Review

Sonochemical fabrication of inorganic nanoparticles for applications in catalysis

Zhanfeng Li a, Tingting Zhuang a, Jun Dong a, Lun Wang a, Jianfei Xia a, Huiqi Wang a, Xuejun Cui b, Zonghua Wang a,

a College of Chemistry and Chemical Engineering, Shandong Sino-Japanese Center for Collaborative Research of Carbon Nanomaterials, Instrumental Analysis Center, Qingdao University, 266071 Qingdao, China
b College of Chemistry, Jilin University, 130012 Changchun, China

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ABSTRACT

Catalysis covers almost all the chemical reactions or processes aiming for many applications. Sonochemistry has emerged in designing and developing the synthesis of nano-structured materials, and the latest progress mainly focuses on the synthetic strategies, product properties as well as catalytic applications. This current review simply presents the sonochemical effects under ultrasound irradiation, roughly describes the ultrasound-synthesized inorganic nano-materials, and highlights the sonochemistry applications in the inorganics-based catalysis processes including reduction, oxidation, degradation, polymerization, etc. Or all in all, the review hopes to provide an integrated understanding of sonochemistry, emphasize the great significance of ultrasound-assisted synthesis in structured materials as a unique strategy, and broaden the updated applications of ultrasound irradiation in the catalysis fields.

1. Introduction

Catalysis is an important phenomenon to affect the chemical reaction rate in which the activation energy of reactants are changed through the catalysts, and almost covers the whole fields related to chemical reactions, such as hydrogen generation, fuel production, energy storage, pollution cleaning. Ultrasound is a term that refers to a mechanical wave with a frequency greater than the upper limit of human hearing (about 20.0 kHz), and is often generated from the electrical energy using a transducer such as magnetostrictive transducer and piezoelectric transducer.[1-4] Sonochemistry is coined to describe a wide research area in which powerful ultrasound radiation (0.02–10.0 MHz) can induce a few chemical reactions, or it is defined as a nonclassical method by which some molecules or particles may undergo one or more chemical processes.[5,6] Before sonochemistry become a popular practice, the chemical effects of ultrasound have been reported actually, and so far, many sonochemistry-based applications have been being found in synthetic chemistry, organometallic chemistry, material chemistry, biological chemistry, medical chemistry, and industrial manufacturing processes.[7] For example, ultrasound irradiation is often used in polymer chemistry as a mean either to initiate the radical-mediated polymerizations by producing free radicals or to carry out the emulsion polymerizations by emulsifying oil and water phases.[8,9] Ultrasound irradiation is able to initiate the reduction reactions, oxidation reactions, and hydrolysis reactions as a driving force, so that it has been used to purify water by degrading contaminants (e.g., textile dyes);[10-13] Certainly, ultrasound irradiation is also a very efficient method to clean debris from surfaces, which has been widely used in research and industry. Up to now, a list of general applications of ultrasound have been developed unceasingly, and most of them refer to chemistry, material and manufacturing processes.

In this review, the latest developments of ultrasound-mediated effects or reactions in catalysis field will be overviewed, where more emphasis is put on the matters about the synthesis of catalyst materials as well as the sonochemical applications in catalytic processes. The review will provide a fundamental understanding of the basic principles on sonochemical synthesis, demonstrating its powerful and unique aspects to create nano-scale or micro-scale materials. Immediately following this, the review will focus on the fabrication of multimodel or multifunctional catalytic devices and a few catalyst-based applications in the reacting systems, highlighting the recent developments of sonochemistry in catalysis. In the end, the review will point out the
prospective challenges and trends in the programming of sonochemistry-assembled functional materials, and concludes the significance of the ultrasound-assisted synthetic methods in different catalytic applications.

2. Sonochemistry and inorganic materials

In a liquid system, ultrasound irradiation can produce the cavitation events, which accounts for the extreme characteristic conditions of sonochemistry. In the well-studied case, sonication the liquids generates highly active radicals for primary sonochemistry, or induces the conversion of primary radicals for secondary sonochemistry.[14] These radicals can serve as strong oxidants or reductants, initiating various chemical reactions in an aqueous or nonaqueous solution including the reductions, oxidation, or hydroxylation of solutes. Besides, the acoustic cavitation in a liquid often gives rise to numerous physical and/or mechanical effects (e.g., simple heating, shock waves, microjets) accompanied by the chemical consequences, and these effects can affect the frequency and efficiency of chemical reactions in material synthesis.[15,16] Anyhow, the most of applications for ultrasound basically utilize the chemical, physical and/or mechanical effects. For instance, the fragmentation for brittle materials, the emulsification for immiscible liquids, the agglomeration for malleable materials, and the exfoliation of layered materials into 2D layers, the fabrication and delivery of drug systems have often been observed.[17-19]

Inorganic nanomaterials have been explored in many applications ranging from photocatalysis, hydrogen storage, energy storage to sensors, electronics, biotechnology and nanomedicine, and correspondingly numerous methods also have been developed to participate in their synthesis, such as the coprecipitation method, sol–gel method, solvothermal method. As a candidate, the ultrasound irradiation provides a facile route to yield a variety of nanomaterials from inorganic precursors mainly based on the primary sonochemistry, secondary sonochemistry, and/or combined effects. Roughly, the primary sonochemical synthesis refers to some extreme transient conditions (high pressure and high temperature) from the collapse of cavitation bubbles when the secondary sonochemical synthesis widely employs the post-produced chemical consequences in the liquid phase. Table S1 and Table S2 have summarized two kinds of sonochemical synthesis of nanstructured metals from the precursors, respectively.[20-35] Additionally, the physical effects (e.g., heating, microjet, shock wave) and mechanical effects (e.g., shear force, interparticle collisions, rapid mixing, turbulence) from ultrasound irradiation are also important in the formation of nanomaterials. At present, ultrasound irradiation has become a broadly useful tool to prepare single and few layered materials by overcoming the attractive forces between individual layers, e.g., breaking bulk graphite down to 2D graphene structures.[36-40] Certainly, the inorganics-based hybrid nanomaterials including inorganics/inorganics composites, inorganics/organics composites and inorganics/macromolecules composites, have been produced largely via the combined sonochemistry synthesis.[41-45] For instance, Ashokkumar et al. carried out the sonochemical formation of polystyrene/SiO₂ Janus particles on the basis of the phase separation mechanism between the tetraethoxysilane and the growing polystyrene particles.[46] In our studies, the magnetic nanoparticles was either fixed on the surface of carrier supports as a shell or loaded into the inner of carrier supports as a core.[47] In fact, the structure, size, stability and activity of inorganics-based hybrid nanomaterials are important to both the quality of properties and the acceptability of applications, and the relevant research results or viewpoints have been reviewed in detail in other papers. [48-53]

