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# Ultrasound-Assisted Preparation Methods of Nanoparticles for Energy-Related Applications

*Christos Vaitis, Maria Mechili, Nikolaos Argirusis, Eirini Kanellou, Pavlos K. Pandis, Georgia Sourkouni, Antonis Zorpas and Christos Argirusis*

## Abstract

Ultrasound (US) technology is already into the research field providing a powerful tool of producing nanomaterials or being implicated in decoration procedures of catalyst supports for energy applications and material production. Toward this concept, low or/and high-frequency USs are used for the production of nanoparticles, the decoration of catalytic supported powders (carbon-based, titania, and alumina) with nanoparticles, and the production of metal-organic frameworks (MOFs). MOFs are porous, crystalline materials, which consist of metal centers and organic linkers. Those structures demonstrate high surface area, open metal sites, and large void space. All the above produced materials are used in heterogeneous catalysis, electrocatalysis, photocatalysis, and energy storage. Batteries and fuel cells are popular systems for electrochemical energy storage, and significant progress has been made in nanostructured energy materials in order to improve these storage devices. Nanomaterials have shown favorable properties, such as enhanced kinetics and better efficiency as catalysts for the oxygen reduction reaction (ORR).

**Keywords:** ultrasound, sonochemistry, nanomaterials, batteries, fuel cells, photocatalysis, metal-organic frameworks

## 1. Introduction: sonochemistry

Over the last decades, sonochemistry has been a fast developing branch of chemistry, which revolves around the ultrasound (US) effect and acoustic cavitation. USs include frequencies above the audible limit of human hearing (20 kHz). The effects of high-energy US arise from the acoustic cavitation rather than interactions of acoustic waves and matter at a molecular or atomic level. The pressure fluctuations generated by US in a liquid medium lead to the formation, growth, and implosive collapse of bubbles. More specifically, the liquid continuously expands (negative pressure) and compresses (positive pressure) until it reaches a critical diameter, which depends on the nature of the liquid and the US frequency.

The collapse of the bubble is almost an adiabatic process, and it results in a massive buildup of energy within the bubble. The microscopic bubbles can also collapse near the surface of the solid substrate and activate it, split larger particles to smaller

ones or deagglomerate nanoparticles. Other than the elevated temperature and pressure, those localized hotspots can result in powerful cavitation-generated shock waves and microjets, which can cause effective stirring/mixing of the adjusted layer of liquid [1, 2].

The first region is the interior of the bubble itself, which can be visualized as a micro-/nano-reactor, dictated by extreme temperature ( $>5000$  K) and pressure conditions ( $>1000$  atm) along with rapid heating/cooling rates ( $10^{10}$  K/s). The second one is the interface between the bubble and the bulk solvent. The reaction efficiency of nonvolatile solutes depends on their hydrophobicity, which determines their ability to accumulate at the gas-liquid interface [3]. The third region is the vicinity of the bubble, where the bulk solution is at ambient temperature, and free radicals can form in the hot regions.

## **2. Batteries**

As the globe encounters constant rise of energy demand to survive, the need to exploit efficiently renewable energy sources is vital. Electrochemical energy production can be a promising power source, while electrochemical devices constitute an energy storage option as well. Among these devices, batteries possess commensurate attention the last decades, due to their various applications and potential [4].

A battery cell, regardless its shape and configuration, is a device consisted of two electrodes, the anode and the cathode, an electrolyte between them having the role of the ionic conductor and a separator positioned between the electrodes that converts chemical energy to electricity or the reverse if the cell is rechargeable. Thus, the performance of the cell depends on the properties of all the components and the consistency of the system [5]. The current challenges are to advance the energy density of batteries, extend their conversion efficiency and rechargeability, and eliminate the charging time and cost while meeting the safety and environmental standards [5, 6].

In this direction, research has been emphasized toward developing nano-structured materials and implementing them in batteries as they deliver enriched performance, which is unapproachable by conventional materials. Some crucial aspects about nanomaterials are their large electrochemically active surface area, their electronic and ionic conductivity, thermal and mechanical endurance, and flexibility [7, 8]. In order to ameliorate redox reaction rates and accelerate kinetic mechanisms, a wide range of methods have been proposed including the possible incorporation of nanomaterials in each component of a cell [9].

Though the effectiveness of nanomaterials remains undisputed, only a minority of them is currently commercially utilized apparently as a result of the high cost to synthesize and manufacture them [7]. Sonochemistry may provide feasible tools to resolve many obstacles concerning the cost, safety, and environmental liability while fabricating the nanomaterials for batteries. As an example, we refer to Gu et al., who give a nice overview of graphene preparation by exfoliation in liquid media by using US as energy source and compared the results with those from other methods [10]. Graphene has excellent electrical, chemical, and mechanical properties and can, for example, boost the activity of electrodes especially of the oxygen electrodes in Zn-air batteries [11–13].

### **2.1 Li-batteries and Li-ion batteries**

High intensity USs have been used to prepare iron-graphene hybrid electrodes for Li-batteries, whereby it was found that the ultrasonication step is of key

importance for obtaining hybrid electrode material with small particle size and outstanding capacity and cyclability [14].

