14–16].

The direct bandgap ~3.37 eV and existence of various interesting defects further make ZnO nanostructures to be very promising candidates for photodetection and advanced optoelectronics/luminescent technologies [5,17]. Generally, defects are unwanted from a crystallographic point of view, but the science behind them makes ZnO very interesting, opening further new application scopes, for example, defect-induced ferromagnetism, p-type conductivities, etc., in ZnO nanostructures. Actually, defects in ZnO have been a never-ending debate, and a lot of research work needs to be done in future for actual realizations of ZnO's application potentials [5,9,17].

By a non-destructive approach, i.e., just by illuminating with UV light, oxygen vacancies can be created on the ZnO surface, which lead to significant alteration in its intrinsic properties,

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for example, increase in n-type conductivity, switchable wetta-bility (super-hydrophobicity to ultra-hydrophilicity and vice versa), and several other physical and chemical features, enabling its versatile application scopes in various interdisciplinary research fields [18,19].

Physical robustness of any material is probably the first and foremost requirement for realization of different applications, and in this respect, ZnO is a very rough and tough material. Par-ticularly, ZnO material is physically very strong, for example, it has Young's modulus (bulk crystal) ∼150 GPa and is quite stable up to very high temperatures (∼1800 °C), etc., hence a very promising material to work within almost any environmental conditions [20,21]. However, it can be easily chemically dis-solved in acidic solvents (below pH ∼ 6) and reactive vapors or gases, which is sometimes an issue in some chemistry-related applications. But from our recent experiences, it is indeed an advantage because this feature offers an opportunity for ZnO structures to be utilized as sacrificial templates for creating new nano- and microstructures from various other materials.

As far as the biomedical utilizations of ZnO are concerned, one should look back into the ancient medical history a bit [22]. Zinc is one of the most important nutrients for the human body (controls more than 300 metabolic functions) [23] which the body gets from foods, plants, fruits, and meat and also from Zn supplements. Actually, zinc-fly ash was quite much in medi-cal use in ancient times for various fatal illnesses and was quite efficient, too [22]. With respect to advancement in science, ancient Zn-based medications were limitedly understood (still in use in some interior regions in different parts of the world), but with respect to the development of nanotechnology and nanomedicine, ZnO materials are under debate toward their scopes in biomedical engineering. The zinc-fly ash used in ancient times was probably in some form of nanomaterials (the term 'nanotechnology' was unknown in those times), but the presently developed ZnO nanomaterials are being debated for biomedical utilizations including their high nanoscale-level cytotoxicities on cancer cells [24]. There exists a separate world for its biomedical relevance, but a lot of new aspects of ZnO nanostructures still needs to be investigated [24]. In our best opinion, although a huge literature exists, even a lot more has to come in the direction of ZnO nanomaterial-based research and applications.

It is important to mention that the global zinc oxide produc-tion amounts to several Million Tons (>40 MT) by different chemical companies as per Global Zinc Oxide Market Report 2017, which already demonstrates the broad research and appli-cation scopes of ZnO material. The developed ZnO material is in the form of powder (frequently in mm and μm length scales but also in nm for special applications) which is mainly used by var-ious industries, for example, electronics, chemical, rubber, tex-tile, pharmaceutical, cosmetics, etc. in form of additives, fillers, etc. [25]. The surface area (to volume ratio) plays a key role in most of the applications, and, therefore, nanoscale ZnO materi-als have recently become rather very important,hence their dif-ferent synthesis strategies [25]. A careful literature review suggests that ZnO material in powder form has been indepen-dently utilized by several industries in various possible ways, and its roles have been independently discussed in respective

fields, such as in physics, chemistry, biology, engineering, and medicine. However, it is tough to find a common ZnO structural platform that is of interest for every field. Manifold applications have been the driving force behind the growth of various ZnO nano-and microstructures,which the ZnO (materials) commu-nity has already paid major attention to but several requirements are still challengeable.

As far as the growth is concerned, a large variety of ZnO nano- and microstructures with almost any complex imaginary shape can be easily found in the literature [5,17]. It all depends upon the kinetics in the synthesis processes, and, actually, a large vari-ety of synthesis strategies have been adopted for various ZnO structures. Physical synthesis strategies have key advantages over wet chemical and biological approaches as they do not involve strong chemical reagents, but at the same time, obtained nanos-tructural varieties are limited [26]. Also, the easy accessibility of the extraordinary nanoscale features with respect to general applications (e.g., building a nanodevice based on single nano-wire) is another issue, and for that, advanced integration tech-nologies are required, such as sophisticated clean room processing, in addition to, synthesis that makes the overall fabri-cation process highly expensive [20,26]. To overcome the utiliza-tion complexities, several conventional and unconventional nanostructure synthesis strategies, for example, directly on the micro-chips/substrates, have been adopted, but the large-scale fabrication is still being debated [26–28]. Three-dimensional (3D)-architectured materials, built from micro- or nanoscale building blocks—such as ZnO tetrapods, multipods, etc., exhibit optimal stability and high free volume to meet many of the tech-nical requirements in contrast to conventional 0D, 1D, and 2D nanostructures. But the versatile synthesis of these 3D-architec-tured materials in desired quantities is a highly challenging task [20,21]. The versatile nano- and microstructuring abilities of ZnO could play a very prominent role in materials science engineering and technology, and the unique potentials of ZnO tetrapods are briefed in this review.

Since almost the middle of the 19th century, the tetrapod shape has been unique in the coastal engineering as waterbreak for efficiently attenuating the water waves. Typically, it is made out of four arms interconnected together via a central core at angles ranging from ∼105° to 110° with respect to each other. Their unique 3D morphology offers easy accessibility of nanos-cale features as surface areas of individual arms that are easily accessible irrespective of how they are placed. The tetrapod shape is indeed a very big advantage. Forces applied along one arm are transferred to the others, leading to high stability. Even if a large number of tetrapods are accumulated together, they anony-mously construct a unique macroscopic interconnected architec-ture with very high porosity (almost impossible to achieve with spherical nanoparticles) [20,26]. The concrete tetrapods were mainly popular in coastal engineering, but nano- and microscale ceramic tetrapods rather exhibit unique potentials toward advanced nanotechnology. Zinc oxide material has unique abil-ities for nanostructuring in this respect, as varieties of tetrapods and multipods can be easily grown just by following synthesis strategies, for example, the flame transport synthesis approach [20,21,26]. Very importantly, a ZnO nanotetrapod is basically built out of four 1D ZnO nanorods (significantly discussed by lit-

erature), hence all those physical and chemical features from 1D nanorod shape are already included in the tetrapods. The unique 3D spatial tetrapod geometry, which is a combination of these four 1D nanorods (interconnected together via a central core), makes it very special in terms of properties and surface accessibility (nanorods will form agglomerated bundle if placed together). Tetrapod shape of ZnO material is probably the most important structure from the application point of view, and this review highlights only some key applications.

It is necessary to emphasize that the tetrapod-shaped ZnO nanostructures are not something new to the community. Actually, a lot has been discussed about their growth mechanism including molecular dynamics simulations and using advanced transmission electron microscopy tools in almost the last 25 years, but a clear understanding of the growth is still lacking [2,4–7,29–78]. Generally, the growth of tetrapod-type nanocrystals from inorganic hexagonal-wurtzite materials initiates via formation of octahedral seed nuclei [54] or zinc-blende (ZB) core [78], but several other models have also been proposed. The recent detailed theoretical studies [67,69] provide fundamental insights into the tetrapod growth mechanism; however, it has to be again experimentally confirmed, and maybe some advanced *in-situ* characterization tools can close the debate that is yet open. Tetrapod growth has already been considered by a large number of published papers. The key aim of this review is to emphasize mainly on application scopes of tetrapod structure from ZnO in various science and engineering disciplines.

The large attention about tetrapods' growth itself indicates their high technological relevance for various applications, but their mass scale fabrication was a big technical challenge that has been successfully achieved by the recently introduced flame transport synthesis (FTS) approach by us [20]. Synthesis by wet-chemistry approaches mostly involve strong chemical reagents that definitely leave their fingerprints behind; however, physical routes (vapor deposition, vapor–liquid–solid, microwave, etc.) suffer from limitations like fabricating nanostructures with any desired size, shape, and quantity (for example, ZnO tetrapod shape would be difficult to synthesize, yield is poor), and they involve high cost, too. Synthesis strategies involving catalytic nanoparticles are already out of scope as synthesis of large quantities of ZnO tetrapods will be questionable (multistep process, high cost, etc.), and, additionally, the catalytic particles act as defects that might be undesirable for certain applications. Self-catalytic processes are rather advantageous in this context, and Table 1 provides a brief overview of some of these synthesis methods. From the long list of ZnO tetrapod synthesis methods, only the most relevant processes have been compared in Table 1. Process simplicity, size of tetrapod, size distribution, yield, cost-effectiveness, etc. are, probably, the most crucial parameters for utilization of these tetrapods and a careful comparison from Table 1 suggests that microwave and combustion methods at least exhibit the potentials for large-scale ZnO tetrapod productions and could open their scopes toward industrial applications. The developed FTS approach at Kiel University (which is a further

TABLE 1

Overview of some catalysis-free growth processes for ZnO tetrapods toward upscalability.

Method [Refs.]	Conditions	Size, Quality, Yield
Vapor-phase [64]	Zn sublimation in air oxygen mixture; pressurized electric furnace ($\sim$920 °C); multistep process	ZnO tetrapods with long arms (30–200 μm); poor yield
Wet chemistry [34]	Growth in a chemical vessel (200–300 °C); zinc hydroxide, ammonia hydroxide and chloride solutions; specially designed silver lined tube	Tetrapod arms; broad size distribution; poor yield
Hydrothermal [79]	Aqueous solution, $ZnSO_4$ and NH_3 in reactor @100 °C; washing required (150 °C hot air)	Uniform tetrapods; multistep process; poor yield
Thermal evaporation [75]	Zn sublimation in the tube furnace (800–1000 °C); Zn filled quartz boat in tube	Mixed tetrapods; broad size distribution; poor yield
Evaporation & recondensation [54]	Zn evaporation; tube furnace (1100 °C); in air	Mostly tetrapods; total size range 300 nm–15 μm; arm dia: 30–650 nm; low yield
Chemical vapor deposition [59]	Zn sublimation in tube furnace (630 °C); on Si substrates; air + O_2 mixture environment	Asymmetrical tetrapods; very low yield
DC thermal plasma [76]	DC plasma reactor; N_2 gas; fast process (10 ms); simple process; direct conversion of Zn powder into ZnO nanostructures	Mixed structures including tetrapods; broad distribution; high yield (overall, nearly 100%); very less tetrapods
Vapor phase growth [72]	Zn evaporation; tube furnace (700 °C); carrier gases (Ar, O_2); gravimetric separation; processing time $\sim$ longer	Arm (length $\sim$ up to 2 μm, dia 100 to 300 nm); aggregates; Zn traces; yield high; broad size distribution
Microwave [73]	Zn oxidation; tube furnace (4 Torr, up to 600 °C), microwave (400 W, 2.45 kMHz, $\sim$1000 °C), vacuum, carrier gasses (Ar, O_2); processing time $\sim$ 30 min	Tetrapods arm (length $\sim$ 0.5 μm, dia $\sim$ 50 nm); crystalline; yield $\sim$ 75%; broad size distribution
Combustion method [52]	Combustion of Zn microparticles in reactor in air; continuous synthesis approach; multistep process	Uniform nanotetrapods; relatively broad distribution (size); lower yield
Flame transport synthesis [20,26]	Conversion of Zn microparticles into tetrapods; sublimation and regrowth (solid–vapor–solid process); muffle/backing furnace ($\sim$900 °C); air environment; single-step process; (i) using sacrificial polymer (PVB), (ii) direct growth. PVB process: micro- and nanotetrapods; arm dia 200 nm–2 μm; arm length; 1–15 μm; (4 gm Zn: 1 g ZnO-T); (ii) direct growth; arm dia: 100 nm–1 μm; length: 2–20 μm; 10 g Zn wire: 3 g ZnO-T	Tetrapods in large quantities; powder form; uniform narrow size distribution; highly crystalline; PVB process: yield $\sim$ 25%; direct growth: yield $\sim$ 30% (Entirely tetrapods in both) Purchase from: Phi-Stone AG Kiel, Germany (our FTS based Start-up Company)

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simplified version of combustion process) offers a simple, cost-effective, and solvent-free growth of versatile micro- and nanostructures from various metal oxides (ZnO, SnO_2, Fe_2O_3, Al_2O_3, Bi_2O_5,...), including mass-scale production of micro- and nanoscale ZnO tetrapods [20,21,26]. In the FTS process, the metallic Zn microparticles are directly converted into ZnO tetrapods in the flame (inside the muffle furnace) at a high temperature via solid–vapor–solid (SVS) growth process [26]. The growth process for ZnO tetrapod structures in FTS approach has been discussed in detail in previous works [20,26]. Just by varying the experimental conditions in the FTS approach, the arm morphologies of tetrapods can be tailored from nano to microscale and also from low to very high aspect ratios [26]. Since there are no chemicals involved, the FTS-synthesized ZnO tetrapods and nanos-

tructures offer the accessibility of almost true ZnO surface properties that make it very interesting for various applications [21,26]. The ZnO tetrapod growth process by FTS technology is very cost effective, and it can be easily upscaled. Based on ZnO tetrapod growth FTS approach (Table 1), a startup company (called as Phi-Stone AG) has been launched at Kiel, Germany, which is upscaling the synthesis process, and hence a progressive step toward the realization of ZnO tetrapods in various possible real day-to-day applications [21].