3. Applications in the catalysis field

Sonication is a cogent tool for catalysis reactions, where the shear force and intense shock waves produced by ultrasound irradiation allow a faster mass transfer to cause a better contact of reactants. Specific to the preparation process of catalysts, ultrasonic treatment is usually able to increase the catalytic activity by changing the crystallinity. For example, the thioglycolic acid-assisted sonochemistry has been used to produce amorphous long Ag₂S nanowires, and the novel silver chalcogenides had good photoelectric and thermolectric properties which could be widely applied in optical and electronic devices.[54] In many literature, the sonochemistry-assisted synthesis of inorganic nanomaterials from precursors has been summarized and highlighted, as well as the special role of surface-active materials.[55-57] Here the current state of sonochemistry and ultrasound-synthesized inorganic catalyst will focus on the enhancement of catalytic properties for the reactions such as reduction, oxidation, degradation, polymerization, and so on (Fig. 1).

4. Reduction

Inorganic catalysts are advantageous to numerous reactions for many reasons such as unique electronic effects, high surface areas and energies, potentially lower cost and even possible reuse without regeneration (i.e., making the catalysts more stable), and especially, many metal or metal-based nanomaterials are able to serve as heterogeneous catalysts in the reduction processes, e.g., hydrogenation, deoxygenation, alklylation, and amination. Usually, the agglomeration of as-prepared catalysts easily occurs due to the van der Waals force or the sintering bonds, causing the limitation of catalytic activity and selectivity from the reduction of active sites.[58] In order to achieve the high performance of catalysts in a heterogeneous reaction system, it is important to improve the controllability in size and structure, increase the surface area and active sites, and enhance the mass transfer at liquid–solid interfaces.

In fact, the synthesis of inorganic nanomaterials under ultrasound irradiation goes through some physical and chemical effects powerfully producing abundant active sites, so various attempts have been made to create metal catalysts and metal-based catalysts by the sonochemical reduction of metal ions (e.g., Pt(IV), Pd(II), Ni(II), Au(III)), and the product morphology has been controlled using complicated procedures, such as the polyol process and the thermolysis of metal complexes. [59,60] Besides different morphologies, various nanostructures and compositions in connection with active sites also can be yielded with the help of the sonophysical and sonochemical effects. Fig. 2 shows the sonochemical synthesis of metal catalysts and metal-based catalysts as well as the physical effects of ultrasound irradiation on the heterogeneous catalyst surface. Meanwhile, the combination of solid support (e.g., alumina, zeolite and silica) and metal nanoparticles may be able to

![Fig. 1. Main reaction types affected ultrasound-synthesized inorganic catalysts.](image-url)
resolve the aggregation issue by the mechanical effects of ultrasound since the composite structure can isolate the metal nanoparticles on the surface of supporting material and reduce the particle size. Consequently, the metal catalysts and metal-based heterogeneous catalysts produced from ultrasound-assisted approaches can provide an increased surface area and highly selective surface for the reduction reactions.

## 4.1. Sonochemical synthesis of metals and reduction catalysis

Metal catalysts are active under certain conditions owing to the corrosion stability and strong acceleration capability. For example, Platinum (Pt) can be employed as an all-round catalyst in a wide range. In everyday life, Pt was commonly used in catalytic converters to deal with the automotive exhaust, because it could catalyze the total oxidation of hydrocarbons and carbon monoxide.\[61-63\] By the ultrasound-aided formation of most-disordered amorphous phase with active centers, the activity of Pt catalysts can be increased for the organics decomposition, and moreover, the catalytic activity is dependent on the ultrasonic intensity and the ultrasonic duration. In Sulman’s report,\[64\] the reduction rate of C = O groups in the sulfuric acid solutions containing Pt catalysts was improved by prolonging the sonication time from 15 s to 30 s at an ultrasonic intensity ranging from 0.1 W cm\(^{-2}\) to 1.0 W cm\(^{-2}\), whereas the ultrasonic treatment lasting for 60 s or 120 s at a higher ultrasonic intensity (3 W cm\(^{-2}\)) led to a decrease in the catalytic activity. Such deactivation of Pt catalysts might be explained by the reconstruction of active centers that was associated with an appreciable morphological modification of the catalyst surface upon an increase in ultrasonic intensity and duration. Radziuk et al. once demonstrated the effect of ultrasonic treatment on the catalytic activity by making clear whether the particle size and crystallization affected the reactivity of Pt nanoparticles, where three highly monodisperse Pt nanoparticles were obtained after a sonication separately in water, PVP aqueous solution, and ethylene glycol solution by the citrate method.\[65\] In this study, the catalytic properties of Pt nanoparticles were evaluated by the electron-transfer reaction between thiosulfate ions and hexacyanoferrate (III), in which the formation of hexacyanoferrate (II) ions and tetrathionate ions was achieved. When the same catalytic reaction was carried out with three kinds of Pt nanoparticles, the ethylene glycol-modified nanoparticles produced by a 20 min sonication demonstrated the highest catalysis, and the modified nanoparticles with PVP or ethylene glycol for 20 min drove a faster catalytic reaction than those for 60 min. This phenomenon was due to the weak crystallinity of nanoparticles in sonication, and in turn demonstrated amorphous nanoparticles more strongly accelerated the reactions than the crystals, or in short, the nanoparticles with less crystallinity were able to become a better catalyst. However, it was in surprise and remained an open question that amorphous and crystalline Pt nanoparticles in water drove the catalytic reaction a bit less slowly than that in PVP.