Olivine-structured  $\text{LiFePO}_4$  is a very promising cathode material; has benefits such as nontoxicity, low cost of raw materials, and good structural stability at high temperature; is safe; and has relatively high-specific capacity ( $170 \text{ mA h g}^{-1}$ ) with a flat discharge-charge potential (3.45 V vs.  $\text{Li}^+/\text{Li}$ ) [15, 16]. However, the low diffusion coefficients ( $10^{-17}$  to  $10^{-14} \text{ cm}^2 \text{ s}^{-1}$ ) of the Li-ions lead to a poor rate performance of  $\text{LiFePO}_4$ , and the poor electronic conductivity ( $10^{-9}$  to  $10^{-8} \text{ S cm}^{-1}$ ) is hindering its practical applications and must be tackled [15–17]. The preparation of nanomaterials for cathodes in Li-ion batteries (LIBs) has been proved to be one of the effective ways to overcome the problem of the slow Li diffusion and facilitate the reaction kinetics on the cathode. It is well known that porous structures can also increase the electrode/electrolyte interface area ensuring effective electrolyte permeation in cathode materials and substantially improve the performance of  $\text{LiFePO}_4$  and thus of the LIBs [17, 18]. It has been demonstrated that the adoption of ultrasonic-assisted impinging stream reaction is an effective method to produce positive electrode precursor particles for LIBs with high electrochemical performance [19].

$(\text{NH}_4)\text{Fe}_2(\text{PO}_4)_2(\text{OH}) \cdot 2\text{H}_2\text{O}$  has been prepared as positive electrode material for LIBs. The ultrasonication step was followed by a hydrothermal treatment step [20].

Apart from  $\text{LiFePO}_4$ , the preparation of Li-Mn-O electrode materials for secondary Li-batteries has been examined. Kim et al. fabricated mesoporous  $\text{LiMn}_2\text{O}_4$  nanospheres with upgraded properties and observed their performance in 50 cycles [21]. Sonochemical treatment of the surface of a corresponding Li-Mn-O electrode by coating particles with a porous film of MgO enhances its electrochemical properties, especially in high temperatures [22].

$\text{Mn}_3\text{O}_4$  is used as a precursor in the preparation of  $\text{LiMn}_2\text{O}_4$  and can be synthesized using US in a direct step.  $\text{Co}_3\text{O}_4$  used as key material in energy applications can be prepared by the same procedure [23].  $\text{Co}_3\text{O}_4$  nanoparticles (NPs) can be obtained by sonochemical synthesis also out of ionic liquids or azo ligands, using  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  as starting material [24, 25]. In both reports, the diameter of the particle size of  $\text{Co}_3\text{O}_4$  could be decreased lower than 50 nm.

A plethora of carbon morphologies has been extensively investigated as potential material appropriate for anode electrode in LIBs. Carbon spheres constitute an example applicable in LIBs [26, 27]. It has been demonstrated that the use of US provides an opportunity to prepare the mentioned material in a nontoxic accessible manner under mild conditions and competent dimensions (150–400 nm) [28].

Furthermore, recently Kumar et al. [29] outlined the progress in sonochemical synthesis of carbon dots, while Gedanken et al. [30] presented an advanced hybrid electrode of Cu foil coated by a layer of  $\text{Sn@C-dots@Sn}$  NPs ranging from 50 to 200 nm. These NPs were formed via sonication and contributed in promising cycling endurance of the cell.

A novel approach for the preparation of electrodes is the use of composite materials based on graphene. Therefore, Fe(III) oxide was sonochemically coprecipitated on graphene nanosheets in order to obtain nanocomposites for rechargeable Li batteries with stable charge-discharge kinetics for ca. 120 cycles [31]. Wu et al. also prepared magnetite NPs on reduced graphene by using a one-pot US-assisted method. These nanocomposites allow for high performance lithium ion storage devices [32].

Reduced graphene oxide (RGO) nanosheets dispersed under ultrasonic irradiation in NV ( $\text{Ni}_3(\text{VO}_4)_2$ ) NPs prove to eliminate their agglomeration; thus, the highly conductive electrode fabricated by the composite NV/RGO can preserve 88% of its initial capacity ( $117.22 \text{ mA h g}^{-1}$ ) after 1000 cycle tests [33].



Polyacrylonitrile (PAN) can be used as a component of solid composite electrolyte lithium battery [34]. A sonochemical method has been used to prepare negative electrode materials containing encapsulated intermetallic NPs in PAN. The use of US leads to very small particles of  $\text{CoSn}_2$ , which favors the formation of amorphous Li-Co-Sn and  $\text{CoSn}_2$  alloys, while the carbonaceous matrix helps to maintain the small particle size. The resulting  $\text{CoSn}_2$ -carbonaceous phase electrode ( $\text{CoSn}_2@\text{C}$ ) shows improved electrochemical behavior and is stable upon cycling (ca.  $450 \text{ mA h g}^{-1}$  after 50 cycles) in comparison with reports on pure crystalline  $\text{CoSn}_2$  [35].

$\text{Cu}_2\text{O}$ -based graphene composites have been prepared and tested for use as anode materials in lithium ion batteries [36] with superior performance than  $\text{Cu}_2\text{O}$  and can be used also for photocatalytic applications, sensors, and energy storage, especially for supercapacitors [37].