Tetrapods exhibit very promising technological potential in terms of applications, but it is very hard to find a detailed article that lists their capabilities. A few do exist but with only limited information in pieces. The motivation of the present article is to give a detailed overview to the readers about future research
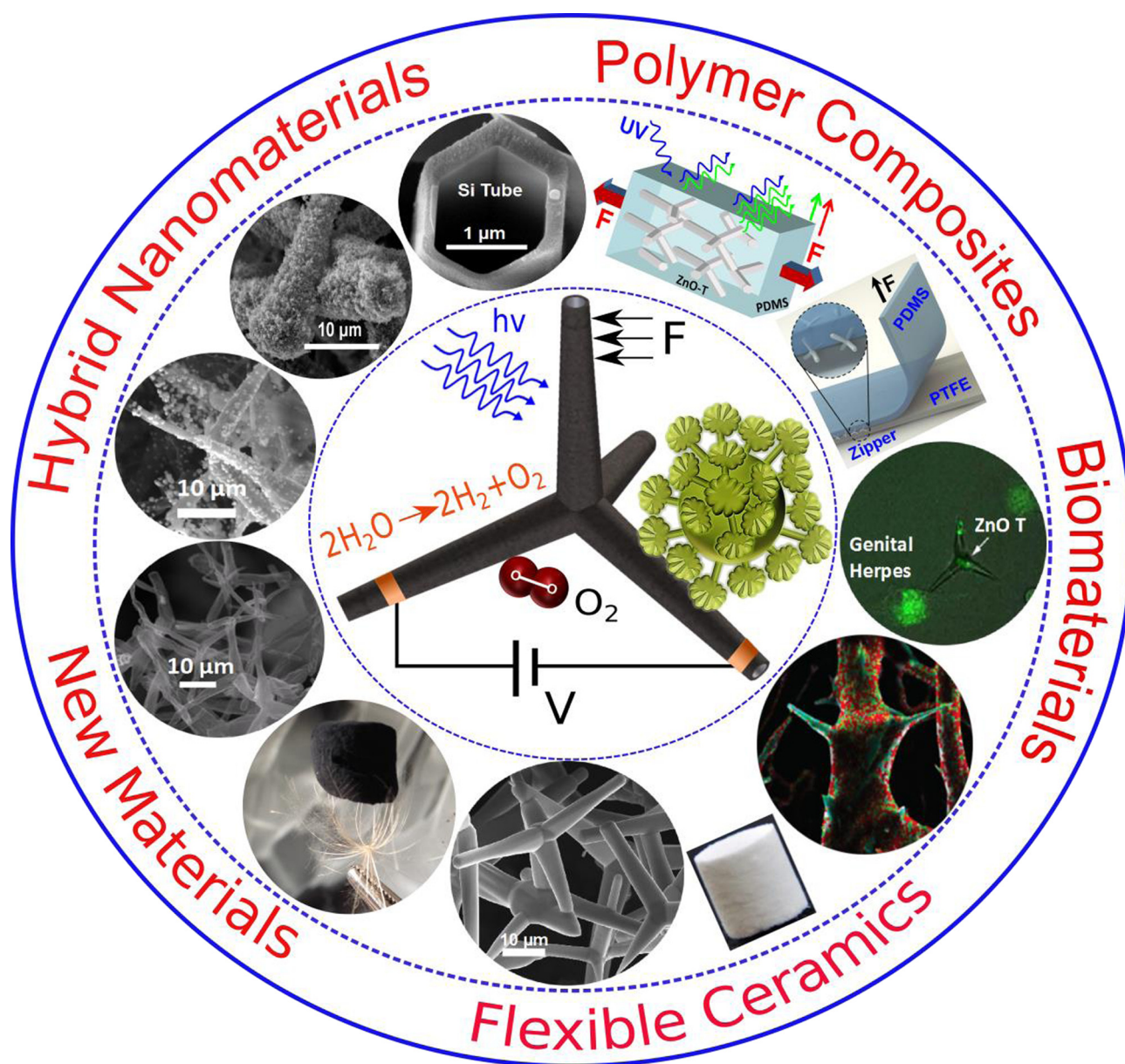

FIGURE 1

Overview of different research areas where ZnO nano- and microtetrapods could play a very important role. They can be efficiently utilized in a lot of innovative applications as well as toward growth of new and hybrid multifunctional 3D micro- and nanostructured materials (many more applications are yet to be realized in future). [The here used Figures have been reproduced with permission from published papers which have been cited in this review.]

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scopes, nanostructuring possibilities, and advanced applications with ZnO tetrapods. Recently, the ZnO tetrapods have been grown by FTS approach in large amounts and have been utilized in several innovative applications, and a glimpse of various possible opportunities is only demonstrated here. Figure 1 presents a brief overview of application scopes of ZnO tetrapod-shaped structures in different directions; however, a lot more (probably beyond our imaginations) has yet to come. The tetrapodal shape is unique in the sense that irrespective of how they are placed, one arm is ever pointing upwards, and hence it offers easy and simultaneous accessibility of excellent nanoscale 1D mechanical, electrical, optical, luminescent and other interesting features. The 1D arms are very strongly interconnected together via a central crystalline core that helps them to retain their three-dimensional shape irrespective of harsh handling or being under tough environmental conditions. Such geometry makes them very interesting because nanoelectronic devices from ZnO tetrapods with reliable electrical contacts can be easily fabricated and used for almost any kind of sensing applications (photo, gas, chemical, biological, etc.) [26,27,79]. The sensing response is mainly reflected as a change in particular property (luminescent, electrical, stress, etc.) when the sensing elements get in contact (physically, chemically, and mechanically) with the surface of ZnO tetrapod arms in the sensor device [80–83]. Because of the complex 3D shape, the ZnO tetrapods are better linker/filler candidates toward fabricating advanced composites in contrast to conventional spherical and 1D nanostructures that suffer agglomeration issues [84–88].

Structured ZnO materials have been significantly discussed in ancient medical practice [22] which needs to be revisited again using modern tools. The developed ZnO tetrapods have already shown very promising potentials against viral infections and several other fatal diseases [89–91]. ZnO nanostructures have got innumerable applications in chemistry in different forms; the ZnO tetrapods open further application avenues toward advanced chemistry because of their complex morphology, enabling fabrication of highly porous materials. Additionally, these ZnO tetrapods could be electrospinned together with polymers for developing rose-spike inspired biocompatible fibers with unique biocompatible features for advanced biomedical applications [92]. Porous 3D nanomaterials are currently in the mainstream of materials research because they offer easy accessibility of nanoscale features, and the complex shape of ZnO tetrapods offers simple fabrication of various macroscopic highly porous flexible ceramics [20,21]. The sacrificial nature of ZnO tetrapods is very advantageous as they can also be used to design other new materials in very simple and efficient ways. The sacrificial template-based strategy offers a large number of nanostructuring opportunities in terms of combining inorganics (metals, oxides, nitrides, phosphides, carbides, etc.), carbon (carbon nanodots, fullerenes, graphenes, single/ multi-walled carbon nanotubes, nanodiamonds, etc.), organic, polymers, zeolites, etc. materials together in the form of hybrid 3D nanomaterials for multifunctional applications. It might appear hyperbolic, but it is reality. Indeed, it is very tough to list all the possible application opportunities of ZnO tetrapods, and hence to give a feeling to readers in this field, we have summarized a list of application keywords of ZnO tetrapods in Table 2 (including all those applications where powder is being used, tetrapods can be preferably applied). However, there might be many more missing names that could be on board and will be realized in future. Table 2 will give a good motivation to general readers who are wondering about where these several million tons of ZnO materials are consumed and how important tetrapods could be for future technologies. The

TABLE 2

ZnO tetrapod material: application keywords overview in various fields.

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Electronics	Nanodevices; Photo Detection; Field Emitters; Gas Sensing; Biosensor (Glucose, Enzyme; Phenol, H_2O_2, Cholesterol, Urea, DNA, Protein, Markers, . . .) Devices; Piezotronics; Spintronics; Electromagnetic Shielding; Smart Devices, . . .
Photonics	Luminescent Devices; Light Scattering Elements; Imaging Technologies; UV Lasers; Light Emitting Diodes; Waveguides; Whispering Gallery Modes; Advanced 3D Optics; Future Lightening Technologies, . . .
Composites	Linkers – Joining Polymers; Advanced Polymer Composites; Self Healing/ Reporting Composites; Antifouling Coatings; Antireflective Coatings; Hydrophobic/Hydrophilic Polymer Coatings; Self-heating Coatings; Smart Textiles; Resins; Cross-Linker/Vulcanizer for Elastomers; Rubber Engineering Technology, . . .
Chemistry & Environment	Paints; Pigments; Inks; Catalysts; Photocatalysis; Water Purifications; Water Treatment; Advanced Membranes; Separation of Chemical; Food Meet & Vegetable Packaging; Environmental Sensing & Monitoring; Advanced Filters, . . .
Energy	Supercapacitors; Batteries; Solar Cells; Self-powered Devices; Nanogenerators; Energy Harvesting Devices; Power Electronics; Blue Energy; . . .
Engineering & Technological Industries	Light Weight Constructions; Additive Manufacturing; Adhesion Technologies; Ceramics; Space Technologies; Wood Engineering & Technology, Cement & Concrete Technology; Soft Robotics; Textile Engineering; Bulletproof Glasses; Dental Implants, . . .
Pharmaceutical Agriculture	Cosmetics; Creams; Powders; Wound Dressing Tapes, . . .Fertilizers; Plant Growth; Food Production; . . .
Biomedical	ROS Generation; Dental Implants & Pastes; Antiviral; Antibacterial; Antimicrobial; Antifungal; Antiallergic; Antidiabetic; Antitumor; Anticancerous; Antiseptics; Antioxidants; Immune Promoters; Wound Healing; Biomedical Imaging (Florescence Microscopy, MRI; PET); Drug Delivery; Gene Delivery, . . .
Ceramics & Glass	Flexible Ceramic Materials; Advanced Glasses; Porous Ceramics; Hybrid Ceramics; Ceramics Science & Technology, . . .
As Sacrificial Templates (New Materials)	New Tetrapods & 3D Nanomaterials from: Inorganic & Organic Materials; Semiconductors; Carbons; Polymers; Zeolites; Stretchable Hybrids; Porous Scaffolds; Cell Templates; Porous 3D Biomaterials (DNA, Proteins, . . .); Future Materials Engineering and Nanotechnology, . . .

