

# Utilizing the broad electromagnetic spectrum and unique nanoscale properties for chemical-free water treatment

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Clean water is critical for drinking, industrial processes, and aquatic organisms. Existing water treatment and infrastructure are chemically intensive and based on nearly century-old technologies that fail to meet modern large and decentralized communities. The next-generation of water processes can transition from outdated technologies by utilizing nanomaterials to harness energy from across the electromagnetic spectrum, enabling electrified and solar-based technologies. The last decade was marked by tremendous improvements in nanomaterial design, synthesis, characterization, and assessment of material properties. Realizing the benefits of these advances requires placing greater attention on embedding nanomaterials onto and into surfaces within reactors and applying external energy sources. This will allow nanomaterial-based processes to replace Victorian-aged, chemical intensive water treatment technologies.

## Addresses

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**Current Opinion in Chemical Engineering** 2021, **33**:100709

This review comes from a themed issue on **Nanotechnology: nano-materials for energy and environmental applications**

Edited by **Dionysios D Dionysiou, Suresh Pillai and Sami Rtimi**

For a complete overview see the [Issue](#)

Available online 28th July 2021

<https://doi.org/10.1016/j.coche.2021.100709>

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## Introduction

Nearly 1 billion people worldwide lack access to clean water, and billions have limited but highly impaired drinking water. Globalization trends are fundamentally changing how water is used. Rapid urbanization is stretching the distance between centralized water treatment facilities and water uses, resulting in days to weeks of travel times in pipes before water reached end users. During this time, water quality degrades in corroding, leaking, and poorly maintained pipe networks [1]. Population growth and higher affluence increases per capita water demands, stressing the once plentiful pristine water supplies and necessitating more distant and often quality-impaired water supplies that were previously overlooked as suitable for drinking water. Active ingredients in pharmaceuticals, personal care products, biologicals, solvents, disinfectants, and so on. find their way into industrial and municipal sewerage systems, and eventually into downstream drinking water supplies [2\*\*]. Water supplies are also impacted by agricultural fertilizers, herbicides, and veterinary pharmaceuticals in concentrated animal feed operations (CAFOs). The Victorian-age unit processes commonly employed at centralized water treatment facilities are often adequate at meeting basic water purification standards but they are weak barriers for chemicals of emerging concern (CECs). Consequently, the industrial and home point-of-use (POU) water market is over \$17B annually and growing by >10% annually [3].

Industrial water needs and sustainability goals are also shifting. From beverage producers to semiconductor manufacturers, and hospitals to computer data centers, companies are reducing their reliance on tap water by installing sensors and treatment technologies to purify water on-site, and maximizing water reuse within their facilities and producing water quality suitable for its specific application (i.e. 'fit-for-purpose' water).

To minimize treatment costs, Victorian-aged water treatment unit processes rely heavily on chemical transport, storage, and addition and produce sludge. However, these design and operating philosophies do not scale well in decentralized systems because concentrated chemicals are toxic to transport and store and require advanced operator certifications. Chemical-free water treatment offers more scalable and safer solutions for potable and wastewater reuse applications, treating water to fit-for-purpose quality in urban as well as decentralized systems. Similar drivers for chemical-free water treatment also are present in mining, energy, or farming industries that are 'off the water (and power) grids.'

This *Current Opinion* introduces opportunities for novel, scalable, and chemical-free water purification technologies that remove different pollutant classes from water. These technologies harness energy from across the broad electromagnetic spectrum using nanomaterials that exhibit unique functional properties. The mechanisms behind fundamental nanoscale interactions with energy present enormous opportunity to shift long-held paradigms that have limited drinking water and wastewater treatment to traditional hub-and-spoke centralized constraints (i.e. one municipal water treatment plant from which hundreds of miles of pipes deliver water to users) that are failing to meet water demands of a growing planet.

## Harvesting energy across the electromagnetic spectrum using nanotechnology

Figure 1 illustrates the broad electromagnetic spectrum and provides examples of water treatment technologies that harness this energy. While electron beams using ionizing radiation ( $\sim 10^{-12}$  m and  $\sim 1$  MeV) [4,5] and deep ultraviolet light ( $\sim 185$  nm) [6] have been examined for water treatment applications, the system costs remain high unless integrated with other oxidants [7]. Instead, we focus on leveraging nanomaterial interactions with more energy-efficient ranges of the electromagnetic spectrum from 250 nm (UV-C;  $10^{16}$  Hz) through radio waves ( $\sim 10^4$  Hz) to target specific biological pathogens and inorganic or organic pollutants in water. The size, shape, and chemical composition(s) of individual and agglomerates of nanomaterials offer highly tunable properties capable of capturing, redirecting, and utilizing energy from across the electromagnetic spectrum.