Various reports investigate copper (II) oxide ( $\text{CuO}$ ) and  $\text{CuO}$ /carbon composites as a possible anode material for LIBs [38–41]. Studies exploiting sonochemical methods for fabricating these materials involve the synthesis of copper complexes in an ultrasonic bath and the following calcination of compounds between  $400$  and  $500^\circ\text{C}$ . In this way,  $\text{CuO}$  particle size can be decreased until  $12.1 \text{ nm}$ . However, the specific structure and dimensions of particles differ depending on the precursor and the treatment conditions [42–44]. Hajnorouzi proposed a new method called “direct sonoelectrochemistry” incorporating ultrasonic irradiation in the process of electrolysis of a Cu tip and a physical top-down method, “US ablation” with Cu foil as the starting material to produce  $\text{CuO}$  NPs [45]. In comparison with conventional electrochemical methods, the produced amount of NPs was increased, and their dimensions were controlled, while the total time of preparation was reduced.

Nanoporous silicon structures are considered to be an attractive material in the design of LIBs as they have a large theoretical specific capacity [46–48]. Bedini et al. reported the synthesis of hydrogenated amorphous Si NPs under ultrasonic irradiation in mild conditions [49]. The product was highly porous with dimensions of particle ranging from  $1.5$  to  $50 \text{ nm}$ .

Two-dimensional molybdenum disulfide ( $\text{MoS}_2$ ) NPs have high potential implementation not only in LIBs but also in sodium-ion [50], Li-sulfur [50], zinc-ion [50, 51], and Mg batteries [52]. Liquid-phase ultrasonic exfoliation method can be an attractive process to disperse nanosheets of  $\text{MoS}_2$  in various solvents [53]. One more layered 2D material that can be obtained with the contribution of US is  $\text{V}_2\text{O}_5$  nanosheets according to Li et al., who fabricated and evaluated the electrochemical performance of the respective electrode [54].

Among the oxides of manganese, manganese dioxide ( $\text{MnO}_2$ ) finds application as energy storage material in alkaline batteries, rechargeable lithium batteries, and dry cells. Highly dispersed and nonagglomerated nano  $\alpha\text{-MnO}_2$  with a needle form of  $1\text{--}2 \text{ nm}$  diameter and up to  $50 \text{ nm}$  length have been synthesized by ultrasonication of an aqueous manganese(III)acetate solution with pH close to 7 followed by mild drying [55]. Reduction of  $\text{KMnO}_4$  has been also investigated as an alternative manner to exploit ultrasonic irradiation to prepare  $\text{MnO}_2$  [56, 57]. Okitsu et al. [56] provided useful data in order to comprehend the mechanism of basification, assisted by  $\text{H}_2\text{O}_2$  molecules formed during sonication, while Gnana Sundara Raj et al. [57] used also polyethylene glycol so as to achieve reduction and prepare spherical  $\text{MnO}_2$  particles with dimensions from  $10$  up to  $20 \text{ nm}$ . This proved to exhibit proper electrochemical endurance (after 500 cycles, 87% of the initial capacitance was preserved, while in the end of 1000 cycles, 78% of the initial specific capacitance was preserved).

Not always is it possible to obtain the result one is looking for, during the preparation of nanomaterials using US. Ganesh Kumar et al. did not obtain lithiated manganese oxide suitable for lithium batteries by treating Mn(III) salts using US and hot-hydrolysis, but the study showed the superiority of the ultrasonication regarding the adjustment of particle properties [58]. In another attempt of the same group,  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  was synthesized sonochemically as cathode with high redox potential for LIBs with better cyclability [59].

## 2.2 Zn-air and Zn alkali batteries

Zinc-air batteries (ZABs) exhibit a high energy density being at the same time a low-cost product. Therefore, a tremendous interest is present in meeting the demands for flexible and portable electronics. A novel porous-structured poly vinyl alcohol (PVA)-based nanocomposite gel polymer electrolyte (GPE) with silica ( $\text{SiO}_2$ ) was synthesized and used as electrolyte in a flexible ZAB. The fabricated porous material exhibited a high ionic conductivity ( $57.3 \text{ mS cm}^{-1}$ ), excellent water retention capability, and improved thermal and mechanical properties under ambient condition, and the ZAB showed an excellent cyclability, discharge performance, and power density [60].

It has been reported that cerium metallic particles deposited on Zn anode for alkali batteries lead to an improved electrochemical performance, whereby US power and sonication time influence strongly the battery efficiency, increase the corrosion resistance of the anode, and suppress the Zn-dendrite formation [61].

Regarding the oxygen reduction reaction (ORR), highly efficient cathodes for ZABs have been prepared based by decorating  $\text{Fe}_2\text{P}$  on 3D N,P-codoped porous carbon. The later has been prepared using pore-forming agents [62]. Further, bimetallic oxides like perovskites can be immobilized on different substrates and used as air electrodes in ZABs. As an example, one can use nafion, which has anti-fouling properties and is very interesting in electrochemical application owing to its interesting electronic and catalytic properties. As an example, we refer to Chen et al., who have immobilized  $\text{SrWO}_3$  on nafion by using US [63].

Nickel-iron layered double hydroxide (NiFe LDH) constitutes one more competitive catalyst with potential use in air cathodes, due to its layered structure. Sonication-assisted liquid exfoliation has been proposed to be competent to deliver highly functional NiFe LDH/CB nanosheets considering their oxygen evolution (OER) catalytic properties and stability [64].