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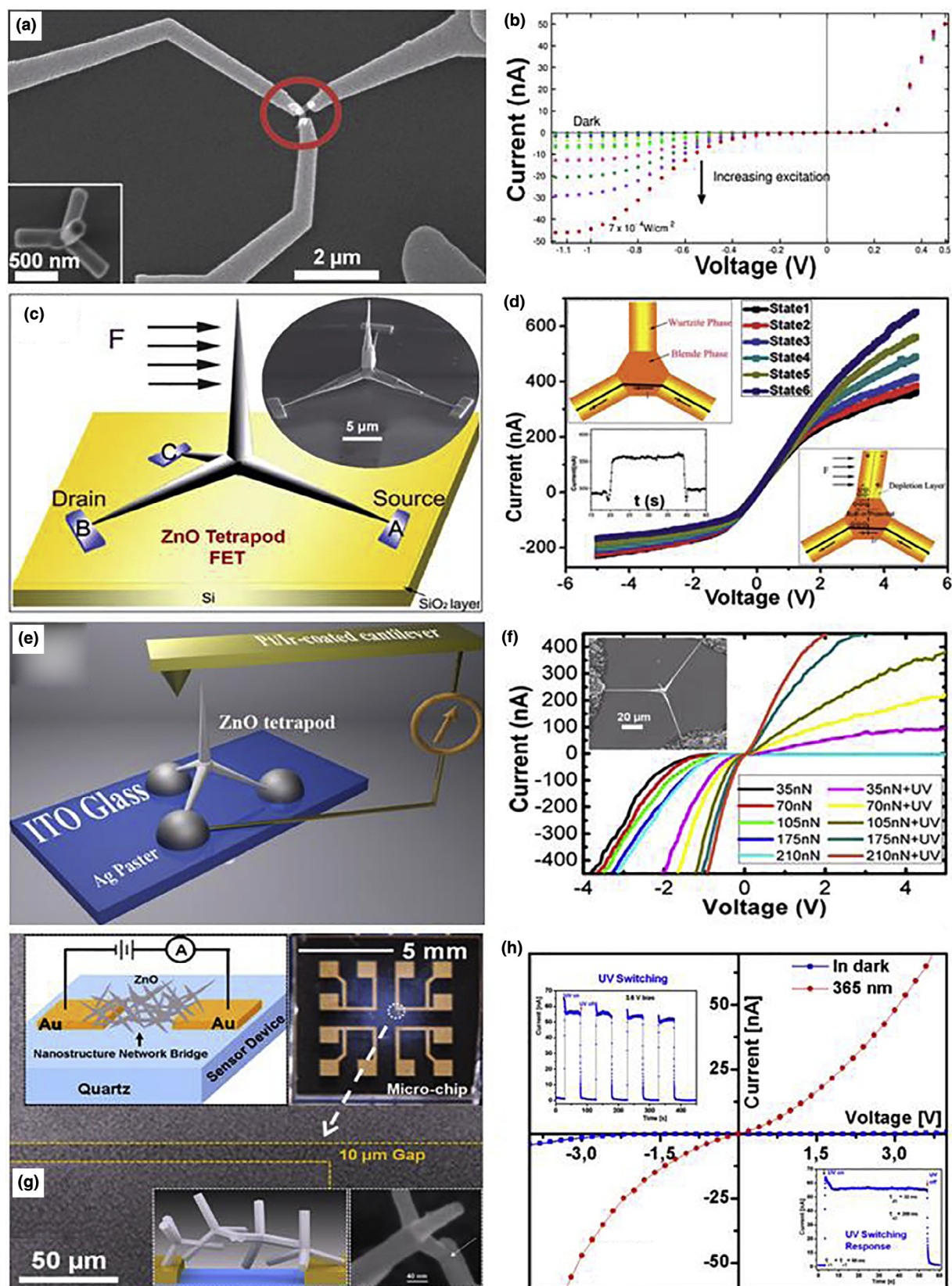
FIGURE 2

ZnO tetrapods for advanced electronic sensing devices: (a and b) Two terminal ZnO tetrapod-based electronic device and its UV-sensing response. (c and d) Logic gate field effect transistor (FET) device for force sensing based on piezoelectric effect. (e and f) Electronic sensing device combined UV light and force. (g and h) Interconnected ZnO tetrapod network-based fast UV sensor. [Reproduced with permissions from: (a, b and e, f) American Institute of Physics [98,106], (c and d) Royal Society of Chemistry [103], (g and h) Wiley VCH [27].]

glimpses of a few recent important application windows of ZnO tetrapods are briefed in the following sections.

Functional nanoelectronic devices

Nanostructures from ZnO exhibit interesting electrical characteristics due to their typical n-type conductivity arising from versatile defects, mainly the oxygen vacancies [9]. Also, the direct bandgap of ~3.37 eV facilitates these nano- and microstructures to easily absorb the UV visible photons efficiently. Because of both features, i.e., n-type conductivity and UV-sensitive bandgap, an electronic device can be efficiently used for versatile sensing purpose if it can be fabricated using adequate nano- and microstructures. 1D nanostructures from ZnO additionally possess piezoelectric properties due to their non-centrosymmetric crystal structure. Hence an electronic device based on 1D ZnO structures could be really utilized for multifunctional purposes. Tetrapod ZnO crystals [49,53,79–81,83,93–110], which constitute four 1D nanowires (interconnected together via a central core), are thus very beneficial in terms of electronic device fabrication because of their 3D spatial shapes (briefly mentioned in the beginning). Simple, as well as advanced, nanoelectronic devices based on ZnO tetrapods can be fabricated, in which all the functionalities from 1D ZnO nanostructures can be easily exploited. For example, Newton et al. fabricated a single-ZnO nanotetrapod p-n junction diode (Figure 2a) that showed enhanced UV light sensitivity [81,98]. The sensitivity was enhanced with respect to illumination power (Figure 2b), and a very high responsivity of $\sim 1.7 \times 10^4$ A/W was reported [98]. The enhancement in sensitivity under UV illumination is mainly due to the photoinduced charge carriers and increase in the width of conduction channels (reduced barrier height) [27]. In an attempt, Sun and co-workers fabricated a two-terminal (Figure 2c) ZnO nanotetrapod (SEM image as inset in Figure 2c)-based logic device that could sense the applied stresses on the upward arm as a function of change in electrical current (Figure 2d) [103]. The logic states were mainly regulated by built-in potential at the tetrapod junction induced by a piezoelectric effect under bending. The central core of the ZnO tetrapod exhibits zinc-blende phase; however, the 1D arm is the hexagonal-wurtzite phase (inset, top left-Figure 2d). When a force is applied, the 1D arm bends in one direction, leading to an increase in forward current due to injection of more electrons (inset, bottom right-Figure 2d) into the cubic core (because of piezopotential) [103]. The current follows the applied force. If the direction of the force reversed, the current reversed, too (inset, bottom left-Figure 2d); therefore, such a device can be easily used as a logic device based on piezoelectric functionality [103]. In an attempt, Wang et al. [106] fabricated a single-ZnO tetrapod-based electronic device, in which combined functionalities, i.e., piezoelectric and photoswitching that are called 'piezo-phototronic effect', were utilized for force sensing using a conducting atomic force microscopy (C-AFM) device (Figure 2e). Typically, I–V characteristics of the device (inset Figure 2f) under UV light and different forces in Figure 2 f demonstrate that the piezo-phototronic functionality of ZnO tetrapods can be efficiently used for various kinds of sensing, including force, light, etc. [106] In a very innovative way, Gedamu et al. [27] fabricated an interconnected ZnO

tetrapod network-based electronic device on micro-chip (Figure 2g) using the simple B-FTS (burner-flame transport synthesis) approach, which showed an excellent (very rapid) UV light-switching response (Figure 2h). The interconnections within the tetrapod arm facilitate a continuous path for carrier migrations, and the device showed very fast response/decay (32 ms/200 ms times, respectively—the fastest reported UV-sensing device at its time) [27]. Several ZnO tetrapod-based electronic devices have been fabricated for various kinds of optical, laser, optoelectronic, field emission, and sensing (force, light, gases, microwaves, chemical, biological, environments, etc.) related applications (Table 2: Electronics) [19,26,40,42,49,93–96,100,111–125]. To enhance the functionality, these tetrapods can be further hybridized with other metal oxides, or their surfaces can be integrated with nanoparticles from different metals, carbons, organics, perovskites, zeolites, etc., for achieving efficient sensing performances [102,107,109,110,118,126–128]. In the context of sensing using metal oxide nanostructures, selectivity is a very important measure that requires careful studies. Especially ZnO-based sensing devices require rather more attention because it is very sensitive to any changes in the surroundings, e.g., lightening, moister, pressures, etc., particularly in nanoscopic dimensions. Generally, special cares are expected during sensing studies with nanodevices, but due to robust nature and nano- and microscale size, the tetrapods (in pure and hybrid forms) might be better alternates.

Advanced optoelectronics: defects and whispering gallery modes

The direct wide bandgap and n-type conductivity of ZnO make it a perfect candidate for luminescent and optoelectronic technologies. Defects in ZnO, as mentioned already, are the topic of debate, and they indeed play a very important role in many applications (Table 2: Photonics) [9,129]. The defects in ZnO are generally characterized by photoluminescence (PL) measurements under different experimental conditions, including low-temperature studies, but their exact information is yet to be discovered because some of them undergo creation/annihilation process during characterization itself [19,40,114,130,131]. Advanced approaches like time-correlated single-photon-counting (TCSPC) modules [132] could reveal more exactly about the possible defect levels in ZnO; however, the aim of the present review is to give some general idea of defects in ZnO. The possible defect levels in the ZnO bandgap are shown in Figure 3(a), and PL study is the most adopted strategy to understand these defects. A typical PL spectrum from ZnO contains two peaks: one around the bandgap energy (exciton luminescence) and the other is a broad peak in the green region of EM spectrum, which is collectively from all types of defects [9,18,19,114,131]. Sometimes, a few additional peaks (Figure 3b) over the broad green band are also observed in the ZnO PL spectrum [40,133,134], but, mostly, they have been ascribed to certain kinds of defects, which is not always true because they could also be due to the shape characteristics causing, e.g., frequency doubling. For example, in hexagon-shaped ZnO nanowires/needles, the light is internally reflected, and, under resonance conditions, strong absorption occurs which is called whispering gallery mode
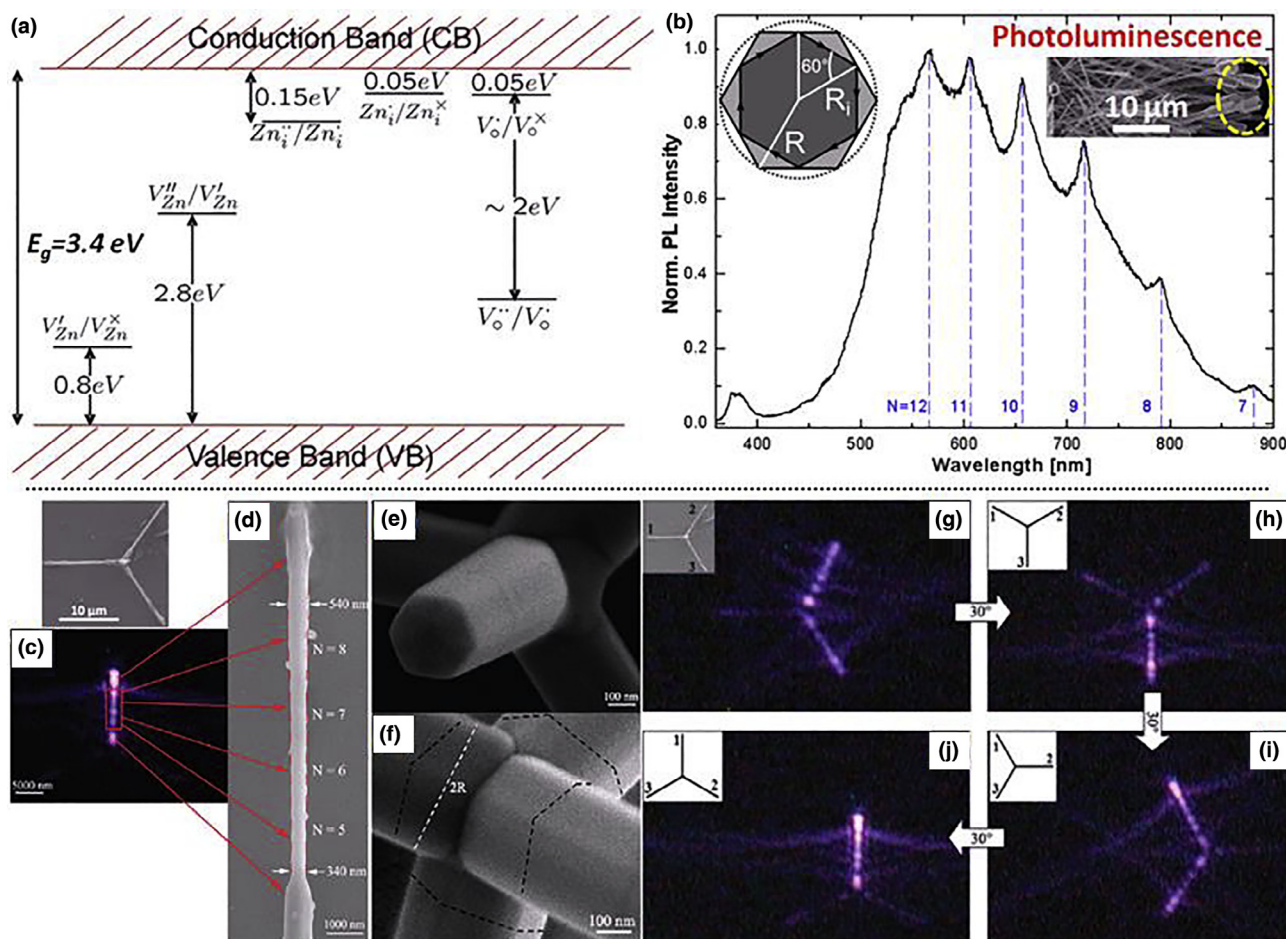
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FIGURE 3

Defects and whispering gallery modes in ZnO: (a) Defect levels scheme in ZnO energy band diagram. (b) PL spectrum on the hexagonal tip of a ZnO nano- and microneedle (SEM image as right inset in b). Additional peaks over broad green luminescence (due to defects in ZnO) are due to WGM resonances, the characteristic of hexagonal shape (left inset in b). (c) Different SH-WGM modes (CCD camera image) on the arm (d) of a ZnO tetrapod (inset image c). (e and f) Hexagonal shape and orientation of arms of grown ZnO tetrapods (SEM images). (g–j) SH-WGMs in ZnO tetrapods at clockwise orientations by 30° (incident light always vertically polarized). A change in orientation from perpendicular to parallel for arm 1 is clearly visible (g–j). [Reproduced with permissions from: (a) Elsevier [6], (b–j) American Chemical Society [134,141].]