Like Pt, noble metal nanomaterials are of great interest owing to their enhanced catalytic activity for several important chemical reactions, especially with an aid of other metal materials. However, it is difficult to commercialize such catalysts for their cost effectiveness and efficiency, so the alloys of noble metals and non-noble metals or transition metals (e.g., copper, nickel, iron) have been highly attractive in recent years because they may provide cost-effective catalysts while preserving the overall performance. Mercury (Hg), as we know, is toxic but will become a safe material in electrochemistry and catalysis fields upon the amalgamation with some other metals. Gedanken et al. achieved bimetallic Hg/Pd alloys (HgPd 1:1, HgPd 2.5:1, and HgPd 4:1) by sonicating an aqueous Pd (II) nitrate solution with liquid mercury,\[66\] and explored the catalytic activity of as-synthesized nanoalloys by using the catalytic reduction of 4-nitrophenol and other nitrophenol derivatives. In the presence of NaBH\(_4\), the nitrophenol reduction occurred involving the successive process that the alloy catalysts absorbed the hydrides onto the surface and further released and transferred active hydrogen to the nitro group. Compared with the two other Hg/Pd nanoalloys (HgPd 2.5:1 and HgPd 4:1), HgPd 1:1 with a smaller particle size showed an excellent catalytic activity, reaching 100% for the 4-nitrophenol reduction within 70 s (Fig. 3), and the rate constant was up to \(58.4 \times 10^{-3}\) s\(^{-1}\) at room temperature. Besides, the Hg/Pd catalyst

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**Fig. 2.** Sonochemical synthesis of metal catalysts and metal-based catalysts as well as the physical effects of ultrasound irradiation on the heterogeneous catalyst surface.
exhibited superior stability and reusability to other noble metal-based catalysts. Recently, Aminabhavi et al. reported a green synthesis of three-dimensional hexagonal-like zero-valent Cu materials via the sonolysis of copper (II) acetate in a medium consisting of ethylene glycol/ethanol (1:1). [67] Then the zero-valent Cu nanostructured materials with high purity (greater than 99%) were used to investigate the reduction of nitrate in the polluted water. During the reduction reaction, the nitrate removal reached up to about 90% after 30 min, clearly demonstrating the high efficiency of pure-phase Cu nanomaterials obtained under ultrasound irradiation for environmental remediation.

In the field of electrocatalysis, alloy nanoparticles containing Pt also have attracted enormous interest not only for their low material cost by reducing the Pt amount but also for their enhanced catalytic activity, durability and selectivity. Based on the sonication of metal salts in an argon purged non-aqueous solution containing a strong reducing agent, Gümceti et al. have prepared bimetallic nanoparticles consistent with Pt$_3$Ni stoichiometry by adjusting the mole ratio of Pt$^{4+}$ ion and Ni$^{2+}$ ion. [68] By assessing the catalyst activity toward O$_2$ reduction, the findings showed that the Ni atoms in the surface layer of Pt$_3$Ni could weaken the bonding of OH species on Pt sites, thereby increasing the energy needed for oxide formation and decreasing the energy for oxide reduction. By the rotating disk electrode studies, the activated Pt$_3$Ni-sono nanoparticles demonstrated 2–3 times higher oxygen reduction activity than the commercial Pt/C catalyst according to both specific activity and mass activity. Kwon et al. have obtained the trimetallic nanoparticles ((Pd,Co)@Pt) with different elemental compositions by the ultrasound-assisted polyol synthesis of Co(acetylacetonate)$_2$, Pd(acetylacetonate)$_2$ and Pt(acetylacetonate)$_2$, where the nanoparticles had Pt-enriched surface with Pd and Co forming the core. [69] In the electrocatalysis of oxygen reduction reaction, the onset potentials of (Pd,Co)@Pt nanoparticles were higher than the commercial Pt/C sample, and it also displayed higher specific activity and mass activity than pure Pt. This positive effect on the electrocatalytic properties was explained as the modification of Pt electronic structure by the strain and ligand effects of Co core substrate, when the electrocatalytically active Pd could also function as a co-catalyst for the oxygen reduction reaction. Osaka and coworkers have used the sonochemical synthesis to prepare a series of non-platinum nanoparticles including Pd, Au, Pd-Au and Pd-Co, [70] and as immobilized indium-tin oxide electrode, they showed widely different activities for oxygen reduction in alkaline solution. In Kwon’s report, the composition-tunable PdM@Pt/C (M = Mn and Fe) core–shell-like electrocatalysts were synthesized by a one-pot sonochemical approach, [71] and in comparison with Pt/C, the samples showed enhanced electrocatalytic activity and durability for oxygen reduction.

Fig. 3. I) Time-dependent UV–Vis absorption spectra for reduction of 4-nitrophenol catalyzed by Hg/Pd alloy at molar ratios of (a1) 1:1, (b1), 2.5:1 and (c1) 4:1, and corresponding conversion plots of the reaction kinetics (a1, b1 and c1). II) Illustrative catalytic mechanism for 4-nitrophenol reduction to 4-aminophenol by Hg/Pd bimetallic alloy nanoparticles. III) Reusability and stability of Hg/Pd bimetallic alloy catalyst for reduction of 4-nitrophenol. Reproduced with permission. [66] Copyright 2020 Elsevier.
4.2. Sonochemical synthesis of metals/inorganic supports and reduction catalysis