## Exploiting advanced materials and the electromagnetic spectrum for water treatment

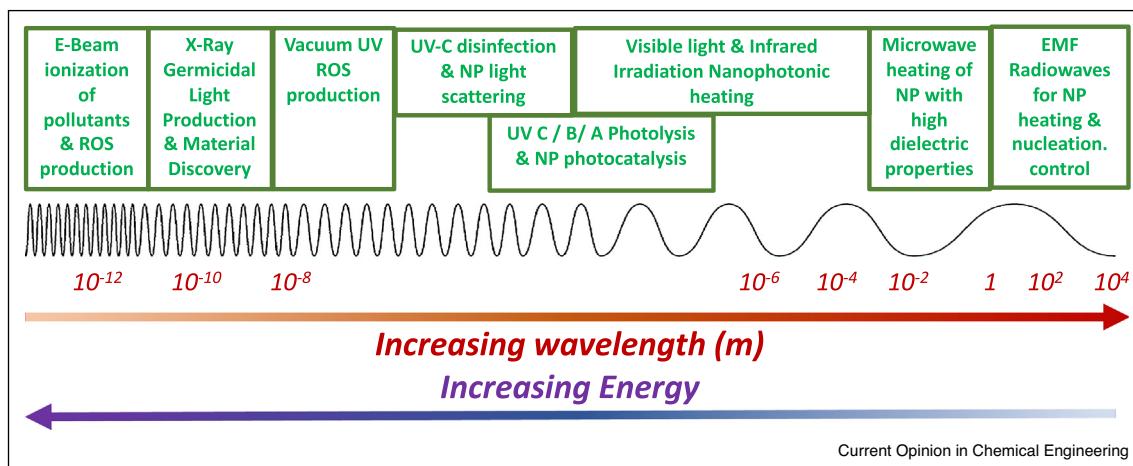
### Pathogen disinfection and biofilm mitigation using silica nanoparticles with UV-C wavelengths

Pathogenic virus, bacteria, and protozoa in drinking water pose water-borne health risks. Non-infectious bacterial biofilms that grow on surfaces in water treatment processes, piping, and household plumbing can reduce operational performance and can harbor other pathogenic organics (e.g. *Legionella pneumophila*). DNA and RNA in living organisms absorb light between 230 and 280 nm, so UV-C irradiation can cleave these bonds and prevent organism replication [8,9]. While low-pressure or medium-pressure mercury-vapor lamps can provide UV-C light to water flowing through small reactors, the advent of nano-enabled light-emitting diodes (LEDs) overcomes barriers associated with delivering UV-C light into other reactor geometries where biofilms often persist [10]. Example geometries include small diameter tubing used in everything from reverse-osmosis membrane channels to dentist offices or household faucets. Light produced by a point-source LED can be spread over large areas using flexible optical fibers. When coated with  $\text{SiO}_2$  nanoparticles (NPs), fibers can side-emit UV-C light, creating a *glow-stick* of UV-C light that inactivates pathogens [11] and prevents biofilm growth [12]. The NPs on the surface of the optical fiber interact with the evanescent wave propagating outside the optical fiber and cause UV-C scattering out of the fiber, through a UV-C transparent fluorinated organic polymer cladding, and into the water or onto surfaces. Modulating NP diameter, mass loading, refractive index, and placement on flexible optical fibers has the potential to provide chemical-free disinfection in locations previously un-reachable by conventional UV-C light sources.

### Photocatalytic oxidation of organic pollutants using UV-B/A to visible wavelengths

Heterogeneous catalysis using NPs that have a bandgap capable of producing reactive oxygen species (ROS;  $\text{HO}^\cdot$ ,  $\text{O}_2^\cdot-$ , etc.) can oxidize organic micropollutants in water. There are thousands of material-discovery focused UV to visible light photocatalyst publications every year, yet only a few consider integrating the NP into treatment processes [13]. Rather than being solely a materials challenge, the barrier to implementing photocatalytic NPs in water treatment has been the need to separate and remove suspended or slurry mixtures of photocatalysts (1 g/L) [14] from solution by filters before the water is suitable for drinking and to enable catalyst reuse for many years [15]. The high catalyst doses used slurries results cause high turbidity reduces the ability of light to pass through water; thus, turbulent flow regimes are needed to constantly transport the catalyst near to the light source. Ceramic membrane-based reactor systems are effective to

Figure 1



Electromagnetic spectrum ranges that can be used in conjunction with nanotechnology to enable disinfection, pollutant oxidation or reduction, and localized thermal driven desalination (frequency ( $f$ , Hz) =  $C/\lambda$ , where the  $C$  is speed of light ( $3 \times 10^8$  m/s) and  $\lambda$  is wavelength of energy (m); Hertz (Hz) have units of  $\text{sec}^{-1}$ ).

remove from water aggregates of nano-photocatalysts used in slurries [16].