(WGM) resonances [135,136]. WGMs are therefore characteristics of nanostructural shape and dimensions, and they have got unique potentials toward waveguides, single-mode lasing, and telecommunications, including advanced optoelectronic applications [135–138]. Actually, the intensity of WGMs can be selectively enhanced by decorating its surface with metallic nanoparticles having absorptions in the desired frequency range, such as plasmonic gold nanoparticles [139] . The tetrapodal geometry exhibits unique light-scattering abilities [140], and the WGM resonances in these structures could be significantly useful for advanced optical technologies, especially in a 3D interconnected tetrapodal network form. For example, Zhang et al. [141] have reported different second harmonic (SH) WGM resonances in hexagonal rods of ZnO nanotetrapod experimentally (Figure 3c–j), which demonstrates that intensity of particular mode can be enhanced by selecting appropriate dimensions and the input laser power. Defects and WGMs in 1D and other complex-shaped ZnO nanostructures were the two schools of thoughts that have been propagating parallel in the community. Actually, the WGMs could not get much attention and might be

mistaken for defect- or dopant-related peaks in the spectrum. At least, for the 1D-based ZnO nanostructures family, the possibility of WGMs should not be ignored apart from defects, but the WGMs have recently got much attention. It is therefore recommended that both the defect- and the WGM-related aspects should be simultaneously explored by the related ZnO community. With respect to tetrapods and other complex ZnO shapes, WGMs are fairly new, and detailed investigations are required for pure and dielectrically hybridized structures under different polarizations, laser powers, etc.

Smart polymer nanocomposite materials

Polymer-based composites are probably the most utilized material components ranging from our day-to-day life stuffs to advanced equipments in airplanes or space, which has become possible mainly by the availability of various kinds of filler nanoparticles (Table 2: Composites). Therefore, the role of filler particles is rather very important, and their various nanostructural forms (0D, 1D, etc.) have been in practice. In this respect, tetrapods with 3D shape exhibit a special role toward engineer-
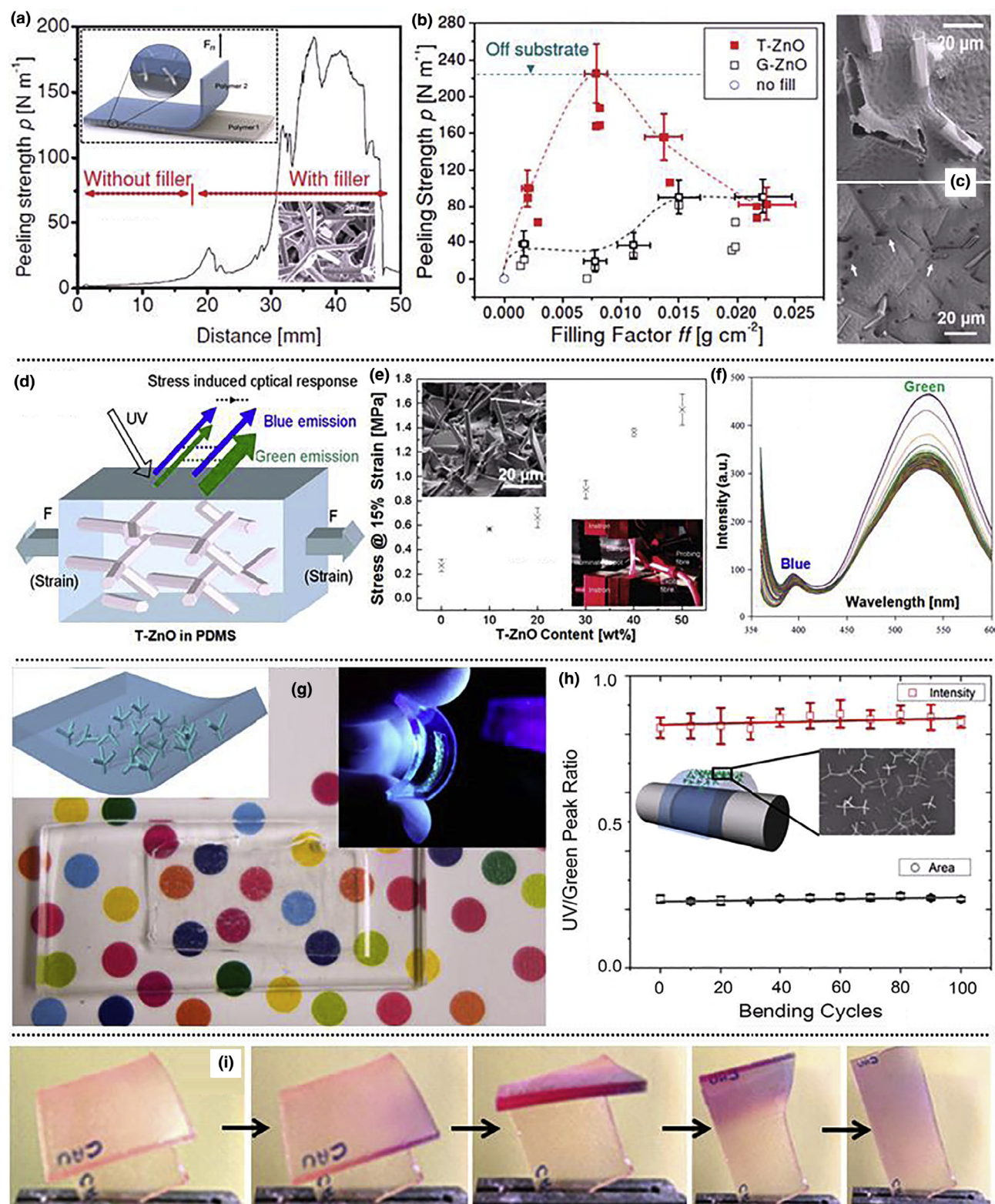
FIGURE 4

ZnO tetrapods for advanced self-reporting/healing polymer composites: (a–c) Linker element for joining the unjoinable polymers [84]. (d–f) Intelligent filler candidates for self-reporting polymer composites [85]. (g and h) Regular arrangement of tetrapods in polymer-enhanced mechanical, luminescent, and self-reporting behavior [88]. (i) ZnO tetrapods improve the self-recovery response of spiropyran-based polymer composite. [Reproduced with permissions from: (a–f) Wiley VCH [84,85], (g and h) American Chemical Society [88] (i).]

ing the properties of polymer-based composite materials in contrast to conventional spherical nanoparticles or one-dimensional nanostructures such as nanofibers [87,142–149]. It is very well

known that filling the polymers with appropriate fillers in the form of composite leads to a significant improvement in their overall properties, and they indeed are being utilized in many

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applications. However, the conventional fillers (0D and 1D structures) have strong agglomeration tendencies in contrast to tetrapod-shaped nanostructures that do not agglomerate irrespective of how they are put together [87,150]. Also a lesser amount of tetrapod-shaped fillers, than conventional fillers, is required to achieve similar improvement properties of the resultant polymer composite. With spherical fillers, getting a very uniform distribution is an issue, at the same time 1D long fibers result in unidirectional improvement in properties (along their length). In contrast the tetrapod-shaped fillers improve the overall properties of the composite in all three dimensions because of their unique spatial complex shape [87]. ZnO tetrapods, specially, are very inert with respect to most of the day-to-day used polymer (e.g., Silicone, Teflon, etc.), and there is no chemical interaction between the surface of ZnO tetrapods and the polymer; their semiconducting properties are simultaneously accessible even though they are embedded in a polymer matrix. On the other hand, the special 3D shape introduces extraordinary mechanical properties in the composite. For example, in a ZnO tetrapod–polymer composite, if one arm is stretched, the other arms compress toward each other, but then the polymer in-between pushes back in the opposite direction. Such a concept using tetrapod-shaped fillers is thus very helpful for designing rough and tough composite materials with engineered properties for advanced technologies. Not only this, some aspects like joining two un-joinable polymers (e.g., silicone and Teflon) which was actually a challenge, can be easily achieved by following this purely interlocking strategy with tetrapod-shaped fillers [84,86]. A typical concept for using the ZnO tetrapods as linking elements (zippers) is shown as inset in Figure 4a, in which they are embedded at the interface between the two polymer layers. After integration, the adhesion strength between the two polymer layers (silicone and Teflon) was increased significantly (Figure 4a). The overall peeling strength from tetrapodal ZnO (T-ZnO) structures was compared with 1D ZnO rods (Figure 4b) and tetrapodal shape indeed exhibits an important role in the improving adhesion between two polymers. The adhesion is mainly due to shape-induced mechanical interlocking (Figure 4c) at the interface because no chemical interactions between ZnO surface and polymers were observed [84]. Such ZnO tetrapod-based polymer (e.g., PDMS) composites are quite unique, in the sense, because of the least chemical interactions between them, the properties of the polymer are significantly altered, but semiconducting features of ZnO tetrapods are still intact. However, the entire composite experiences the deformation in case an external stimuli is applied, but the occurrence/propagation of any internal damage is reflected as a relative change in the electrical, luminescent, etc., properties of ZnO tetrapods [85]. Such tetrapod-based polymer composites have thus the ability to report about any damage occurring internally and could lead to designing the new class of self-reporting and smart composites [85]. A typical concept for designing the self-reported composites using ZnO tetrapods is shown in Figure 4d– f in which the applied stress on the composite is reflected as a change in luminescence (Figure 4f). With an increase in the T-ZnO filling fraction (wt%), the Young's modulus of the nanocomposite also improved (Figure 4e) leading toward better mechanical properties [85,87]. The mechano-luminescence response of the tetrapo-

dal ZnO polymer composites can be further enhanced (up to several mechanical cycles) by controlling the distribution of tetrapods within the PDMS polymer as can be seen in Figure 4g and h [88]. Spiropyran molecules have got unique features in terms of conformational transformation (reflected as color change) when subjected to some energy in the form of stress, heat, light, etc., and they can be nicely utilized for self-reporting, healing, and advanced composites (Figure 4i). The required energy for conformational transformation is in the visible range of the electromagnetic (EM) spectrum, which is difficult to provide locally. However, if ZnO tetrapods are also embedded along with spiropyran molecules in the polymer, they can easily provide the necessary energy for conformational transformation because of their broad luminescent emission in the visible region and can also improve the overall mechanical properties of the composite. In a recent work, Shree et al., fabricated a unique ZnO tetrapod-spiropyran-based PTU (polythiourethane)-based composite that responds to any external impact (heat, force, or light) by color change, and it could be excellent composite system for a lot of advanced applications [151]. A large variety of advanced polymer composites using ZnO tetrapods have been fabricated and utilized for various applications, especially robust coatings for underwater appliances (ships, marines, etc.) [142,152–153] and many more have to be further realized. It is worth to mention that embedding the ZnO tetrapods in a polymer improves its wettability features, too, hence the ZnO- T-based polymer hydrophobic coatings/paints can be easily developed and mounted on all those areas that need to be water proofed. Improving the properties of rubber-based composites, e.g. tire and related industries, has been a big issue, and because of their unique shape, ZnO tetrapods could add wings to this field. Therefore, in milieu of composites, ZnO tetrapods have got a lot of scope toward fabricating various interesting composites [85–87, 142,144,150,152–155], electronic-skin [156], and smart-textiles [157] and, therefore, will introduce several novel and broad research fields in future.