Compared to the pure metal counterparts, heterogeneous metal catalysts doped with inorganic compounds or complexes are active under certain conditions, and has an enhanced activity and selectivity and an increased tolerance to some simple substances and compounds. [72-74] The sonochemically treating platinum catalysts (e.g., Pt/C, Pt/Al₂O₃, Pt/SiO₂ and Pt/montmorillonite) could lead to an substantially increased enantioselectivity in many processes. In the case of ethyl pyruvate hydrogenated to ethyl lactate, the hydrogenation rate with treated catalyst was increased by an order of magnitude compared with the untreated one, and the yield of targeting product reached up to 100%.[75] Such enhancement in activity after ultrasonic treatment should be owing to the formation of plentiful reactive different-ligand complexes which were favored apparently by the decreased size of catalytic nanoparticles and the changes in their morphology. Analogous conclusion was reached for the sonochemical treatment of catalytic Pt/Al₂O₃-quinidine system in acetic acid.[76] In Venezia’s study,[77] an Au-Pd/SiO₂/Al₂O₃ catalyst showed a high turnover frequency for the hydrogenation of toluene in the presence of dibenzothiophene. The tantalizing conclusion supported the concept that the metallic compound-based nanocomposites might have much more different catalytic characteristics than their monometallic parent nanoparticles. And the combinatorial screening of catalytically active materials made the metallic compound-based nanocomposites applied in a very broad research area ranging from the splitting catalyst for water to the catalyst for bulk and fine chemical production.

Abbas et al. employed a surfactant-free sonochemical approach to synthesize morphology-controlled Fe₂O₃/ZrO₂ nanocubes with various Fe/Zr molar ratios,[78] and then decorated highly dispersed Au nanoparticles on the Fe₂O₃/ZrO₂ surface by another ultrasound treatment. The as-synthesized Fe₂O₃/ZrO₂ nanocomposites were capable of becoming catalysts for Fischer-Tropsch synthesis, where the liquid fuel and organic chemicals were produced from CO and H₂ syngas. The catalytic results demonstrated that the Fe/Zr molar ratio played an important role on the catalytic activity, and an increased amount of Fe made for the improved catalytic performance, while the deactivation of catalyst might occur mostly ascribed to a decrease in Fe active sites. Interestingly, Au dopant brought a significant enhancement in the catalytic activity of Fe₂O₃/ZrO₂ nanocubes. When 2.5 wt% Au nanoparticles were coated on the catalyst as a promoter, the conversion ratio of CO was raised significantly with a product selectivity of liquid hydrocarbons instead of CH₄, and the selectivity ratio of C₅+ reached a maximum value of 79.5% at 270 °C (Figure S2). It was mostly ascribed to the improved dispersion and reducibility, the sharp increase of pore size in catalyst, and the blocked hydrogenation process on Fe active site surface. However, the Au concentration in the catalyst increased to 5 wt % would cause the catalyst deactivated owing to the aggregation and poisoning of particles. Prakash et al. sonochemically synthesized porous MnCO₃O₄ nanospheres coupled with graphene sheets aiming to serve as a hybrid cathode material for nonaqueous Li-O₂ batteries.[79] In comparison to the Pt/C catalysts, the MnCO₃O₄/graphene composites displayed excellent cyclability, high rate capability and low overpotential, which was attributed to the mechanism that the porous channels of MnCO₃O₄ nanospheres and the high electronic conductivity of graphene sheets responded for the higher kinetics of lithium peroxide formation and decomposition or the enhanced oxygen reduction and oxygen evolution.

In order to carry out CO₂ hydrogenation to methanol and find out a few appreciable effects of Cu/Zn ratio on the turnover frequency and selectivity towards methanol, Dassireddy et al. prepared Cu/ZnO/Al₂O₃ (CZA) catalysts by three different synthesis methods including co-precipitation method (CP), ultrasound-assisted method (US), and sol–gel combustion (SC)/solid-state (SS) method.[80] After investigating the preparation methodology influencing on the copper particle size, the metal interactions, the exposed surface area of copper phases, the ratio of Cu⁰/Cu⁺, and hydrogenation reactions, they got many conclusions, e.g., using different metallic precursors in the preparation reduced the Cu/Zn interaction and improved the dispersion and surface area of Cu⁺ particles on the catalyst surface; The presence of Cu⁺ species in a high concentration level caused a good methanol selectivity under the operating conditions rather than an extremely high selectivity towards CO in the conventional industry; Among all the preparation techniques (Figure S3), the ultrasonic synthesis route provided both the increased basic active sites of CuO-ZrO₂ catalyst and the significant selectivity towards methanol by improving the dispersion of copper particles without changing the intrinsic activity. For purpose of selectively catalyzing the reduction of NO with ammonia, Xu et al. synthesized a V- Ce-Ni/TiO₂ catalyst by an ultrasound-assisted impregnation method,[81] and further prepared V- Ce-Ni/TiO₂-NP and V- Ce-Ni/TiO₂-HP separately by N₂ and H₂ non-thermal plasma-treatment. The characterization results indicated that the treated catalysts had higher specific surface area, smaller particle size, and more uniform distribution of active sites on the surface than the V-Ce-Ni/TiO₂. When the catalysts were used in the reaction of NO with ammonia, the NO conversion would be above 90% for the V-Ce-Ni/TiO₂-NP catalyst at the temperature ranging from 195 °C to 414 °C, wherein 100% conversion was maintained at 230 ~ 350 °C. This operating temperature window after the non-thermal plasma-treatment was widened obviously compared with V-Ce-Ni/TiO₂ though the catalysts temperature range of V-Ce-Ni/TiO₂-NP was provided in the study.