Other reactor designs immobilize photocatalysts on surfaces. For example, photocatalytic NPs of  $\text{TiO}_2$  [17] or graphitic carbon nitride ( $\text{g-C}_3\text{N}_4$ ) [18] attached on glass or polymeric optical fibers have increased quantum yields by  $>10\times$  in micropollutant oxidation compared against slurry reactors. The low and even energy distribution along the optical fibers prevents energy oversaturation within the NP (i.e. more light irradiation striking the photocatalyst than can be absorbed to generate an excited electron and thus decreasing the observed quantum yield of the system) [17,19]. Because light does not need to be transmitted through water or dense catalyst slurries, energy use is more efficient. Additionally, UV-A and even visible light conveyed within the optical fiber directly reacts through refracted light and also through interactions with evanescent wave energy to activate NPs on the surface (i.e. interface with water), and ROS produced within the interface degrades the pollutants.

Another novel reactor configuration involves embedding photocatalytic NPs within porous electrospun polymer mats, and then placing the mats within a sequencing reactor for two operational steps termed ‘trap-n-zap’ [20]. First, in the absence of light, micropollutants are adsorbed from flowing water onto and into the porous hydrophobic polymer (i.e. ‘trapped’). Second, water flowing through one reactor containing the polymer mats is temporarily halted, and the mats irradiated with UV-A light, photocatalytically degrading the previously adsorbed micropollutants (i.e. ‘zapped’). Production of ROS can remove micropollutants and can also enhance

pathogen inactivation in water, as demonstrated in a photo-electro-catalytic reactor using titania nanotubes [21]. While recent reviews suggest that photocatalysis may be constrained to niche applications [14•] rather than large scale (millions of gallons per day) water treatment applications, there are a growing number of viable reactor platforms capable of utilizing less expensive, more effective catalysts and wavelengths at the boundary of UV-A to visible light wavelengths.

Advances in photocatalyst materials, including the use of single atom catalysts, to enhance their light absorption and charge separation properties are also noteworthy [22] and expand their application to the destruction of recalcitrant and recently concerning pollutants such as perfluoroalkyl and polyfluoroalkyl substances (PFAS) [23••]. For example, atomically dispersed Pt on SiC photocatalysts effectively degrades PFAS via hydrodehalogenation pathway [24]. Another notable advance in materials includes wide-bandgap photocatalysts such as  $\text{Bi}_3\text{O}(\text{OH})(\text{PO}_4)_2$  [25] and boron nitride (BN) [26•] that also effectively degrade perfluorooctanoic acid under UV 254 nm irradiation. Catalyst applications must consider these reactor-scale applications because they influence the energy efficiency of photocatalytic processes.

#### Desalination using solar light coupled with energy-harvesting nanoparticles

The desalination of high-salinity waters with total dissolved solids (TDS)  $>70$  g/L is challenging for widespread pressure-driven technologies such as reverse osmosis. Thermal distillation can treat water containing higher TDS, even at ambient pressure, because its performance is less influenced by salinity. Typical drawbacks

of thermal approaches are having practical, low-cost access to thermal energy and the relatively low thermodynamic efficiency of the process, which relies on energy-intensive phase changes [27].

Membrane distillation can be direct-driven by solar thermal energy to reduce the energy consumption and hence cost of desalination [28], or it can be coupled with solar photovoltaic systems [29\*\*]. Distillation membranes do not ‘boil’ water (<100°C), but they allow water vapor to diffuse across the polymer using a temperature gradient of only 20°C–40°C. Nanophotonic-enhanced direct solar membrane distillation (NESMD) uses photothermal NP coatings on the membrane to harvest sunlight, generate localized heat, and deliver thermal energy directly to the membrane surface all at once [30\*\*,31,32]. Carbon black NPs, which absorb a broad spectrum of UV-vis-IR energy, exhibit greater localized heating from solar energy than more well-recognized photonic NPs, such as gold NPs, that absorb and resonate at narrow wavelengths — varying with the NP size and shape [33,34]. Nanocellulose, a biodegradable and renewable nanomaterial, can harness nearly 80% of the available solar energy for use in desalination [35].