Biomedical engineering

Because of their exceptional physical and chemical properties, nanomaterials have got enormous perspectives toward biomedical engineering, and that is why, nanobio-based interdisciplinary research has been trending for almost the last two decades. Several strategies have been followed to develop efficient drugs, the so-called 'nanodrugs', and up to some extent, a few approaches have delivered successful results; however, this field of nanobio has to witness a lot more to reach on certain conclusion. The precondition for an effective drug is the least cytotoxicity at dosage targeted for the desired therapeutic effects. Despite their promising therapeutic effects, nanoscopic structures from several materials are out of scope because of high cytotoxicity issues. Only a few materials, e.g., gold etc., surpass, but apart from cytotoxicity, they need to overcome several other challenges, like cost-effective synthesis, etc. ZnO material is very advantageous in the sense that its nanostructures (with adequate sizes and shapes) exhibit very low toxicity as found by many studies [92,158–160]; even nanowires were found to be completely biocompatible and biosafe [161]. A remarkable low toxicity is observed from micro-
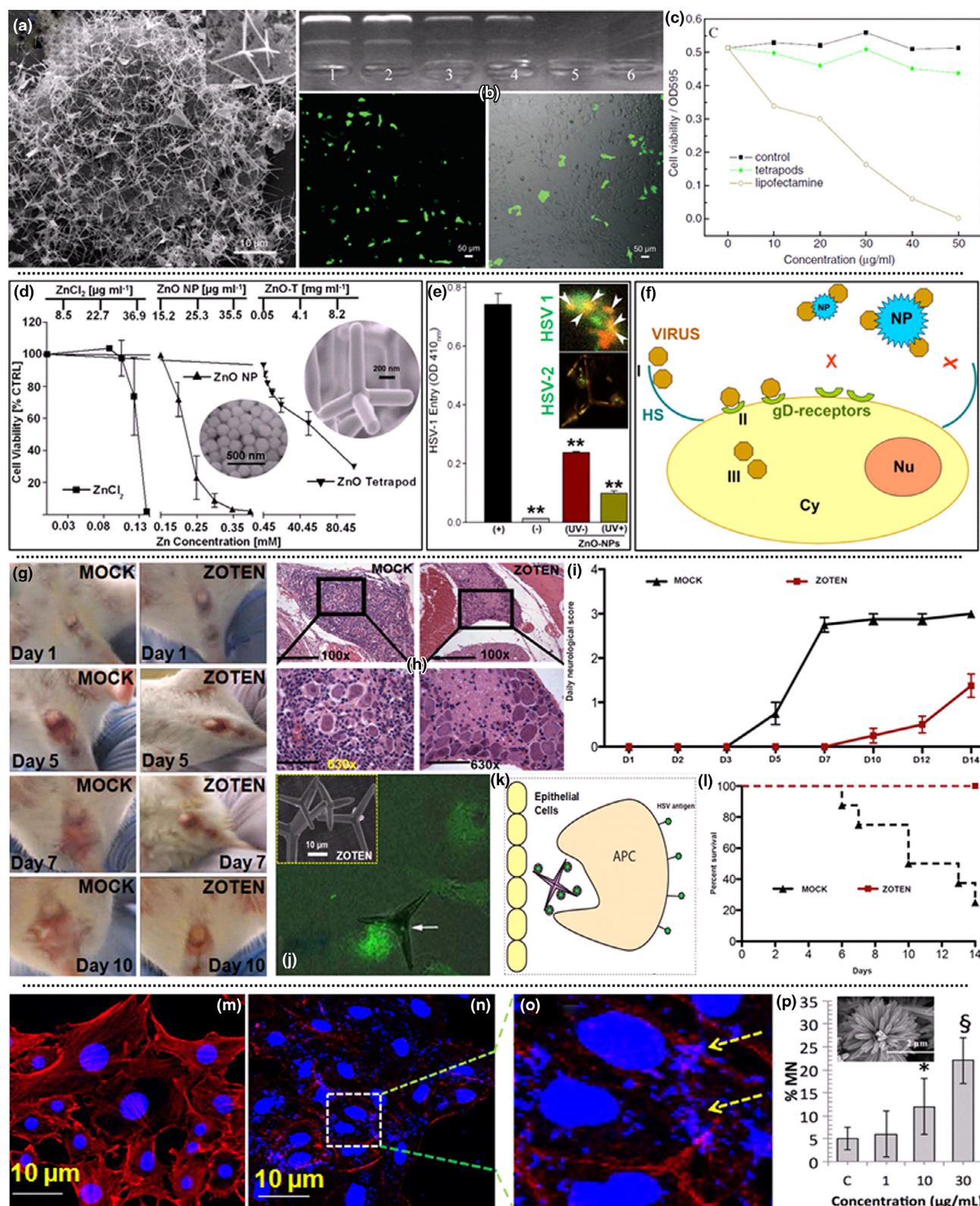
FIGURE 5

Biomedical applications of ZnO tetrapods: (a–c) Plasmid DNA delivery [154,158]. (d) Cell viability study demonstrating lower cytotoxicity of nano- and microscale ZnO tetrapods as compared to spherical ZnO nanoparticles and ZnCl$_2$ powders [159]. (e and f) Capturing of HSV-1 viruses by ZnO tetrapods and virus-binding mechanism [89]. (g–l) *In vivo* animal studies for role of ZnO tetrapods against genital herpes virus [91], (m–p) anticancerous potential of self-styled ZnO structures against glioblastoma cancer [166]. [Reproduced with permissions from: (a and b) Wiley VCH [158], (c) IOP Publishing [154] (d) PLoS Library [159], (e and f) Elsevier [89], (g–l) American Association of Immunologists [91], (m–p) Nature Publishing Group [166].]

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and nanoscale ZnO tetrapods on healthy cells as well [159], which are prepared using the solvent-free FTS approach developed at the Kiel University [20]. Adverse effects of ZnO seem to be observed only at unrealistic high doses like 1 g/kg [162,163]. This is important as micro- and nanoparticles, especially the spiky ones, are always suspicious to cause cancer or asbestos-like effects. Probably, the good biocompatibility of ZnO, including ZnO tetrapods, results from the fact that Zn is an essential trace element for humans (15–30 mg/day recommended by world health organization-'WHO' for a male adult [164]) and ZnO can be easily metabolized by the body in many ways. Moderate acids (pH < 5.5) can decompose ZnO completely.

ZnO has been a traditional therapeutic for skin diseases in India, known for at least two millennia [22]. "*The Canon of Medicine*" by Avicenna et al., (1025 AD), describes many applications of ZnO, including skin cancer. Today ZnO nanomaterials are an everyday ingredient in many creams, powders, and ointments [25]. Most biomedical effects are believed to be based on hydrophilic, antiseptic effects and the solution of zinc. Because of micro- and nanoscale size and unique 3D morphology, the ZnO tetrapods find more application flexibilities in biomedical engineering in contrast to conventional nanomaterials (spherical nanoparticles, 1D nanowires, etc., which suffer from agglomeration issues), and their 'nanobio' potentials have been least exploited. To the best of our literature knowledge, Leng Nie et al. first demonstrated the use of functionalized ZnO nanotetrapods for plasmid DNA delivery (Figure 5a–c) [154,158]. The surface of ZnO tetrapods (Figure 5a) was coated with silica and amino groups. Plasmid DNA easily binds to functionalized tetrapod surfaces due to electrostatic interactions between positively charged amino groups and negatively charged phosphate groups from DNA. The ratio of functionalizing agents (silica and amino groups) is very important as it ensures binding of enough DNAs because only above a certain ratio, the DNA binding could be confirmed (top-Figure 5b). Cells (A375) can also easily bind to functionalized tetrapods with amino groups [158]. The unique binding capability of functionalized ZnO nanotetrapods with respect to DNA, as well as cells (A375), could facilitate unique plasmid-DNA delivery. These ZnO nanotetrapods exhibit relatively low cytotoxicity (Figure 5c), and hence could be utilized for related applications [158]. Surface functionalization of ZnO tetrapods was the most crucial task in plasmid-DNA delivery, and it would be better if this step can be skipped. A direct utilization of ZnO micro- and nanotetrapods might be preferable for certain nanobio applications, which has been our strategy. Inspired by the biomedical potential and extremely low cytotoxicity (Figure 5d) of ZnO micro- and nanotetrapods, we targeted a unique mechanism for capturing different viruses (Figure 5e and f) with oxygen vacancies on our ZnO tetrapods [89]. The tetrapodal ZnO can be easily equipped with oxygen vacancies to create polar surfaces with positively charged defects, which we intended to trap the virus with its functional glycoprotein groups on the surface like a fly with a flypaper (Figure 5e). This immobilization was successful and the binding mechanism could be confirmed by illuminating the T-ZnO crystals with UV light in ambient air to create more oxygen vacancies (more viruses are bound with the surface) by the known auto photocatalytic process (Figure 5f) [89,90,165]. Subsequent trapping was much more

effective [90]. To confirm the evidence, we continued with *in vivo* animal studies and it was observed by Shukla et al., that the immune system picks up viruses from the T-ZnO and performs a tri-functional vaccination (Figure 5g–l) [91]. Furthermore, the wound healing was much faster in animals treated with ZnO tetrapods (Figure 5g) [91]. The use of ZnO tetrapods reduced the development of chronic infection (Figure 5h and i) and the ZnO-treated animals survived longer (Figure 5l). Viral particle bound with ZnO tetrapods is easily taken up by dendritic cells (Figure 5j and k) [91]. After successful animal studies, first observations on human patients were also performed, which again confirmed the results in congruence with the animal studies. Thus, it is very important to perform systematic studies and to widen them for further similar viruses and other species. The ongoing experiments with human papillomavirus (HPV), ZIKA, μ-AIDS, Dengue showed promising results, but studies with respect to many more viruses have to be explored. Actually, viruses exhibit certain kinds of glycoprotein groups at envelopes (called virion) that facilitate their bindings with existing surface (polar) defects on ZnO tetrapods, and this could offer excellent binding possibilities even for the fatal HIV viruses, too, and thus a broad therapeutic window for severe diseases, too. This is not limited to viruses; the recent work [166] about the response of self-styled ZnO nanostructures against glioblastoma cancer cells (Figure 5m–p) opens further a broad the perspective about use of ZnO tetrapods in biomedical engineering. From the recent studies, it has been observed that these ZnO tetrapods can be electrospinned together with biocompatible polymers in the form of rose-spike like fibers with enhanced antibacterial and other biocompatible features, which have opened a lot of new application avenues toward biomedical engineering [92,160]. Therefore, tetrapods (Table 2: Biomedical) have got a very promising future.