In recent years, the magnetically heterogeneous nanomaterials with matrix structures have generally developed as the recyclable catalysts, which could be very thoughtful to assist an effective separation and recovery by an external magnetic field, especially in a liquid-phase reaction. Karamou et al. prepared the CoFe₂O₄/Pd(0) magnetically recyclable catalyst by a sonochemical method,[82] where the reduction of Pd(II) was accomplished with poly(ethylene glycol) prior to the synthesis of CoFe₂O₄. Then the CoFe₂O₄-Pd(0) was used to catalyze the hydrogenation of 4-nitroaniline with NaBH₄. Through the related UV–Vis spectra, the initial solution containing 4-nitroaniline and NaBH₄ showed a dominated band, which originated from –NO₂ group. In the absence of catalyst, such band intensity decreased very slowly, suggesting that the hydrogenation of 4-nitroaniline by NaBH₄ was quite weak. After the addition of CoFe₂O₄-Pd(0), the hydrogenation of 4-nitroaniline was greatly accelerated. From the successive absorption spectra in the presence of CoFe₂O₄-Pd(0), the 4-nitroaniline-catalyzed hydrogenation reached the completion very fast, and a new band appeared during the reduction, proving the formation of 4-phenylenediamine. Comparatively, CoFe₂O₄-Pd(0) had a higher catalytic activity than Pd catalyst by accelerating the electron transfer from NaBH₄ to Pd particles in the CoFe₂O₄-Pd(0) and finally to the 4-nitroaniline. The catalytic activity of CoFe₂O₄-Pd(0) catalyst was also proved by the hydrogenation of 1,3-dinitrobenzene into benzenediamine. Besides, the reusability of CoFe₂O₄-Pd(0) was examined in the study. After carrying out 10 repeated runs in the hydrogenation reaction of 4-nitroaniline, the decrease in the catalyst activity was only 4%, which suggested that there was no significant loss of catalytic activity after the multiple uses or the recycling.

Snoussi et al. have taken advantage of the versatile sonochemistry-assisted pathway to successfully sonohybridize a core/double-layered shell nanocomposite denoted by Fe₂O₄@NH₂-mesoporous silica/polypyrrole/Pd (Fig. 4),[83] where the synthesis was designed in a three-step process with the synthesis of magnetic core, the coating of mesoporous silica, and the sonochemical deposition of Pd(0)-doped polypyrrole (PPy/Pd). Subsequently, the catalytic performances of the nanocomposite were investigated by assessing the p-nitrophenol (p-NP) reduction and the methyl orange (MO) degradation in aqueous media. As a model reaction to investigate the nanocatalyst effectiveness, the
mechanism of p-NP reduction referred to three main steps including the reduction of nitro group to nitroso group, the reduction of nitroso group to hydroxylamine, and the subsequent reduction of hydroxylamine to aniline derivative. The $\text{H}_2$ produced by the reaction between sodium borohydride ($\text{NaBH}_4$) and water would form palladium–hydrogen bonds with Pd atoms in the catalyst, which practically relied on the relation between the antibonding orbital of $\text{H}_2$ and the unfilled d-band of Pd. It was the palladium–hydrogen bonds to complete the different steps of palladium catalyzed reduction. In the reaction, the initial fair greenish color of p-NP solution gradually turned to be colorless accompanied with a decrease of the band intensity of p-NP at 400 nm and an increase of the band intensity at 297 nm owing to the reduced species 4-aminophenol, and more than 94% of the p-NP was reduced within 180 s. For the MO degradation catalyzed by Fe$_3$O$_4$@NH$_2$-mesoporous silica@PPy/Pd nanocomposite,[83] the orange color of dye would turn to be transparent along with the gradual promotion of the reaction, and 99% of the initial concentration was almost entirely degraded within 600 s (Fig. 4). As another persuasive evidence of catalyzed degradation, the UV–Vis band at 463 nm associated with MO decreased rapidly while the band at 247 nm attributed to the degraded form sulfonic acid increased accordingly. With reference to the degradation mechanism of MO, there should be two main steps (Fig. 4): Firstly, the MO molecule was adsorbed onto the catalyst surface, and an intermediate phase allowed the exchange of electron transfer to be combined with the two $\text{H}$ radicals; Then the catalyst united the former mid-body and integrated another two $\text{H}$ radicals again, finally forming the two different amines. Researchers also have carried out the p-NP reduction and MO degradation in the same system, and proved that the two reaction processes could occur simultaneously under the catalysis of Fe$_3$O$_4$@NH$_2$-mesoporous silica@PPy/Pd nanocomposite. Furthermore, neither the yield of p-NP reduction nor the yield of MO degradation was affected by the coexistence.

Maleki et al. presented a novel ultrasound-assisted strategy for the preparation of dithiothreitol-functionalized SiO$_2$-coating Fe$_3$O$_4$ nanocomposites containing the dopant palladium and calcium carbonate (i.e., Fe$_3$O$_4$/Pd/CaCO$_3$-DTT nanoparticles), aiming to design a suitable heterogeneous tool for the precise reduction of S-S bonds,[84] e.g., the protein cleavage and the purification of reduced antibody (Figure S4). To ensure the high catalytic performance of such nano-organic catalyst, the control reactions were carried out by using diphenyl disulfide, following by an optimum condition of 0.01 g agent amounts and 10 min ultrasound (50 KHz and 200 W). And at the optimal conditions, the different disulfide derivatives such as bis(4-chlorophenyl) disulfide, and bis(4-methylphenyl) disulfide, arrived at a high reaction yield (almost 93%). In a real antibody reduction, the designed catalyst still worked efficiently by a synergistic catalytic effect with ultrasound, and its catalytic behavior was freshly recycling.

5. Oxidation

5.1. Oxidation based on ultrasound

Upon the implosion of cavitation bubbles, the produced radicals will be propelled into the bulk solution reacting with the solutes, however, the reaction selectivity is quite difficult to control so that ultrasound is mainly application for the total free oxidation of aqueous pollutants, coined degradation. In order to implement the ultrasound technologies to synthesize a variety of chemicals, it is elusive but highly desirable to control the selectivity of oxidative reactions. Jérôme et al. once studied the catalyst-free oxidation of glucose induced by the high-frequency ultrasound,[85] and found that the reaction selectivity was significantly impacted by the nature of gaseous atmosphere. Under the O$_2$ gas, the glucuronic acid could be formed in a significant amount while the gluconic acid was formed as a major product under the Ar gas.