## 2.3 Other battery systems

Xie et al. prepared active cathodes for  $\text{Ag}_2\text{V}_4\text{O}_{11}/\text{Li}$  battery systems through a reaction between  $\text{V}_2\text{O}_5$  gel and  $\text{Ag}_2\text{O}$  powder, which has been accelerated by using US [65]. The prepared cathodes ( $\text{Ag}_2\text{V}_4\text{O}_{11}$  and  $\text{Ag}_{1.4}\text{V}_3\text{O}_8$ ) exhibited superior electrochemical properties as compared to the ones prepared by this solid-state method.

In Li-S batteries, the sulfur host plays an important role. With respect to this, hierarchically ordered micro/mesoporous carbon (HPC) has been prepared by US-assisted spray pyrolysis obtaining HPC-S cathodes, which exhibited an excellent cycle retention of 77% in tests with 500 cycles at  $2.4^\circ\text{C}$  [66, 67].

## 3. Fuel cells

An electrochemical mechanism for the direct combustion (chemical oxidation) of fuels, which bypasses the intermediate stage of heat generation (so-called “cold

combustion”), allows for the direct conversion of chemical energy of a fuel to electrical energy without the losses due to the Carnot process. This direct energy conversion is possible in devices called fuel cells, and the underlying electrochemical mechanism has analogies in living beings [68].

There are several types of fuel cells, mostly categorized based on the used electrolyte. A second classification is based on the temperature needed by the electrolyte to achieve sufficient ionic conductivity and one speaks about low-, intermediate-, and high-temperature fuel cells.

### 3.1 Low-temperature fuel cells

The most important reaction in fuel cells is the provision with enough oxidant in order to keep the reaction running and thus the electricity production at the maximum level. This reaction is the reduction of the oxygen molecule (oxygen reduction reaction—ORR) as this is the source of the ions either to be transported through the solid electrolyte in solid oxide fuel cells (SOFCs) or to react with the protons arriving through the electrolyte in polymer electrolyte membrane (PEM) fuel cells.

In PEMs, the operating temperature is low, and therefore, the kinetics of the ORR is not high enough without the use of catalysts [69].

We prepared using the sonoelectrochemical method a Pt and carbon black-based nanocomposite as electrocatalyst for PEM fuel cells. We used pulsed electro-deposition in combination with pulsed ultrasonication to obtain Pt NPs on carbon black substrates, and we have shown the beneficial role of polyvinylpyrrolidone (PVP) against the agglomeration of the produced NPs [70].

Despite the reports of many research groups that Pt-based materials are considered to be the best electrocatalyst for ORR in fuel cells, there is no doubt that their reserves in nature are very limited making them expensive. Further, their durability is not as high as needed to use them in commercial applications. Therefore, reduction of the Pt consumption and most importantly their replacement with nonprecious metal catalysts in the ORR are considered essential. Therefore, the development of non-Pt or metal-free ORR electrocatalysts is extremely important and urgent [71].

Pd-based catalysts are one of the most attractive choices for the replacement of Pt catalysts as their cost is significantly lower, and at the same time, they possess a high catalytic activity for ORR not only because of the Pd itself but also due to synergistic effects between the Pd and the other components and supports [72]. Until now, different Pd-based composite materials have been proposed and investigated as catalysts for ORR [73, 74].

A very useful overview on sonochemically prepared multicomponent electrocatalytic materials for low-temperature fuel cells is given by Lee and Kwon [75]. Most of the efforts are focusing on the partial replacement of Pt by low-cost metals, for example, Ni [76], or the Pt replacement by Pd and respective nanoalloys with low-cost metals (Mn and Fe as core-shell with Pd) as well [77]. Carbon-supported Sn NPs for electrochemical applications and especially for improving the kinetics of the ORR have been sonochemically synthesized and showed high reduction overpotential for the ORR mainly due to the high surface area of the resulting carbon-supported Sn electrode [78].

Further improvement in the catalytic activity of the developed catalysts is expected through core-shell architecture materials and also through the use of active supports with high porosity leading to high active centers on the catalyst surface. Unique Pd@Pt/C core-shell NPs as methanol-tolerant catalysts have been prepared by Zheng et al. in a sonochemical multistep approach [79]. The high



performance of the Pd<sub>3</sub>Pt/C catalyst is ascribed to the unique combination of preferable growth of the Pd (1 1 1) plane, small particle size (~4 nm), unique core/shell structure, and the electronic effects between Pd and Pt.

Alternative electrocatalytic materials for the ORR have been also prepared starting from biomass and turned out to be promising alternatives to noble metal catalytic materials. The resulting catalysts exhibit an excellent catalytic activity as compared to commercial catalysts with reduced methanol crossover [80].

Also, oxides of transition metals have been sonochemically prepared as electrocatalysts for the ORR. Highly active porous MnO<sub>2</sub> with superior electrocatalytic activity as compared to commercial Pt/C catalyst has been sonochemically prepared and tested by Zuo et al. as a promising catalyst for direct methanol fuel cells [81].

US has been used also for the preparation of electrolyte membranes for PEMs. Nanocomposite membranes based on sulfonated polybenzimidazole (PBI) with cellulose and silica precursors have been made with improved mechanical properties and decreased methanol permeability [82].

Zuo et al. prepared a composite cathode material for alkaline fuel cells based on MoS<sub>2</sub> decorated with Pd using a simple sonochemical route [83]. They found that the new electrocatalyst has better performance than commercial Pt/C catalysts.