The synthesis of customized radiation-absorbing nanoparticles allows accessing electromagnetic energy across a wide spectral region [36]. At visible wavelengths (~400–750 nm), water is mostly transparent, and conductive nanostructures have been used to dissipate light into heat in ultrathin absorbing layers [37] (i.e. ~100 s of nm to ~10 s of μm), generating compact heat sources viable for local water vaporization, especially at higher temperatures [38]. At longer wavelengths, water exhibits larger absorption coefficients. Still, nanopatterned ‘lensing’ metasurfaces can be engineered to reduce radiation losses by transmitting radiation in the spectral region of interest (e.g. visible) while reflecting the wavelength range associated with thermal radiation (e.g.  $\lambda \sim 8$ –10 μm for temperatures between 20°C and 100°C) [39]. Heat losses to the environment represent one major bottleneck limiting the specific energy consumption of thermal desalination techniques. A resonant heat transfer mechanism has recently been coupled with light-driven desalination scalable modules, [40] enhancing the distillation efficiency by 500% and minimizing advective thermal losses [41].

The future of energy-efficient decentralized thermal desalination will probably require the combination of highly efficient broadband electromagnetic absorbers, selective infrared reflectors, and effective heat recovery methods. The specific water production rate (i.e. volume of clean water produced per unit photon energy harvested) depends on the solar thermal conversion efficiency, thermal energy utilization efficiency, solar irradiation intensity, heat recovery efficiency, and reuse strategy employed. There is a potential risk for semi-volatile organic pollutants to pass through distillation

membranes, [42\*] along with water vapor, but innovations in polymer materials coupled with solar pervaporation techniques may mitigate these risks [43]. Coupling solar concentration technologies with multi-effect and multi-stage membrane distillation process designs has the potential to deliver low-cost desalinated water, a highly attractive solution to water supply at locations with no or limited access to water and power infrastructure.

### Thermal degradation of pollutants in solid treatment residuals using microwaves

Microwaves are used in many high through-put industrial manufacturing processes, from ceramics to fast food, but they have only recently been considered for destruction of environmental pollutants. While not applied to pollutants in water, microwaves have been applied to treat pollutants in solid phases such as soils or spent adsorbents used initially to purify pollutants from water. Adding 0.5–5 wt% carbon nanotubes (CNTs), graphenes or carbon fibers to hydrocarbon contaminated before applying microwave fields can volatilize and mineralize the organic pollutants [44]. Nanomaterials with high dielectric constants rapidly superheat and mineralize organic pollutants to carbon dioxide (CO<sub>2</sub>). Rapid mineralization of organic pollutants occurs due to extremely high localized surface temperatures (>1000°C) and ROS produced on the surface of CNTs. The hydrophobic surface of CNTs readily absorbs non-polar organic pollutants; the smallest-diameter CNTs tested (10–20 nm) exhibited the highest catalytic destruction potential at microwave dosages of 450 W at 2450 MHz [45]. Even the most persistent pollutants (e.g. PFAS) can be defluorinated in this manner from activated carbon used as adsorbents that remove PFAS from drinking water [46\*\*]. Microwave treatment of graphitic and other materials with high dielectric constant properties holds tremendous opportunity for catalytic pollutant degradation, although research has yet to quantify the relative cost-effectiveness of microwave.

Application of weak magnetic fields in the presence of nano-scale zero valent iron can increase removal of selenium or trace organics from water [47–49]. They attribute the improved removals to an inhomogeneous magnetic field around the magnetized ZVI, which generated ferrous ions and formed a galvanic couple that lead to localized corrosion. The availability of soluble iron and electron transfer lead to improvements redox reactions and adsorption of selenium to iron solids. Future research is needed to understand the susceptibility of other materials and size dependence of such weak magnetic fields to redox-mediated water treatment processes.

### Using radio waves to control nucleation of scale-forming colloidal precipitates or activate engineered NPs for thermal heating

Electromagnetic fields (EMFs) are emerging as a strategy not only to activate engineered NPs for localized thermal

heating [50] but also to prevent nucleation and attachment of inorganic metal hydroxides, carbonate, or sulfate precipitates. These commercially available applications reduce surface scale and improve membrane performance during water treatment [51]. Benefits of localized heating of NPs using low-frequency EMFs are demonstrated in biomedical applications [52], and EMFs (150 kHz) also accelerate degradation of organic pollutants in groundwater using zero valent iron [53]. The ability of acoustic waves to travel through water is opening new modalities, from particle and precipitate scale mitigation to localized heating that accelerates pollutant degradation.