The removal of sulfur from transportation fuel and petrochemicals has been gaining more attention due to the adverse effects of burning sulfur on human health and the environment, so many ultrasound-assisted oxidative desulfurization processes have been designed to give a promising strategy to reduce the sulfur content.[86,87] Shahhosseini et al. developed a computational fluid dynamic model to investigate the hydrodynamics of sulfur removal reactions in a sonoreactor.[88] Both physical effects and chemical effects induced by ultrasound contributed to the enhancement of sulfur removal rates, wherein the physical effects played a predominant role, and the turbulent kinetic energy from ultrasound also had an important influence in the process. Later on, they exploited a multi-probe continuous flow system with different injection strategies to investigate the ultrasound-assisted oxidative desulfurization. The results indicated that the sulfur removal was improved by increasing the residence time for all nozzle types or increasing the nozzle diameter under the fixed flow rate, and that the injection of aqueous...
phase in the active zone below the horn tip could obtain a greater conversion. Thereinto, there was over 97% sulfur removal achieved when setting the double-nozzle injection with a 1.5 mm nozzle diameter, a 15 min residence time, a 277.2 W electrical power as well as the volumetric flow rates of water/oil phases with a 48.89/244.44 mL/min.

5.2. Oxidation based on ultrasound/catalyst

The introduction of a solid catalyst is a nice strategy to control the selectivity of radical reactions induced by the ultrasound irradiation. In contrast to the homogeneous solution, the formation of cavitation bubbles in a heterogeneous solution occurs preferentially on the particle surface due to the heterogeneous nucleation, and at the same time, the implosion of cavitation bubbles easily generates some high-speed jets of liquid toward the solid surface. Such physical behavior could greatly increase the selective transfer of in situ produced radicals to the surface of solid catalyst, realizing a better control of reaction selectivity. Moreover, the dispersion of catalyst/reactant and the mass transfer will be enhanced by the physical effects such as the turbulent flow and shock waves, resulting in the improvement of reaction rates. It is worth noting that the radicals should interact faster with the catalyst surface than with the solutes in order to optimize the reaction selectivity. Recently in another Jérôme’s report, a CuO catalyst has been used for the glucose oxidation at the 550 kHz ultrasound irradiation under the Ar gas, where the synergistic effects between non-noble metal oxide catalyst and high-frequency ultrasound could independently oxidize glucose to gluconic acid. Within the oxidation process, H· radicals from the sonolysis of water were trapped by the surface lattice oxygen of CuO catalyst, leaving the -OH radicals highly covering on the catalyst surface and making the ring-opening of glucose energetically, which favored the selective oxidation of glucose to glucuronic acid (Fig. 5). Hence, the catalyst combining with ultrasound irradiation caused a dramatic change of the reaction selectivity, making glucuronic acid to be the major product. According to the suggestion from the researchers, optimizing the catalyst particle size could minimize the damage to the catalyst, aiming for the reuse.

With the help of solid catalysts, many organics can be subjected to the oxidation by the sonolysis. Maleki et al. have designed and prepared a new multiwall carbon nanotube-based TiO\(_2\) nanocatalyst (MWCNTs/TiO\(_2\)) via the sonochemical approach,[90] and by using the hybrid nanocatalyst, they completed the selective oxidation of alcohols to aldehydes, ketones and epoxidation in excellent conversions at room temperature under the sonochemical-assisted conditions. Costa et al. carried out the sonocatalytic degradation of EDTA at near-room temperature under Ar/O\(_2\) saturating gas in the presence of Co\(_3\)O\(_4\)/TiO\(_2\) and Pt/TiO\(_2\) nanocatalysts (Figure S5-I),[91] and the Co\(_3\)O\(_4\)/TiO\(_2\) catalyst was found to have a significantly higher sonocatalytic activity than traditional Pt/TiO\(_2\) catalyst, and could oxidize about 90% of EDTA to several acidic intermediates such as iminodiacetic acid, formic acid, oxalic acid, glycolic acid and acetic acid. Compared to noble metal Pt, the interaction of Co\(_3\)O\(_4\) with EDTA was stronger, where the EDTA oxidation involved the radical-driven mechanism as the oxidizing

Fig. 5. I) synergistic effect of high-frequency ultrasound with CuO catalyst resulting in a selectivity switch in glucose oxidation. II) Energy profile for glucose ring-opening process under different conditions. Label of structure: Int1, adsorbed glucose; Int2, product of first step of -OH activation; Int3, adsorbed open-chain glucose; TS1 and TS2, transition states of steps 1 and 2, respectively. Bond lengths in Å for the transition states were indicated. Color code: Large peach and red balls represented Cu and O atoms of CuO substrate, respectively, and small white, gray, and red balls represented H, C, and O atoms of adsorbates, respectively. III) Plot of the selectivity as a function of the conversion of glucose (a) CuO and (b) CuO\(_{HFUS}\) (10 wt% copper oxide, 80 °C, 550 kHz, glucose concentration 20 g L\(^{-1}\), \(P_{\text{acoust}} = 0.36\) W mL\(^{-1}\)). IV) Recycling of CuO\(_{HFUS}\) (80 °C, 550 kHz, 10 wt% CuO, glucose concentration 20 g L\(^{-1}\), \(P_{\text{acoust}} = 0.36\) W mL\(^{-1}\)). Reproduced with permission.[89] Copyright 2019 American Chemical Society. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
radicals were generated by acoustic cavitation and Co(II)–Co(III) redox process. With the aid of Schiff base ligand, Naeimi et al. synthesized a nanocomplex of MoO$_3$ nanoparticles and copper under ultrasound irradiation,[92] and then the MoO$_3$/copper nanocomplex was used to catalyze the atom-efficient and selective oxidation of alcohols in the presence of hydrogen peroxide and ultrasound irradiation (Figure S5–II). In the case, a wide range of primary and secondary alcohols were transformed into the related aldehyde and ketone products with high conversion and excellent selectivity under solvent-free conditions, and the MoO$_3$/copper catalyst could be reused at least six times without any significant loss of initial catalytic activity.