### 3.2 High-temperature fuel cells

Fuel cells working at temperatures higher than 500°C are referred to as intermediate (<700°C) and high temperature (700–850°C) fuel cells. These are proton conducting ceramic fuel cells (PCFCs), molten carbonate fuel cells (MCFCs), and solid oxide fuel cells (SOFCs). In all these fuel cells, the ORR is important, but in general, the use of catalysts is not necessary on the cathode side because of the high service temperatures.

In SOFCs, the ORR is as important as mentioned in the PEM section, but here the temperature is high enough to accelerate the ORR without the use of specific catalysts [84]. SOFC cathodes must be efficient mixed ionic-electronic conductors (MIECs) as they need to transport both electrons and ions especially in intermediate SOFCs (IT-SOFCs) [85].

Once the cathode reaction is providing a sufficient amount of oxygen ions in SOFCs, the anode material is of outmost importance as it has to catalyze the oxidation reaction.

One of the critical components for such a device is hydrogen, which is the fuel to be oxidized. Hydrogen can be produced by not only the classical methods such as reforming of hydrocarbons, gasification of coal or heavy oil fractions, and electrolysis using renewable or nuclear energy sources but also sonochemically and sonoelectrochemically, as reported in a recent review [86]. Other groups have developed electrocatalysts for hydrogen evolution using US. High intensity ultrasonic irradiation of AlNi alloy has led to an electrocatalyst for water splitting with high surface area and changes in its composition, which can be controlled by the selection of the right fluid during sonication [87]. Nitrogen doped reduced graphene oxide supported on N-titania as efficient catalysts for the production of hydrogen through water splitting has been prepared in a combined sonochemical/hydrothermal step [88].

As oil and natural gas supply is well established, feeding SOFCs directly with natural gas would be an ideal solution [89]. For natural gas fed SOFCs, the catalytic activity of the anode materials is critical as it needs not only to accelerate the oxidation reaction but also to prevent poisoning of the active centers by coking and sulfur and to be stable against other components that may be contained in the natural gas.



In our group, several efforts have been made in order to improve the preparation methods of SOFCs [90–94] and SOFC materials [95, 96] with a focus on the anode compartment [97–99]. Emphasis was given on the implementation of US in order to reduce the preparation time or to follow a facile and/or alternative path for materials with improved properties. In most cases, we prepared nanomaterials because they offer special properties to the fuel cells as they are catalytically active to a wide range of chemical reactions. One can prepare novel SOFC anodes by decorating state-of-the-art anode powder with nanometric metals and metal oxides [100]. We decorated anode materials based on GDC/Nickel and YSZ/Nickel cermets with molybdenum and tungsten oxide NPs and improved the catalytic activity and stability of the resulting composite anodes against coking and sulfur poisoning [101].

Not only electrodes for SOFCs have been made using ultrasonication but also electrolytes. Okay et al. prepared samaria doped ceria (SDC— $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ ) using an US-assisted coprecipitation method [102]. It has been found that the lattice parameter of the produced nanomaterial increased with increasing ultrasonic acoustic power and is linearly related to the ionic conductivity of the resulting electrolyte after sintering at 1200°C. Pinjari and Pandit prepared sonochemically at room temperature ceria nanopowders with particle size less than 30 nm with clear benefits regarding energy efficiency and reaction time as compared to the conventional preparation method [103]. Sonochemistry has been also used to prepare Ce(III) nano-sized precursors for nanoceria [104].

### 3.3 Other electrocatalytic applications

USs can be used not only in batteries and fuel cells but also in many other electrochemical and sonoelectrochemical applications. Ultrasonication has been used for the preparation of electrocatalysts for the direct electrooxidation of ethanol. A facile US-assisted method was proposed to fabricate the Pd-Pt alloy/multiwalled carbon nanotube (Pd-Pt/CNTs) nanocomposites for the ethanol and methanol electrooxidation reaction in alkaline media [105].

In another attempt, a catalyst made of graphene supported Ag decorated Pd NPs with exceptional activity and uniformity. In this respect, it has been shown that graphene is very important as substrate as it minimizes the coalescence of the NPs, which would decrease both the surface area and the electrocatalytic activity [106]. A multifunctional nanostructured electrocatalyst has been prepared by replacing carbon copper nanowires by Pd resulting to Pd@CuNWs and supported them by multiwalled carbon nanotubes (MWCNTs) using chitosan (CH) as a binder. Electrochemical catalytic activity and durability evaluation results proved the superiority of the resulting Pd@CuNWs/MWCNTs/CH regarding electrocatalytic activity and long-term stability compared to Pd/MWCNTs and commercial Pd/C electrocatalysts for ethanol electrooxidation [107].

An overview on fundamental studies of sonochemical and sonoelectrochemical nanomaterial preparation is given in recent publications of our group on fuel cells [108, 109] and others on nanomaterials [110].

Silica gels have been considered as appropriate matrices for the preparation of complex center doped materials for a variety of applications such as controlled-release carrier implantable materials for low weight drugs in biological systems and as substitute materials for membrane processes in fuel cells [111, 112].

Ultrasonication can be used for the atomization of methanol in order to have a smooth and continuous feed in direct methanol fuel cells, leading to a high and stable open circuit voltage (OCV) [113] or to enable improvement of direct methanol fuel cells using sonication in parallel with a novel cell design with integrated ultrasonic transducer [114].