### Characterization of nanomaterial interaction with pollutants using X-rays

Electromagnetic radiation with wavelengths ranging from  $10^{-8}$  to  $10^{-12}$  m (i.e.  $10^{16}$ – $10^{20}$  Hz) correspond to the X-ray part of the spectrum. When X-ray light is incident on matter, it has enough energy to eject electrons. X-rays play a critical role in understanding mechanisms of pollutant adsorption to surfaces and characterization of surfaces, using XPS or XANES, exposed to pollutants in water [54–57,58<sup>••</sup>,59]. Machine learning using DFT predictions is now being applied to discover new nano-scale catalyst material properties that could transform the historical empirical or trial-and-error approach to water treatment material discovery [58<sup>••</sup>,59,60].

While biomedical applications have been suggested that use X-rays for bio-imaging [61] or targeted drug delivery [62], using X-rays to degrade pollutants in water remains in its infancy. One application uses X-rays to generate germicidal UV-C light within polymer membrane devices, to control biofilm formation on membranes which impairs their function and energy efficiency to treat water. X-rays delivered through the membrane device from an external source excite chemically stable radioluminescent phosphor materials embedded on/within the polymer membrane. The LaPO<sub>4</sub>:Pr<sup>3+</sup> and YPO<sub>4</sub>:Pr<sup>3+</sup> phosphor crystals were  $\sim 10$   $\mu$ m, because micron-sized crystallites were previously reported in 2004 to be more efficient luminescence for lanthanide-doped phosphors, compared to nanocrystals. However, recent reports suggest strategies to engineer Frenkel defects to act as traps for charge carriers in nanocrystals [63]. While the findings are thought likely to enable new approaches non-invasive medical radiology and inspection of nanoelectronics [64], integration of similar nanocrystals into water purification technologies may unlock yet additional opportunities for targeted release of chemicals or formation of germicidal UV-C light.

### Barriers and future perspectives

The last decade was marked by tremendous improvements in nanomaterial design, synthesis, characterization, and assessment of material properties. Realizing the benefits of these advances requires placing greater

attention developing reactor designs that can safely apply external energy sources to nanomaterials as a replacement for Victorian-aged, chemical-intensive water treatment technologies. A critical barrier is how to add/remove or immobilize nanomaterials and deliver energy between ultraviolet ( $\sim 250$  nm;  $10^{16}$  Hz) and radio waves ( $10^4$  Hz) to achieve fit-for-purpose water quality. From a safety perspective when treating drinking water, nanoparticles should not be thought of as ‘fairy dust’; when adding NPs as a slurry, one should not assume it will be simple to achieve  $\sim 100\%$  recovery from downstream and such applications may be more suited for industrial wastewater rather than drinking water treatment [3]. NPs dispersed in groundwater may be optimal for *in-situ* remediation [65]; however, although using ceramic membranes to recover NPs from slurries has been demonstrated to be economically and technologically viable, our experience suggests that immobilizing NPs on or near porous surfaces is the safest long-term strategy and avoids concerns regarding ingestion of nanoparticles [66<sup>••</sup>]. Immobilization of nanomaterials by be within polymer beads, fibers and membranes, within activated carbon, on optical fiber or metallic electrode surfaces, and so on [20,67–70]. This is especially important for small, home-based, point-of-use products, where customer and industrial surveys indicate safety as being an important attribute [71,72].

Harnessing synergies between nanomaterial properties and energy from across the broad electromagnetic spectrum enables creative solutions to emerge at the nexus of water and energy systems, allowing movement toward chemical-free water treatment. Achieving this ambitious chemical-free water treatment goal requires (i) advances in materials that can be produced at scale, (ii) strategies to integrate, and preferably immobilize, NP within porous reactor ‘architectures’, and (iii) safe and efficient means of delivering electromagnetic energy into reactors.

### Conflict of interest statement

Nothing declared.

### Acknowledgements

This work was partially funded by the National Science Foundation (EEC-1449500) Nanosystems Engineering Research Center on Nanotechnology-Enabled Water Treatment, the Nanotechnology Collaborative Infrastructure Southwest (NNCI-ECCS-1542160), and the National Institute of Environmental Health Sciences of the National Institutes of Health under Award Number P42ES030990. Laurel Passantino provided technical editing.

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