These examples show that T-ZnO crystals enable new therapies and allow more effective treatments like the conventional ZnOpowder or zinc salts. May be these aspects were overlooked in the 20th century by focusing mainly on the chemistry of the ZnO treatment and ignoring widely the structural aspects in the therapeutic window. The ZnO as fabricated in ancient times, by contrast, was very much similar to the fabrication of the tetrapodal ZnO presented by us (flame transport synthesis). Maybe the descriptions in ancient times about the healing potentials of ZnO were much closer to reality than expected. Recent papers [89–91,159,165], as well as own experiments with cell cultures of healthy and cancerous cells, reveal a wide therapeutic window in the cancer therapy, e.g., toxic levels for cancer cells were ∼40 μg/mL, while healthy cells withstand up to 180 μg/mL [166]. The results in viral therapy of T-ZnO, as well as the cancer cell experiments, strongly suggest that the research on metal oxide semiconductor-based therapies, T-ZnO, gives here a starting point. ZnO tetrapods have got a lot of application scopes toward antimicrobial, antifungal, anti-aging, food preservation, cosmetics, etc. Zn is an essential element for the human body because it activates more than 300 enzymes in the body, which is responsible for various metabolic pathways, and thus plays an important role in glucose consumptions and insulin synthesis. [23,167]. Therefore, Zn deficiency in humans causes severe health issues, and this has actually become a very big
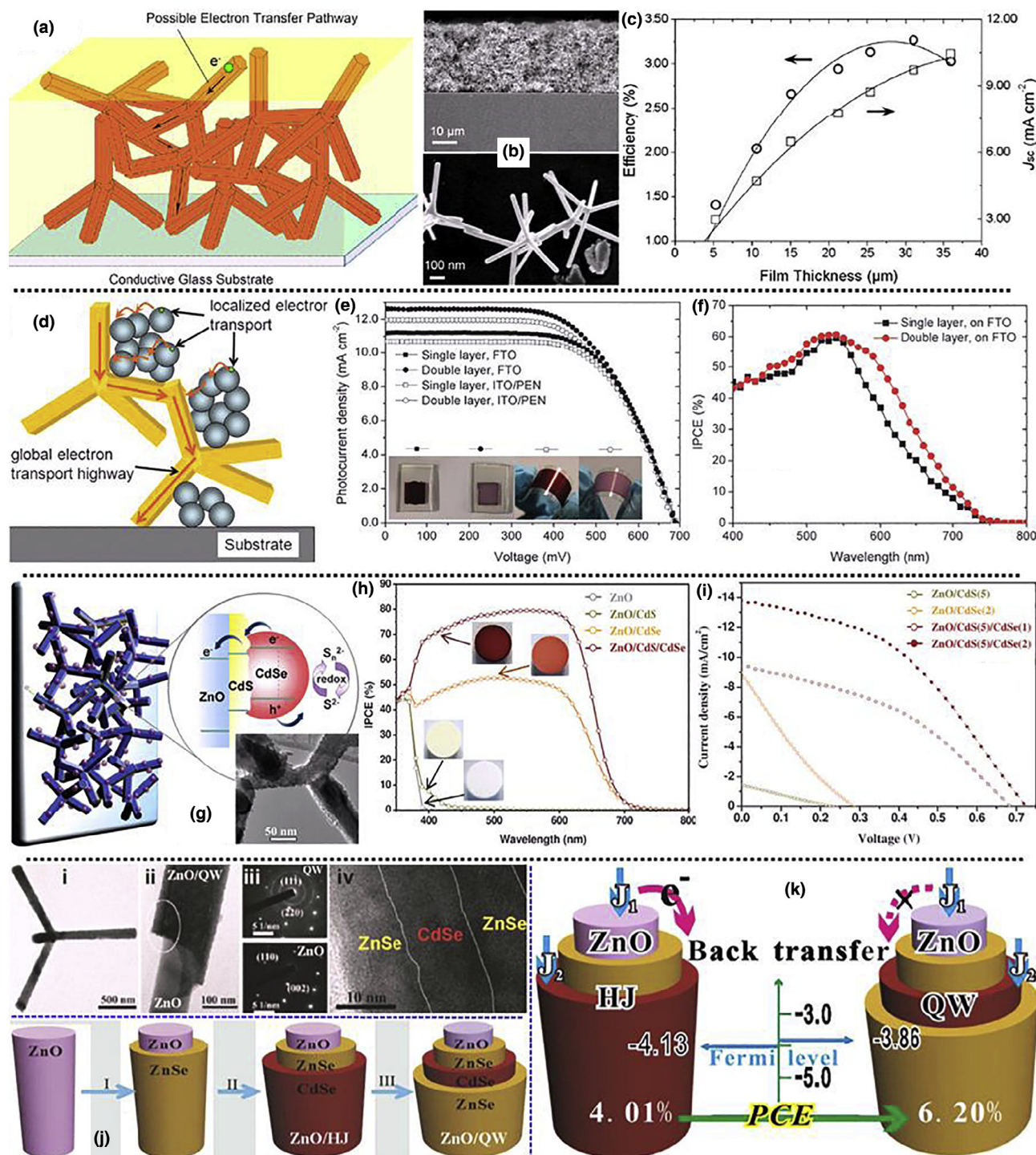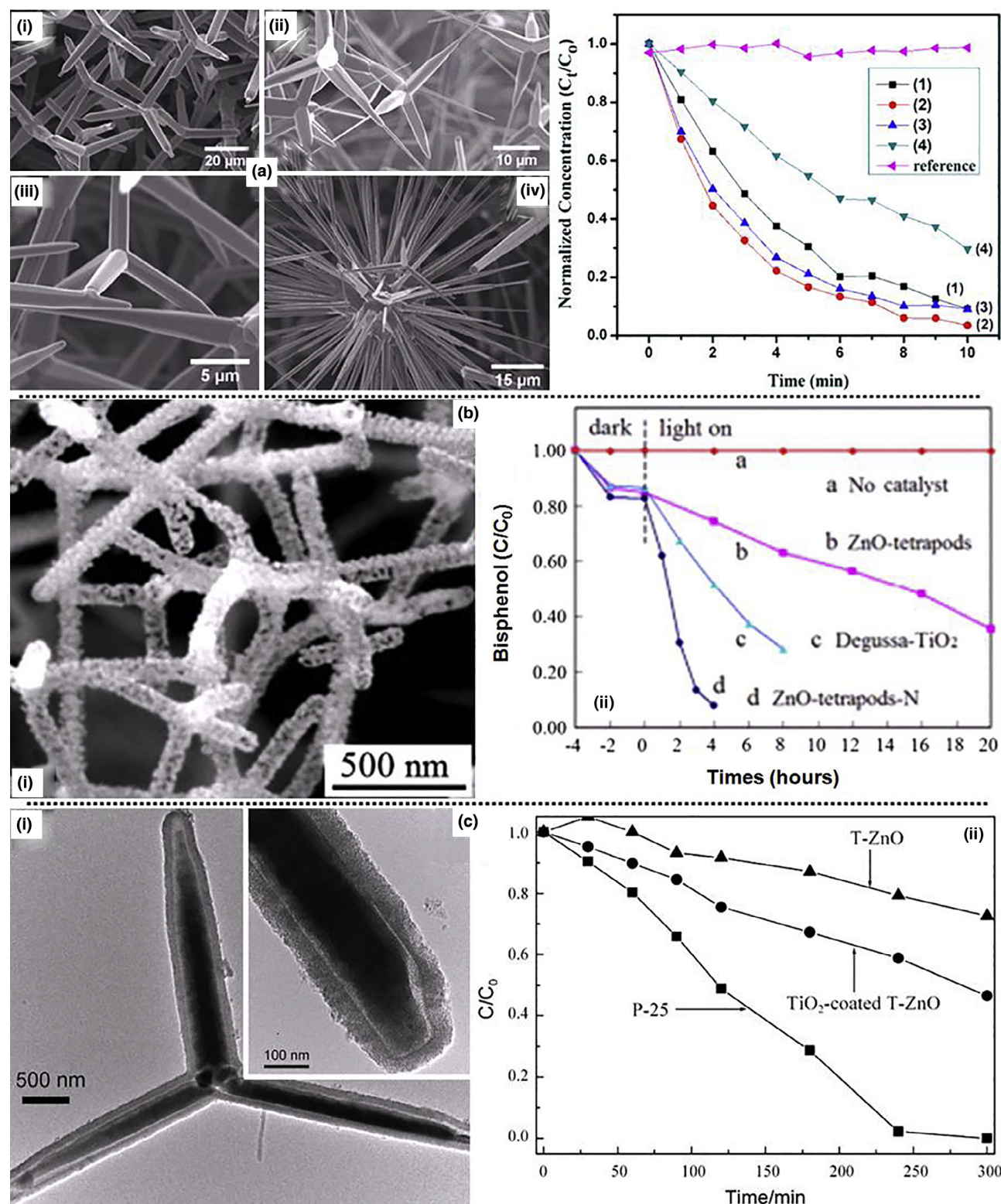
FIGURE 6

ZnO tetrapods for photoelectrochemical energy devices: (a) ZnO tetrapod network-based schematic (photoelectrode) demonstrating the possible pathways for electron migrations in the film up to the substrate [171]. (b) Structural morphology of interconnected ZnO nanotetrapodal film (∼30 μm): cross-sectional and high-resolution SEM views [171]. (c) Plot showing energy conversion efficiency and photocurrent density (short circuit) of the ZnO tetrapod-based DSSC [171,177]. (d) Schematic demonstration of a SnO_2–ZnO tetrapod-based DSSC photoelectrode with ZnO tetrapod network and encapsulated SnO_2 nanoparticles offering global and local pathways for carrier transport [177]. (e) The current density–voltage (J–V) responses of composite and layered ZnO tetrapod-SnO_2 nanoparticle-based DSSC photoanodes [174]. (f) IPCE spectra for the single-layer composite and double-layer-structured DSSC photoanode based on SnO_2 nanoparticle–ZnO tetrapod-based systems [174]. (g) Schematic for charge-transfer mechanism in CdS/CdSe-ZnO nanotetrapod-based photoelectrode [188]. (h and i) The IPCE spectra and current density (J–V) variations of QDSCs corresponding to (i) pure ZnO-T, (ii) ZnO-T/CdS, (iii) ZnO-T/CdSe, (iv) ZnO/CdS/CdSe (insets in h show the digital camera photographs corresponding to different DSSCs) [188]. (j) Fabrication steps semiconductor heterostructure sensitized ZnO-T solar cell. (k) Charge transfer mechanism in quasi QW/ZnO-T based SSSC (in j) [189]. [Reproduced with permissions from: (a–c) Elsevier [171] (d–i) Royal Society of Chemistry [174] (j and k) American Chemical Society [189].]

problem in Asia [24].Some countries have developed Zn supplements, but they do not offer a long-term solution. Grains are the main sources of Zn for the human body, which directly come from the soil. In some counties, for example, India, the Zn level in soil has gone down significantly and increasing its level (which might also improve plant growth and yield) is a very challenging task. The use of spherical nanoparticles has shown promising results [168]; however, several factors like agglomeration, high cost, etc. might limit their real utilization. With the developed cost-effective, simple FTS approach and 3D shape, we believe that these ZnO tetrapods might solve the purpose; however, detailed studies need to be performed.

Energy: solar cells, photoanodes, and others

Energy is one of the most important concerns in today's scenario, and semiconductor materials have played very important key roles. Silicon is probably the most relevant material revolutionizing the energy-harvesting sector in terms of batteries, photovoltaic solar cells, power electronics, etc. Indirect semiconductors are generally preferable for the photovoltaics community because of longer carrier lifetimes, but the direct bandgap semiconductors like TiO_2, ZnO, etc. have also been in the race for fabricating various types of solar cells. Dye-sensitized solar cells (DSSC) based on several direct bandgap semiconductors have been fabricated and studied; however, achieving desired efficiencies and increasing carrier lifetimes have been major concerns. In contrast to conventional thin films, tetrapod shape of ZnO [8,12,13,169–187] has received a significant attention in DSSCs because the hierarchical nature in the interconnected tetrapodal network offers longer pathways (Figure 6a) for the carriers to migrate before they recombine, and hence leading to an enhancement carrier lifetime [171,177]. Chen et al. fabricated a DSSC based on a 30-μm-thick film of interconnected ZnO tetrapod network on the conducting substrate (Figure 6b) and investigated its performance [170,171]. The measurements confirmed that such a ZnO tetrapod network-based DSSC could achieve an efficiency of up to 3.27% (Figure 6c), which is much more than what DSSC-based ZnO nanowire arrays or spherical ZnO nanoparticles achieve [171,177]. The electron transport time for nanotetrapod network-based thin film is around 1–2 orders of magnitude higher than that of nanoparticle-based thin films [177]. The thickness of the tetrapod film (i.e., interconnections existing therein) in the photoelectrode is the most crucial parameter deciding the carrier lifetime, and hence increasing the thickness would be a logical option. However, a large thickness could lead to other experimental issues like crack, stresses, etc., which could degrade the overall performance because of unnecessary charge collections (locally) [177]. To further enhance the performance, some nanoparticles (e.g., SnO_2) can be integrated on the surface of ZnO tetrapods, in the form of a hybrid system, in such a manner that the necessary porosity remains within the network. In such hybrid porous-architectured thin-film-based DSSCs, the ZnO tetrapods offer global highway paths for electron; however, the embedded nanoparticles enhance the local carrier migrations by introducing certain roughness (schematically presented in Figure 6d) [170,174,177]. Chen et al. fabricated a DSSC photoanode with a SnO_2 nanopar-

ticles–ZnO tetrapods composite system following two different strategies: (i) varying SnO_2/ZnO ratios in the photoanode [170] and (ii) a layered hybrid structure (SnO_2 nanoparticles/ZnO tetrapods) by pressing on the top. The typical current density–voltage (J–V) responses of SnO_2 nanoparticles–ZnO tetrapods based on different composite and layered DSSC photoanodes are compared in Figure 6(e), which reveal that the double-layer-structured film on FTO-coated glass exhibits the highest photocurrent density [174]. The incident photon-to-current-efficiency (IPCE) spectra corresponding to the single-layer composite film and a double-layer-structured film on FTO-coated glass substrates (from Figure 6e) are shown in Figure 6(f). Using this strategy, Chen et al. could achieve an efficiency of up to 6.31% (highest at that time) for the composite photoanode with SnO_2 nanoparticles–ZnO tetrapods ratio of 2:1 [170]. Quantum dot (QD)-sensitized solar cells have been much in practice in photovoltaics research, and they indeed can sensitize ZnO tetrapods too. In an attempt, Cheng et al. fabricated the CdS/CdSe QDs-ZnO tetrapods solar cell (Figure 6g) and compared the performances of different QDs: The performances of ZnO- T-based DSSCs (pure ZnO-T, CdS/ZnO-T, CdSe/ZnO-T, CdS/CdSe/ZnO-T) are shown in Figure 6h and i [188]. ZnO tetrapods again can offer better carrier transport (than 0D and 1D ZnO nanostructures), and solar power conversion efficiency (maximum) of ~4.24% was obtained for CdS/CdSe/ZnO-T DSSC in contrast to other QDSCs [188]. Yan et al. in this context fabricated a quasi-quantum well (ZnSe/CdSe/ZnSe heterostructure) semiconductor-sensitized ZnO tetrapod-based solar cell (SSSC) that showed (Figure 6j and h) an efficiency of 6.2% [189]. Such a quasi-semiconductor quantum well (QW)-based strategy offers a lower carrier transport resistance and a higher recombination resistance, leading to a much more enhanced carrier diffusion length, and hence an improved lifetime. Qiu et al., in this regard, proposed a strategy for restructuring the arms of tetrapods by growing ZnO nanowire on them and doping with nitrogen to use them as an active network toward photoelectrochemical water splitting [176]. They mentioned in the abstract that the nitrogen doping in ZnO leads to bandgap narrowing, but it might be an effect due to incorporation of defect levels within the bandgap, leading to absorption within visible range. The secondary branching on the ZnO tetrapod arm significantly improves the roughness that significantly contributes towards more light harvesting within the network. Therefore, such nitrogen-doped structured ZnO tetrapods network are very good candidates for efficient visible light absorption, and hence very good photoanodes for water splitting applications. The IPCE for nitrogen-doped ZnO tetrapodal networks has been found to be much higher than the nitrogen-doped conventional ZnO thin films and ZnO nanowire arrays [176]. The branched ZnO nanotetrapod network is preferable in terms of efficiency in contrast to normal ZnO tetrapod network because it can trap more light in it (more hierarchical architecture). A nitrogen-doped secondary-branched ZnO tetrapod network is rather better because its efficiency is the highest among all the pure and N-doped ZnO-based systems (normal ZnO tetrapod network ~ 1.7%, branched ZnO tetrapods network ~ 3.6%, N-doped branched ZnO tetrapods network ~ 10.1%), and hence very good photoanodes for photoelectrochemical water splitting [176]. Therefore, the hierarchical nature of the ZnO tetrapods