## 4. Photocatalysis

Photocatalysis is a phenomenon based on redox reactions, which take place at the surface of a semiconductor material under UV or visible light irradiation. The photocatalytic activity of the catalyst depends on its ability to create electron-hole pairs, which are then taking part in a redox reaction to generate hydroxyl and superoxide radicals, which are able to undergo secondary reactions [115].

The improvement of the photocatalytic efficiency is a strategy, which was developed to push the absorption onset of  $\text{TiO}_2$  toward longer wavelengths (anatase band gap, 3.2 eV) by doping  $\text{TiO}_2$  with anions and/or cations and metal ions [116–118]. Zinc oxide can be either a n-type or a p-type semiconductor with a wide band gap ( $E_g \approx 3.3$  eV at 300 K), while its composites are very interesting materials because of possible synergistic effects on photoelectrochemical properties and photocatalytic activity [119, 120]. The primary ways to improve the photocatalytic effect can incorporate a sonocatalytic technique [121], doping [122], or stratified films [123, 124].

### 4.1 Environmental and energy applications

The photocatalytic degradation of organic pollutants such as dyes, pesticides, and pharmaceutical waste is a crucial application for the safety of the ecological system, mainly due to their toxicity and degradation complexity. The main application areas in catalysis are photocatalytic electrolysis of water, environmental protection, and solar cells. The pollutants in wastewater can be roughly divided into organic and inorganic pollutants, where organic compounds can be degraded by  $\text{TiO}_2$  photocatalytic technology [125].

Converting  $\text{CO}_2$  waste into valuable carbon fuels is undoubtedly one of the most viable and economical alternatives to reduce the  $\text{CO}_2$  emissions and resolve the energy crisis. UV irradiation and visible light have been used as sources of excitement for semiconductor catalysts to produce energy-bearing products such as methane, methanol, carbon monoxide, formic acid, and formaldehyde. Photocatalytic reduction of  $\text{CO}_2$  can not only reduce the carbon dioxide emissions but also solve the energy crisis [126–128]. Some of the catalysts that can be used for the photocatalytic reduction of  $\text{CO}_2$  include  $\text{WO}_3$  [120],  $\text{ZnIn}_2\text{S}_4$  [129],  $\text{CdS}$  [130],  $\text{Cu}_2\text{O}$  [117],  $\text{CuInS}_2$  [131, 132], and  $\text{BiVO}_4$  [133].

### 4.2 Sonochemical synthesis of nanocatalysts

Stucchi et al. used sonochemistry to both form NPs from the precursor and achieve a good distribution on the  $\text{TiO}_2$  decoration surface [117]. In fact, US energy accelerates the diffusion of the dissolved substance into the reaction system and also affects the selective adsorption of the surfactant on copper, causing elongation or compression in certain directions, thus affecting the morphology of the particles. The utilization of Cu, CuO, and  $\text{Cu}_2\text{O}$  NPs on  $\text{TiO}_2$  surface can greatly enhance the photodegradation of acetone and acetaldehyde [118].

$\text{CdS}/\text{TiO}_2$  can be prepared at a relatively low temperature ( $70^\circ\text{C}$ ) with small particle sizes (11 nm) using US in a short time (1.5 h) [130]. On the other hand, the use of conventional methods requires at least 20–24 h and elevated temperatures ( $200$ – $400^\circ\text{C}$ ). The properties of complex core-shell materials are combinations of the properties of both materials in the core and the shell. Those materials can be used in photovoltaic cells, optical sensor photocatalysts, and catalysts. In addition,  $\text{CdS}/\text{TiO}_2$  NPs can selectively bind heavy metal ions, such as Cr (VI), on their surface [134].

The irradiation of  $W(CO)_6$  in diphenylmethane in the presence of an Ar- $O_2$  mixture for 3 h can lead to tungsten oxide NPs consisting of both orthomolecular and monoclinic  $WO_2$ , partial oxidation of which produces tricyclic  $WO_3$  [135].  $WO_3$  acts as a catalyst in reducing  $CO_2$  in fuels ( $CH_4$  and  $CH_3OH$ ) with significant catalytic efficiency [136]. The introduction of CdS on  $WO_3$  can enhance carbon dioxide adsorption and increase  $CH_4$  selectivity, while the existence of two different regions can minimize undesirable back reactions of the photocatalytic products [137]. Those material CdS/ $WO_3$  can also use for the photocatalytic degradation of organic dye rhodamine B [138].

Xin et al. synthesized  $ZnIn_2S_4$  nanosheets with hexagonal and cubic structures. The samples were prepared and used to form methyl formate by photochemically reducing  $CO_2$  to methanol. The efficiency of the hexagonal form was better than the cubic one. In addition, both hexagonal and cubic nanosheets exhibited much higher activity than  $ZnIn_2S_4$  microspheres prepared by the hydrothermal method [129]. The  $ZnIn_2S_4$ - $In_2O_3$  structure is effectively used as a photocatalyst in  $CO_2$  reduction, by offering a large surface area for  $CO_2$  adsorption, while it exhibits abundant active sites for surface catalysis, leading to significant CO production rate and high stability [139].

Copper can also be used to prepare a  $CuInS_2$  NP structure. The study of various parameters, such as the different crystallographic structures of sulfur, the concentration of precursors, the reaction time, and the power of ultrasonic radiation on the morphology and particle size, showed that the crystallinity of sulfur plays an important role in the morphology of  $CuInS_2$  [131, 132]. Reducing  $CO_2$  to solar fuel can be essential for both decreasing  $CO_2$  emissions and increasing energy production. This photoelectrochemical reduction of  $CO_2$  to methanol is carried out by using p- $CuInS_2$  as a photocathode [140].