The oxidative desulfurization of diesel fuel could not convert more than 70% of dibenzothiophene to polymer because the polymer deposition on the surface of the particles makes oxygen lack, so Shahhosseini et al. used an ultrasound-assisted oxidative process to enhance the fuel desulfurization in the presence of polyoxometalate such as H$_2$PV$_3$Mo$_3$O$_{12}$Si$_2$O$_5$, H$_2$PV$_2$W$_{10}$O$_{40}$/SiO$_2$.[93] Compared with the 70% desulfurization rate in a 6 h oxidative process, the ultrasound-assisted oxidation could reach a 90% desulfurization rate in 3.5 h. In the Han’s study,[94] the photocatalytic CdO took place of the polyoxometalate to apply in the ultrasound-assisted oxidative technology of organic sulfur removal from the diesel as well, and under the optimal condition, this oxidative approach was efficient for sulfur removal and reached a 99.47% desulfurization degree. Alternatively, iron materials have been also used in the ultrasound-induced catalytic oxidation, for example, the oxidation of 1-phenylethanol to acetophenone was carried out in the presence of hydrogen peroxide and ultrasound irradiation (Figure S5–II). The Pt-Au/C catalyst exhibited extraordinary electrocatalytic performance attributed to the synergistic effect of Pt and Au, and even its catalytic activity was over 150 times higher than Pt/C catalyst when the atomic ratio of Pt and Au in the sample was set as 32:68. In the density functional theory calculations, the neighboring Au on Pt effectively decreased the reaction energy barriers in Pt-Au structure significantly facilitating the cleavage of O–H bond in the direct pathways not in the indirect pathways (Fig. 6), which indicated that the oxidation reaction occurred more easily in the direct pathways. Kim et al. deposited palladium oxide (PdO) on the surface of silica nanoparticles at room temperature and atmospheric pressure by using a sonochemical process.[98] Such PdO-doped silica

5.3. Oxidation based on ultrasound-produced catalysts

5.3.1. Oxidation of organics

Apart from the catalysis from the combination of sonolysis and catalysts (Table S3), the solid materials produced by ultrasound irradiation are very outstanding to catalyze numerous oxidation reactions (Table S4). Camacho et al. used the sol–gel method and ultrasound method to synthesize the Pt/zeolite-carbon composites with three different zeolites as a support of Pt nanoparticles,[96] and investigated the effects of Pt/zeolite-carbon on the electrocatalytic activity for the methanol oxidation reaction in acid media. Compared to Pt/merlinoite-carbon, Pt/analcime-carbon and Pt/carbon, the Pt/faujasite-carbon exhibited higher electrochemical activity for methanol oxidation since the faujasite zeolite had higher specific surface area and Pt/faujasite-carbon enhanced the formation of smaller Pt clusters with a homogeneous dispersion. Wang et al. designed and synthesized Pt-Au/C catalyst for the electrooxidation of formic acid, where an ultrasound-assisted method enabled Pt and Au to be loaded on the carbon black in uniform and dense without any surfactant.[97] The Pt-Au/C catalyst exhibited extraordinary electrocatalytic performance attributed to the synergistic effect of Pt and Au, and even its catalytic activity was over 150 times higher than Pt/C catalyst when the atomic ratio of Pt and Au in the sample was set as 32:68. In the density functional theory calculations, the neighboring Au on Pt effectively decreased the reaction energy barriers in Pt-Au structure significantly facilitating the cleavage of O–H bond in the direct pathways not in the indirect pathways (Fig. 6), which indicated that the oxidation reaction occurred more easily in the direct pathways. Kim et al. deposited palladium oxide (PdO) on the surface of silica nanoparticles at room temperature and atmospheric pressure by using a sonochemical process.[98] Such PdO-doped silica

Fig. 6. I) Electrochemical measurements of Pt/C, Pt-Au/C and Au/C catalysts in an aqueous solution of 1 M formic acid and 0.5 M H$_2$SO$_4$ at 25 ± 1 °C: (a, b) Anodic polarization curves in formic acid electrooxidation normalized by Pt and total metal weight respectively. The insets are enlarged views of the curves of Pt/C and Au/C; (c) Comparison of oxidation currents recorded at peak positions of the direct pathway in (a) and (b); (d) Chronoamperometry curves with a logarithmic Y-axis measured at 0.05 V. In the below were Atomic ratios and metal contents of Pt/Au/C structures. II) The DFT calculation schematic of formic acid (HCOOH) oxidation: via (a) the direct pathway and (b) the indirect pathway in the middle of Pt and Au slabs; via (c) the direct pathway and (d) the indirect pathway on Pt slab. The energy barriers are provided in each step. Reproduced with permission.[97] Copyright 2018 Elsevier.
nanocomposite showed higher catalytic activity and selectivity than unsupported PdO nanoparticle when applied as a nanocatalyst for selective alcohol oxidation reaction in the presence of molecular oxygen. With the aid of PdO-doped silica nanocomposite (40 mg, Pd content = 3.3 mol% of substrate) under an oxygen atmosphere at 90 °C, a nearly complete conversion of 2-naphthymethanol to 2-naphthaldehyde was obtained over the period of 10 h.

To develop an efficient V-based catalyst for the CO2-oxidative dehydrogenation of ethane to ethylene, Haghighi et al. modified the MCM-41 materials with various metal oxides (MgO, Al2O3, ZrO2) prior to the VOx dispersed over the supports under ultrasound irradiation.[99] The obtained catalysts displayed an improved catalytic performance owing to the alteration of structural properties such as crystallinity, VO2 dispersion, size distribution and acid-base properties, and they effectively gave 43% ethylene yield in the presence of CO2 at 700 °C when containing MgO and ZrO2. Considering for the important practical application of detecting formaldehyde in indoor environment, Niu et al. sonochemically prepared a novel composite based on platinum and tungsten oxide for the electro-oxidation of formaldehyde, where the local atomic structure of commercial WO3 was regulated into the highly active sub-stoichiometric WO2.98 through a facile thermal treatment.[100] The Pt-WO2.98 exhibited a better electro-chemical activity than both Pt-WO3 and pure Pt, and reducing the Pt content in the catalyst improved the catalytic activity. When used in an equipped formaldehyde sensor, Pt-WO2.98 displayed high sensitivity, and good reproducibility and stability. In the Nair’s study,[101] the commercial ZnO nanoparticles were deposited in the inner wall of fluorinated ethylene propylene (FEP) microtube with an ultrasound-assisted process, which was mainly attributed to the physical changes on the FEP surface occurring during the ultrasound irradiation. The as-modified photo-catalytic microtube was used for the oxidation of benzyl alcohol to benzaldehyde, and compared to the batch photocatalytic reactor, the photocatalytic microtube displayed a better specific conversion rate and selectivity for the established oxidation, even though there was a lower change in the catalytic selectivity after multiple reaction runs.