FIGURE 7

Photocatalysis response of pure and hybrid ZnO nanotetrapods: (ai–aiii) SEM images of a ZnO tetrapod with different arm morphologies, (aiv) SEM images of a typical ZnO multipod. (av) The photocatalytic responses of ZnO structures (ai–aiv) showing that tetrapods with sharp needle-like arms exhibit the highest activity [26]. (b) SEM image (bi-left) of nitrogen-doped ZnO nanotetrapods, and (bii-right) corresponding photocatalytic response (in comparison to pure ZnO tetrapods, Degussa-TiO$_2$) [204]. (c) TEM image (left-ci) of a TiO$_2$ nanoparticle-coated ZnO nanotetrapod, and photocatalytic activity (right-cii) of pure and TiO$_2$ nanoparticle-coated ZnO tetrapods [202]. [Reproduced with permissions from: (a)-American Chemical Society [26], (b and c)-Elsevier [202,204].]

and the possibility to architecture their arms again, including easy doping and surface functionalization opportunities, could make them very promising candidates for photoelectroenergy [8,12,13,41,176,178,181–183,185,190–193], supercapacitor [194], including other energy-related applications, and a large scope is open in this direction for future innovative and efficient energy technologies (Table 2).

Chemistry: photocatalysis, water purification, filters, antifouling, and other applications

Nanostructures from ZnO are very important toward applications in chemistry because of their extraordinary features like UV-sensitive bandgap, photoluminescence, charge separation, electron trapping, Lewis acid/base reaction capabilities, and strong attraction with metals . [44,57,195–197]. These properties exhibit important roles in photo-catalysis, photoelectro-catalysis, piezo-photocatalysis, and thermo-catalysis [57]. Applications like photocatalytic, water purification, removal of heavy elements like chromium, arsenic, uranium, etc. from ground water, etc. are very big deals nowadays for which ZnO nanomaterials exhibit significant potentials, but again, the challenge lies toward morphologies of the involved ZnO nanostructures and of course their cost-effective fabrications [26]. The most important requirements are that: (i) the accessible surface area from ZnO nanostructures must be as high as possible and (ii) the involved ZnO nanomaterial must be re-usable [26,44,57,198]. The conventional spherical and rod-shaped ZnO nanostructures lack both the capabilities that are nicely fulfilled by the highly porous 3D network (built from interconnected ZnO tetrapods) [26,199]. Additionally, the facetted surfaces (hexagonal) are more chemically active, too, which most of the complex shaped, branched structured ZnO tetrapods exhibit [26,44,57]. Thus, because of their high surface accessibility, the ZnO tetrapods and their highly porous, 3D interconnected networks are very potential candidates for chemistry applications. The ZnO tetrapods and multipods with different arm morphologies have already demonstrated their photocatalytic performance against Methylene Blue dye (Figure 7a) [26]. Complex shaped ZnO structures with an increased surface area lead to improved photocatalytic degradation responses [26]. The photocatalytic response of ZnO tetrapods can be further enhanced by incorporating different defects [200], plasma treatment [201], alloying them with other metal oxides [202], and functionalizing their surfaces different quantum dots, nanoparticles, fullerenes, nanocarbons, perovskites, etc. [146,173,203–205]. For example, the nitrogen-doped tetrapods exhibit an improved photocatalytic (against Bisphenol A dye) response in contrast to pure ZnO tetrapods as shown in Figure 7 b (left-SEM image of N-doped ZnO tetrapods, right-comparison of photocatalytic responses of different ZnO tetrapods) [204]. Alternatively, the arms of ZnO tetrapods can be decorated with other metal oxide nanoparticles/nanolayers to enhance the photocatalysis response. For example, Zhang et al. [202] deposited anatase TiO_2 nanoparticle layer on the surface of ZnO tetrapods and investigated the photocatalytic response against phenol dye. The typical transmission electron microscopy (TEM) images from a TiO_2 nanoparticle-coated ZnO tetrapod is shown in Figure 7c(i), and the corresponding photocatalytic activity is presented in

Figure 7c(ii) in comparison to pure ZnO tetrapods [202]. It can be clearly observed that TiO_2-coated ZnO tetrapods exhibit an enhanced photocatalytic activity.

In principle, the surface of the ZnO tetrapods can be easily and selectively engineered with different nanostructures (metals, metal oxides, carbides, nitrides, nanocarbons, etc.) for their utilization in a large range of chemistry applications, and it would be impossible to list them all here. Additionally, the wettability can be altered by illuminating it with UV light, which is an intrinsic functionality. Together with easily engineerable surface and UV-induced wettability, the ZnO tetrapods and their interconnected porous networks could be efficiently used for various chemistry-related applications. Figure 8 describes a typical model for filtering applications of ZnO tetrapods that could be easily upscaled to a industrial level. Filtering some bigger species out of a smaller in liquids is an easy task as it can be simply done using sieve concept, but filtering smaller species out of bigger in any liquid is often very challenging and cannot be achieved straight forward. For example, filtering viruses from blood is a very crucial task due to huge size differences in two involved biological identities. The viruses are typically a few hundred nanometers (in diameters), however, blood cells are typically a few micrometers (in diameter), and just removing viruses from blood would not be that simple and is a big issue in blood dialysis (because blood cells would also be filtered if sieve concept is used). Since viruses are easily captured with UV-illuminated ZnO tetrapod surface [89–91], the highly porous 3D interconnected networks can be effectively used for filtering viruses from blood (pores are large enough for blood cells to pass through), which has been recently presented as a unique strategy [206]. Actually, the arm dimensions exhibit important roles in observing wettability behaviors with respect to different liquids [207], and, therefore, such highly porous ZnO tetrapod network could be used as efficient filters for filtering the desired liquids, for example, polluted waters, chemicals, oils, defected blood, pharmaceuticals, dyes, etc., using different functionalities of the engineered ZnO nanotetrapods in a very simple model, which can be extended to many other chemistry, environmental, pharmaceutical, and biomedical related applications.

3D nanotechnology: flexible hybrid nanoceramics

Macroscopically expanding porous materials that are made by interconnecting nanoscale building blocks, the so-called 3D nanomaterials, are in forefront in research focus at the moment because of their easy nanoscale features accessibility and utilization simplicities open many more scopes toward real technological applications [20]. Building such 3D interconnected nanomaterials is not so simple, and a lot of strategies have been followed; however, this field is yet to witness realistic technologies. In this respect, we have demonstrated a very simple but quite unique approach for fabricating large 3D interconnected networks by taking the advantage of the hierarchical tetrapodal shape of the ZnO nano- and microstructures produced by flame transport synthesis approach [20]. The complex tetrapodal shape prohibits close packing of these structures. And if optimally compressed together and heated at adequate temperatures (in ceramic scaffolds), the 3D interconnected networks with desired porosities can be fabricated in a very simple manner [20]. The
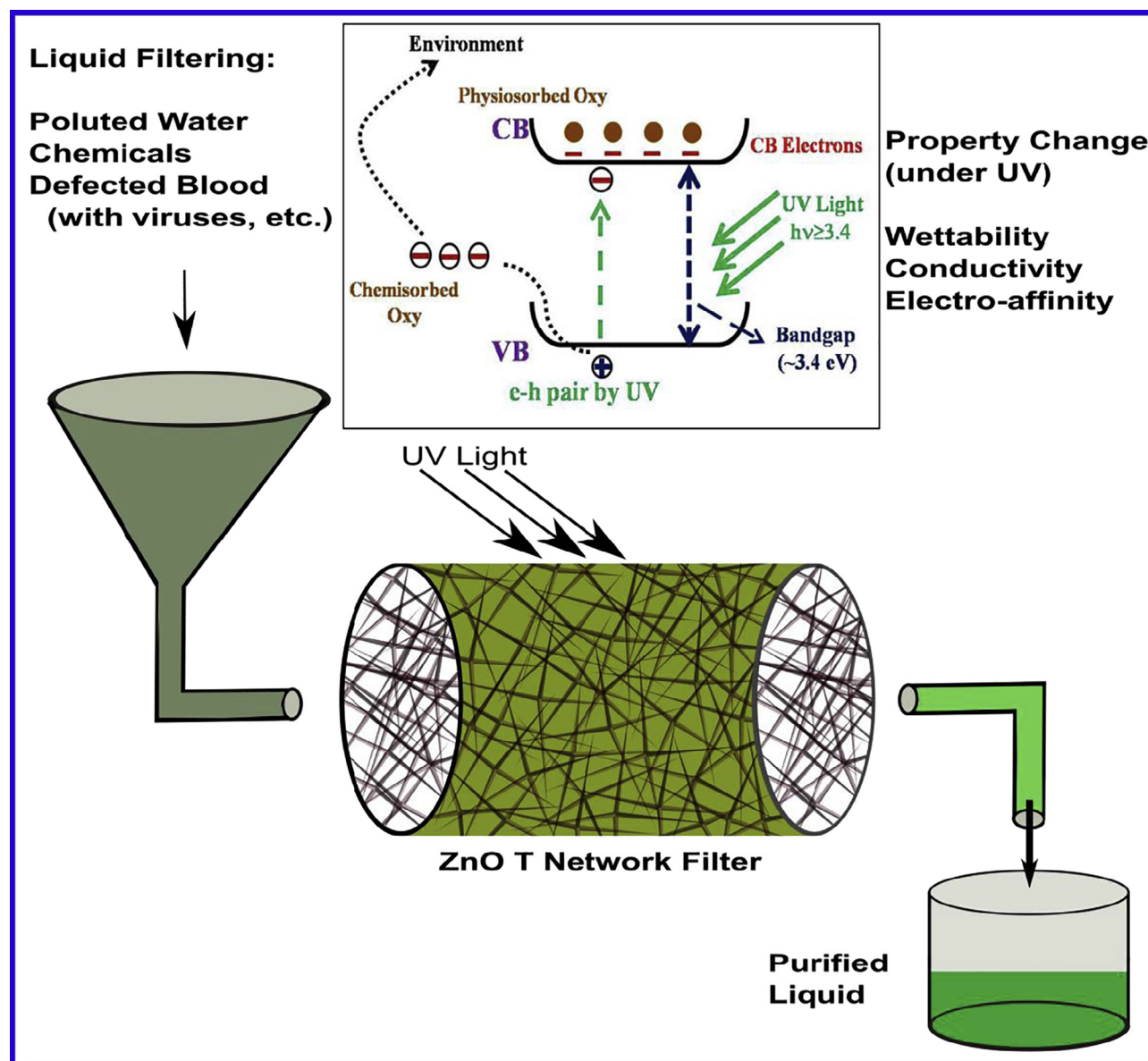
FIGURE 8

Typical concept for using ZnO tetrapod network for filtering chemicals, blood, water purification, and many other liquid-related applications.

typical digital camera image from porous ZnO network tablet is shown in Figure 9a, and the corresponding SEM image showing tetrapodal morphology within the interconnected network is presented in Figure 9b. By varying the initial amount of ZnO tetrapods in the ceramic scaffolds, 3D interconnected networks with desired porosities (high up to 98%) can be easily synthesized as demonstrated in Figure 9 c (inset SEM image in Figure 9 c shows the interconnections among ZnO tetrapods arms). In contrast to their bulk counterparts (which are brittle), these networks are highly flexible and exhibit soft, rubber-like elastic mechanical properties [20]. The 1D arms of the tetrapods contribute to the mechanical flexibility of the network; however, the interconnections formed among them during heating provide an overall mechanical stability to the 3D network tablet [20]. By selecting appropriate scaffold, the desired network shape with density can be easily synthesized, and such kinds of 'flexible ceramic

materials' are of large interest for fundamental science, as well as advanced future technologies (including those in which ZnO nanostructures are being utilized), and few application keywords are listed in Table 2 (Ceramics, Engineering) [20,21].