$BiVO_4$  NPs can be synthesized sonochemically at room temperature at different pH values (3, 5, and 10) of the original precursor without further heat treatment. The morphologies of the final samples are different depending on the pH value of the original precursor. The  $BiVO_4$  sample, which was prepared at a higher pH value, has an advantage in photocatalytic performance. The excellent photocatalytic efficiency can be attributed to the superior crystallinity and the large active surface of the  $BiVO_4$  structure [133], while its photocatalytic activity was studied during the degradation of organic dyes [134].

## 5. Metal-organic frameworks

### 5.1 Properties and applications

Metal-organic frameworks (MOFs) are a new class of porous crystalline hybrid materials that have achieved a tremendous growth over the last decades, with attention not only in chemistry but also in general science and technology. They consist of inorganic metal-based centers (ions or clusters) and organic ligands, assembled through strong coordination bonds in order to create an open crystalline framework with permanent porosity.

These ordered crystalline structures possess physicochemical properties, such as high surface area, open metal sites, and large void space. The easy tuning of the shape, size, and chemical nature of pores has led to unique chemical versatility and various morphologies, such as micro- or nano-spheres, -cubes, -sheets, and -rods [141–143]. Furthermore, accessing the molecular adsorption sites has opened the way to host-guest interactions and the ability to capture materials in both

chemisorption and physisorption states [144]. Due to their controllable composition and targeted preparation, MOFs can be manipulated, so they can be used in specific applications.

MOFs have been very promising in a wide spectrum of applications, ranging from the well-known gas storage/adsorption [145] and separation [146], catalysis [147], sensing [148], and dye/toxic material removal [149] to recently rising fields, such as luminescence [150], membranes [151], and drug delivery [152]. In terms of energy-related applications, they have been used for solar energy conversion [153], supercapacitors [154], batteries [155], and fuel cells [156].

## 5.2 Synthesis methods

MOFs have been traditionally synthesized either at room temperature [157] or via a hydrothermal/solvothermal approach by using electrical heating, an oil bath, or an autoclave at high temperatures, for a prolonged time of hours or even days. Recently, new methods have arisen to avoid these conditions. Similar to conventional, as a heating-based technique, microwaves (MWs) have lately been used widely for the synthesis of MOFs [158, 159], by offering phase selectivity, fast crystallization, and control over the crystal morphology. Electrochemical [160] and mechanochemical syntheses [161] are alternative methods, which appeared in 2005 and 2006, respectively. Other than the above popular methods, slow diffusion [162], reverse micelle [163], and combinations like sonoelectrochemical [164] have been tested as well.

## 5.3 MOF synthesis via US

This section is focused on the effect that US synthesis conditions have on the final product along with the use of sonochemically prepared MOFs in environmental applications with regard to harmful substance removal.  $(\text{Zn}_3\text{BTC}_2) \cdot 12\text{H}_2\text{O}$  (BTC = 1,3,5-benzenetricarboxylate) was the first MOF that was successfully prepared by applying a sonochemical method in 2008 [165], followed by MOF-5 [166] and ZnBDC (BDC = 1,4-benzenedicarboxylate) [167] later that year.

In order to reveal the determining factors of the reaction rates, a kinetic study was performed in 2010, by comparing conventional, microwave, and US syntheses [168]. Fe-MIL-53 was chosen for the comparison due to its mild synthesis conditions. The average reaction time to obtain the product is 1.5–3 days at 70–80°C for the conventional synthesis, 1.5–2.5 h at 60–70°C for microwaves, and 0.5–1 h at 50–70°C for the US, which is a result of increased preexponential factors in the sonochemical method.

Synthesis conditions can heavily affect the quality of crystals, the particle size, the surface area, and the morphology; thus, various studies have been published in an effort to optimize the reaction time, US power, solvent ratios, reagent concentration, and modulators/additives and achieve the best results in targeted applications [169, 170].

## 5.4 US advantages on MOFs

The contamination of the environment is becoming an aggravating problem [171, 172]. As a result of the accelerated expansion of chemical, pharmaceutical, and agricultural industries, many hazardous compounds, such as dyes, antibiotics, and pesticides, reach the aquatic environment. Therefore, many scientists have dedicated their work for the production of materials that can remove harmful substances.



Abbasi et al. compared the sonochemical synthesis of HKUST-1 with a mechanochemical one [173]. The majority of the mechanochemically prepared particles had a size of at least 60 nm, while the US led to particles mainly around 35–65 nm. Their adsorption efficiency was tested via the removal of two dyes. After 24 h, 19.52% of methylene blue and 10.86% of crystal violet had been adsorbed by the mechanochemical MOFs, while the US one had managed to remove 31.91 and 27.43%, respectively. The increased adsorption of methylene blue could be explained due to its smaller size, so it can be captured more easily than crystal violet.

In order to improve the methylene blue adsorption performance of TMU-23, a composite was prepared with graphene oxide (GO) in a US bath within 60 min at room temperature [174]. About 30 mg of GO-TMU-23 (10% GO) was added in 20 mL of 10 ppm aqueous solution, as well as 27 mg TMU-23 and 3 mg GO were also examined separately for comparison purposes. After only 2 min, TMU-23, GO, and GO-TMU-23 have removed 50, 47, and 89% of MB, respectively, while after 15 min, they have removed 78, 90, and 97%, respectively. Another GO composite is GO-Ni-BTC, which was prepared via an US-assisted ball milling technique [175]. Water was used as the only solvent as the coupling effect of mechanical force and ultrasonic waves can promote the reaction without an organic solvent. The Ni-BTC and GO-Ni-BTC were compared by studying the thermodynamics, along with adsorption kinetics by using the congo red dye, resulting in capacities of 2046 and 2489 mg/g, respectively.

$[\text{Zn}(\text{ATA})(\text{BPD})]_{\infty}$  nanoplates (ATA = 2-aminoterephthalic acid, BPD = 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene) were prepared at room temperature in a US bath within the optimized duration of 120 min [176]. The addition of triethylamine accelerated the crystal growth, and crystals could get separated after 60 min, but 120 min was still needed to receive fully uniform nanoplates. The modulator implementation led to an increase in 2,4-dichlorophenol adsorption from 68 to 91%. Pyridine had also been tested as a modulator agent during the synthesis of  $[\text{Zn}(\text{TDC})(4\text{-BPMH})]_n \cdot n(\text{H}_2\text{O})$  (TDC = 2,5-thiophene dicarboxylic acid, 4-BPMH = N,N-bis-pyridin-4-yl-methylene-hydrazine) [177]. Its addition led to better morphology of uniform sheet-shaped nanoplates with a thickness of 20–35 nm instead of NPs without order, while it also increased the removal efficiency of dichlorophenol and amoxicillin from 92.5 to 95% and from 87 to 94.5%, respectively, after 3 h.

The adsorption of rifampicin (antibiotic drug) [178] and imatinib (anti-cancer drug) [179] was tested as well with HKUST-1. The MOF was prepared by both a sonochemical method within 60 min and a conventional one after 24 h at 80°C. The US synthesized particles had an average size of 80 nm, while the majority of the conventional ones had a size over 150 nm. Regarding the uptake properties, the former could adsorb 26.6% of rifampicin after 3 h and 98% after 48 h, while the latter could reach 19% and 59.6%, respectively. Similarly, although a greater time period was needed, after 144 h, 96.7% of imatinib was adsorbed by the US HKUST-1 and 81.1% by the conventional one.

## 6. Conclusions

Among the several types of fuel cells, the use of nanoparticles has been implemented for improving the ORR in cathodes and the stability and poisoning of the anodic catalysts enhancing mainly the mass transfer phenomena. US-assisted preparation methods have been enabling more facile and cost-effective preparation methods of producing mono- and bimetallic nanoparticles in the absence and presence of various surfactants than conventional methods of preparations. The

produced nanoparticles were decorated onto cathode surfaces used in low- and high-temperature fuel cells acting synergistically with the surface toward an enhanced catalytic activity. The use of US and/or sono(electro)chemical methods also produces a controllable variety in the shape of the exposed planar sites of the moieties onto electrode surfaces and was proven to be a powerful tool for reducing metal precursors to mono- or/and bimetallic nanoparticles. Especially, in the case of carbon-supported nanocatalysts, the use of US, in general, has been proposed toward a high-value product production to meet the needs of energy applications.

US-assisted preparation methods are also a very promising tool in developing highly efficient materials for batteries. Significant efforts have been focused on creating functional nanomaterials in a variety of morphologies while decreasing the time and cost of preparation for meeting the commercial requirements. Substantial research has been reported in the field of Li and Li-ion batteries, where certain materials were directly tested in custom-made batteries with promising performance. Concerning other battery systems such as zinc-based and metal-air batteries, research showed promising results, although various nanomaterial candidates for electrodes, electrolytes, or catalysts have been prepared but not thoroughly tested. A more focused research trend in implementing the synthesized US-assisted nanomaterials in battery applications is currently toward a complete range definition of characteristics and stability in order to overcome possible failures and limitations.

In terms of environmental studies, semiconductor nanoparticles and composites prepared via US technology have shown promising results toward photocatalysis. Carbon dioxide reduction has achieved great process on both the reaction mechanisms and the pathways; thus, such materials can display better product selectivity.

Finally, USs have opened the way to fast and facile synthesis of metal-organic frameworks by further offering smaller particle size and enhanced morphologies. Compared to conventional methods, the accelerated nucleation and crystallization times have made sonochemistry very attractive over the last few years, although proper handling is necessary in regard to synthesis conditions for the acquisition and optimization of desired properties.

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## Author details

Christos Vaitsis<sup>1</sup>, Maria Mechili<sup>1</sup>, Nikolaos Argirusis<sup>2</sup>, Eirini Kanellou<sup>1,4</sup>,  
Pavlos K. Pandis<sup>1</sup>, Georgia Sourkouni<sup>3</sup>, Antonis Zorpas<sup>4</sup> and Christos Argirusis<sup>1,3\*</sup>

1 School of Chemical Engineering, National Technical University of Athens,  
Zografou, Greece

2 mat4nrg – Gesellschaft für Materialien und Energieanwendungen mbH, Germany

3 TU Clausthal, Clausthaler Zentrum für Materialtechnologie, Germany

4 Faculty of Pure and Applied Sciences, Open University of Cyprus, Nicosia,  
Cyprus

\*Address all correspondence to: amca@chemeng.ntua.gr

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