Development of new kinds of innovative materials with enhanced functionalities using simple and versatile methods has been an ever-demanding aspect of materials science engineering and nanotechnology. Material fabrication is the first and foremost requirement for any technological realization and here we present a quite unique but very simple strategy for synthesizing the multifunctional hybrids, as well as new nanomaterials, using the advantage of the complex tetrapodal shape of the ZnO nanostructures from flame transport synthesis approach [20,110]. The ZnO nano- and microscale tetrapods and their porous interconnected networks (Figure 9a and c) offer various micro- and nanostructuring opportunities. A roadmap for the
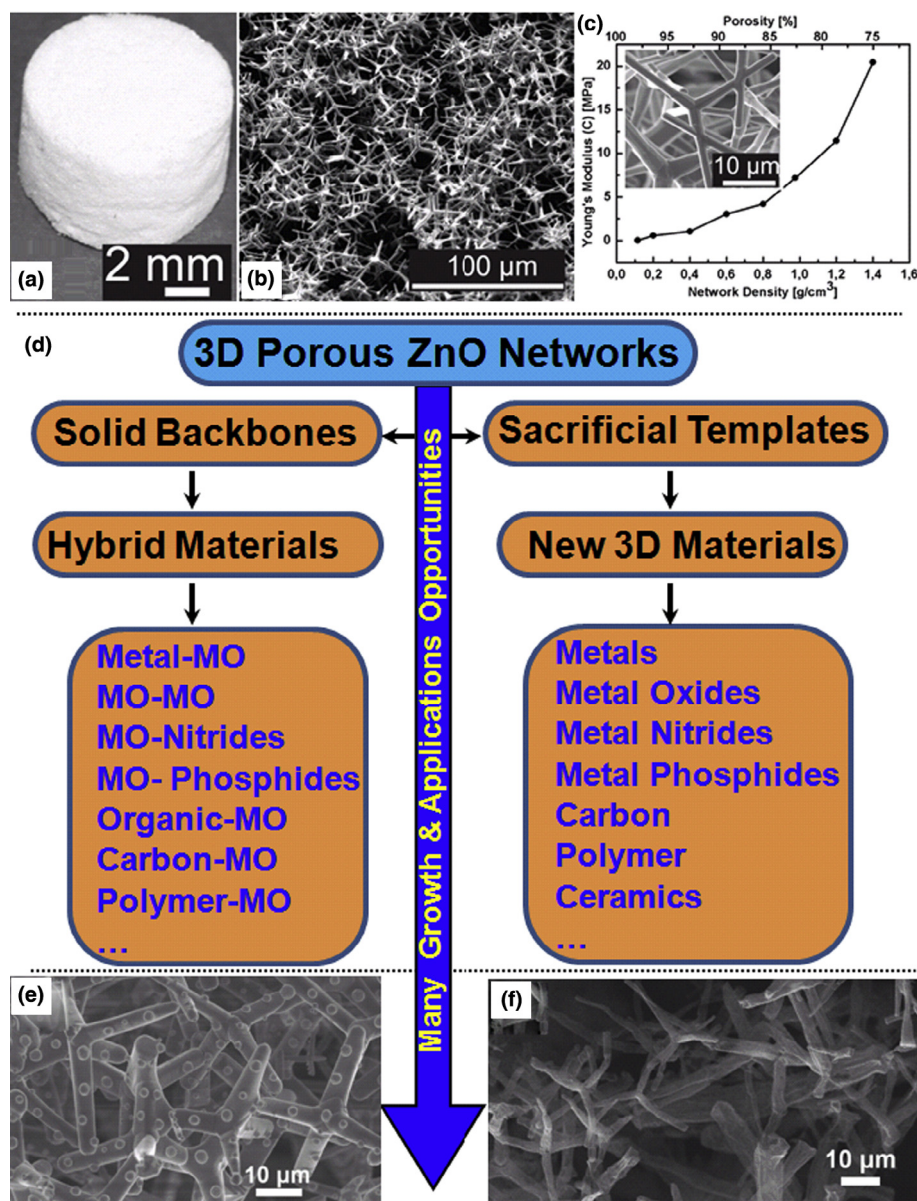
FIGURE 9

Application perspectives of 3D porous interconnected tetrapodal ZnO networks toward future 3D nanoengineering: (a) digital camera image of a 3D template, and (b) corresponding SEM image showing tetrapodal network in the template (a) [20]. (c) Young modulus verses density plot for porous 3D networks (inset SEM image shows the interconnections among tetrapod arms) [20]. (d) Roadmap for utilizations of these tetrapodal networks as solid backbones and sacrificial templates for growth of metal oxide (MO)-based hybrid and new 3D nanomaterials (various permutations and combinations can be adopted). (e) Exemplary SEM image from Au-ZnO hybrid network in which gold nanoparticles are integrated over the surface of the ZnO tetrapod arms. (e) Typical SEM image of carbon-Aerographite tetrapod network obtained from a single-step CVD conversion process. The crumbling nature of tetrapodal arms is due their hollow in nature with very thin walls (~20 nm) [208]. [Reproduced with permission from: (a–c)-Wiley VCH [20].]

scope of these highly porous ZnO 3D networks toward nanoengineering is presented in Figure 9d. The ZnO tetrapods can be used as solid backbones (left panel-Figure 9d) and nanostructures from other materials such as metals, metal oxides, nitrides, phosphides, organic, carbon, polymers, zeolites, cells, viruses, proteins, DNA, genes, etc. can be integrated on their arms by an appropriate synthesis process (physical, chemical, biological), and hybrid nanostructures (including their 3D networks) can be thus easily fabricated for desired applications [20,107–110,2 05,209,210]. For example, the SEM image in Figure 9 e shows the 3D Au-ZnO hybrid tetrapodal 3D network in which Au nanoparticles are strongly integrated at the surface of ZnO tetrapod arms. Fabrication of 3D nanostructures from different materials is in general not so simple and involves lots of efforts, and in this respect, the presented ZnO tetrapodal networks can be efficiently used as sacrificial templates (Table 2) to grow new 3D materials (right panel-Figure 9d). The desired material can be deposited on the surface of the porous template by appropriate technique (physical, chemical, biological, etc.), and the underneath ZnO template can be removed by etching (using acids or in chemical vapor deposition-CVD). Following this strategy, a large number of new 3D micro- and nanomaterials have been

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fabricated, for example, carbon-based Aerographite [208,211], carbon nanodiamond [212], carbon nanotube tube (CNTT) network [213–216], hollow amorphous Si tetrapod network [217], and fabrication of many other complicated materials, such as gallium nitride, hexagonal boron nitride, hydroxyapetite, etc., are under progress. The Aerographite is a hollow nano- and micro-tubular tetrapodal network directly grown by converting ZnO networks in CVD process in the presence of reactant gases at a high temperature in the furnace [208]. Aerographite is an extremely lightweight and ultraporous network material with very interesting electrical, mechanical, biomedical, etc. properties suitable for various applications due to its extreme properties [208,211,218–220]. Because of their extremely high surface areas and hollow microtubular tubular nature, the Aerographite tetrapods can be better filler candidates in epoxies/polymers (than conventional CNTs for example) because of the enhanced interlocking phenomenon [221,222]. Thus, they can also be used as ultraflexible templates for growth of hybrid 3D nanomaterials,

e.g., GaN-Aerographite [223], ZnO-Aerographite [224], and enzyme-Aerographite [225] networks that have demonstrated remarkable applications toward sensing, supercapacitors, etc. Growth and applications are not limited to the above-mentioned ones; a large number of nanostructuring opportunities are available by selecting appropriate permutations and combinations among the choices available in both panels in Figure 9d. Depending on the requirements and growth flexibilities, multi nano-component hybrid materials of any kind (Table 2: Sacrificial Templates) that offer simultaneous accessibility of multifunctional features in 3D macroscopic form can be easily fabricated and utilized for desired applications [213].

Summary and outlook

Tetrapod-shaped nano- and microstructures from zinc oxide and other materials have got a large number of nanostructuring and application opportunities in a very broad field of materials
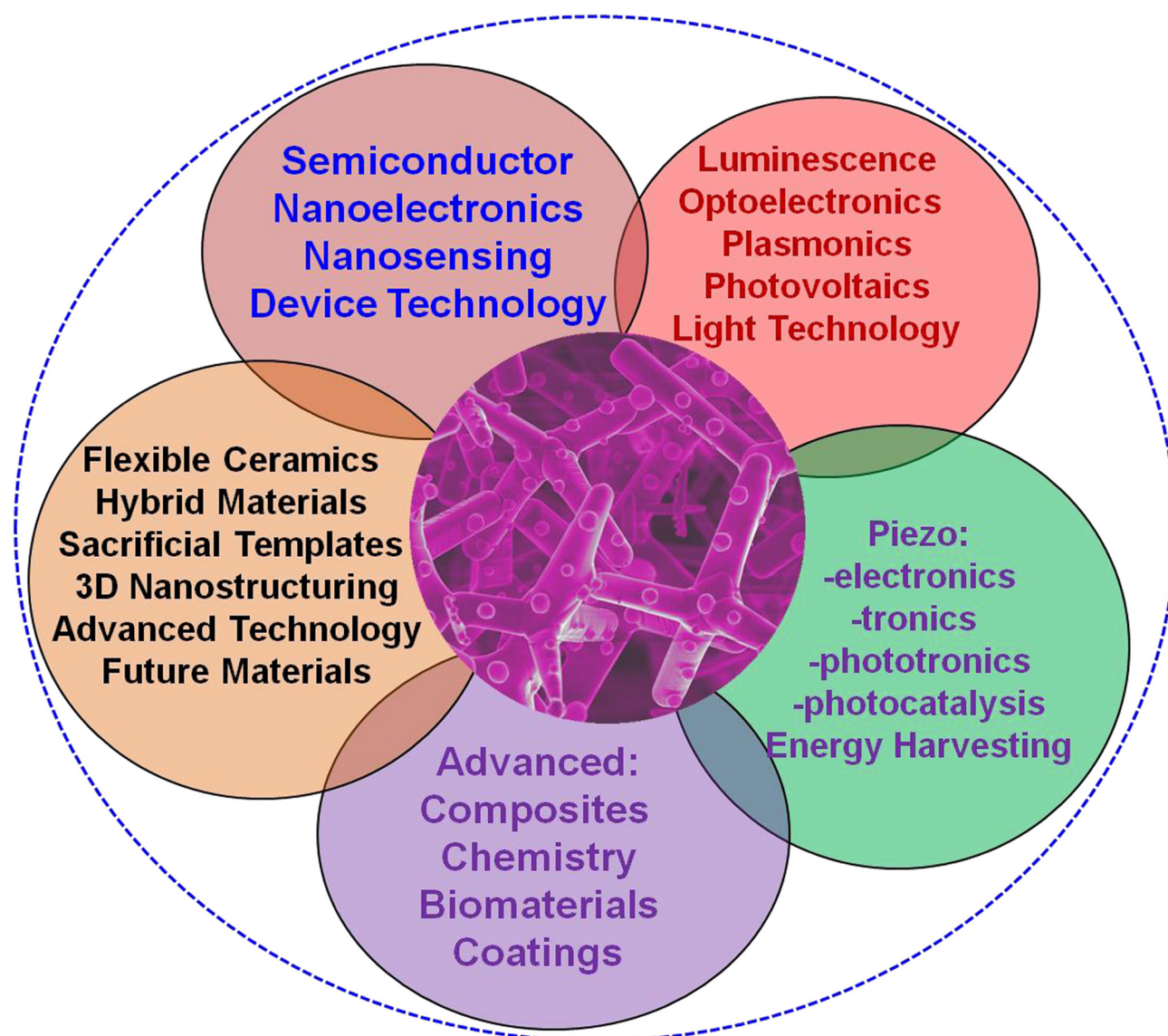

FIGURE 10

Overview about fundamental research interests and advanced technological applications of pure and hybrid ZnO tetrapod-based network materials in different interdisciplinary fields.

science and engineering (Table 2). A few application examples have already been demonstrated here; however, a lot more is on the way yet to appear in the future. Figure10 presents a perspective where these tetrapods mingle several fundamental, as well as interdisciplinary, material fields together at one platform. Since the developed flame transport synthesis (FTS) technology offers easy upscaling for the synthesis of different varieties of ZnO tetrapods (Phi-Stone AG: a start-up company has already been at Kiel, Germany), this field is going to witness real technological applications. Here, we tried our level best to cover all the possible aspects of ZnO tetrapods, but several might be left and many more will appear in future papers, including detailed review articles.

Acknowledgments

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