Ultrasound irradiation has been closely utilized to create two-dimensional materials,[102-106] and the specific structures and physicochemical properties of products (e.g., single- or multi-layered nanostructures, unique electronic properties and thickness dependent band gaps) endow them with unique functions, so several hottest research topics nowadays are being explored in many applications such as semiconductor materials, delivery materials, and catalyt material catalysts. Chen et al. prepared ytterbium-doped molybdenum selenide (YbMoSe2) in the form of nanosheets by using a simple ultrasonic method, and further developed it as an electrocatalyst for the effective sensing of diphenylamine (DPA).[103] Due to the substitution/doping of Yb, the band gap of MoSe2 was decreased when the active sites were increased by the lattice distortion, facilitating an excellent electronic conductivity and electrochemical activity, so YbMoSe2 showed a high level of electrochemical activity, excellent sensitivity and superior selectivity. In the process towards the DPA detection (Figure S6), the unstable free radical DPA - was produced through one electron transfer at first (oxidation peak 1), and it underwent the oxidation reaction further resulting in the formation of diphenyl benzidine dimer (reduction peak 2). The formed diphenyl benzidine dimer was also easily oxidized to form a new radical cation (reduction peak 4 and oxidation peak 5), and finally aroused the formation of poly-DPA (oxidation peak 3 and reduction peak 6).

Generally, graphene materials can function as an oxidant in a catalysis reaction, and upon ultrasonic treatment, the initially stacked graphene layers will be liberated to single- or few-layer sheets, where each layer is rich in oxygen functional groups. Even the introduction of ultrasound irradiation in a catalysis reaction, owing to a turbulent mixing happening with shockwaves, can increase the collision between the reactants and the graphene sheets, in turn aiding in a faster reaction rate. On the side, ultrasound can also supply the requisite energy to induce a thermodynamically feasible reaction because the local high pressure and temperature generated by the cavitation is able to overcome energy barrier.[107] Mahendiran et al. obtained an efficient electrocatalyst for ethanol oxidation in alkaline medium via the decoration of NiO nanoparticles and Pd nanoparticles on the MWCNTs followed by the ultrasound-assisted deposition of MWCNTs composite on the reduced graphene oxide (rGO).[108] Attributed to the synergistic effect of active sites between Pd and NiO, the as-synthesized Pd-NiO/ MWCNTs/rGO showed a long-term electrochemical stability as well as a higher catalytic activity for ethanol oxidation in alkaline medium than either Pd/MWCNTs/rGO or Pd/C commercial catalyst.

In a Mirza-Aghayan’s study,[109] a simple and mild sonochemical procedure was described to realize the direct oxidative esterification of aromatic aldehydes and benzyl alcohols to the corresponding esters, where GO and oxone served as a highly efficient catalytic system in an alcoholic solvent under ultrasound irradiation. The direct oxidative esterification took place in good to high yields with a short reaction time, and in the oxidation process, GO most likely participated in the generation of sulfate and hydroxyl radicals or acted as an oxidant itself though the mechanism was not very clear. In another study,[110] researchers used GO as an oxidizing agent for the generation of aldehydes or ketones via the oxidation of alcohols under ultrasound irradiation, where numerous heterocyclic and aliphatic alcohols were tested by varying the solvents and/or reaction conditions. Similarly, the high yields from ultrasound-aided oxidation were deduced due to an enhanced mass transfer of reactants and products to and from the catalytic surface. A shorter reaction time and even a higher yield would be able to achieve by using potassium hydrogen mono persulfate, iron (II) sulfate and GO for oxidizing alcohols to produce carboxylic acids and ketones.[111] In the case, only 30 min ultrasound irradiation was required at room temperature but could give a 80%-98% yield of products from the oxidation of various alcohols with exception to tertiary alcohols. It was the sonochemical generation of sulfate, hydroxyl radicals and iron (III) ions that deduced for the accelerated oxidation process. Besides, GO has been also applied in an ultrasonic reaction for catalyzing the ring-opening of epoxides to alkoy alcohols. Numerous alcohols could react with styrene oxide to create the corresponding alcohols with a 94% yield within a half-hour ultrasoundation,[112] and as well, the reaction could be performed with good regioselectivity at room temperature, and an increasing catalyst in amount led to an increased yield.

5.3.2. Oxidation of inorganics

Ultrasound-assisted oxidation systems are also used to oxidize the inorganics, especially in the presence of catalyst. Wang et al. prepared Pd-Cu/palygorskite catalysts by a wet impregnation method, where the palygorskite was modified by ultrasonic treatment to be a catalyst support.[113] Under the feed gas with 1.0 vol% CO and 3.3 vol% H2O at room temperature, the Pd-Cu/palygorskite exhibited much higher catalytic activity and stability toward CO oxidation than the catalyst supported on the palygorskite without ultrasonic treatment. The elimination of quartz impurities, the existence of more copper species, the enhanced reducibility of palygorskite, and the proper decrease of catalyst hydrophilicity after the ultrasonic treatment might contribute to the excellent catalytic performance. In another study, Shi et al. used the multi-wall carbon nanotubes confined CuO-CeO2 binary oxide (Cu2Ce1-xO/CNTs) as a catalyst to carry out CO preferential oxidation.[114] After the catalyst was prepared by an ultrasound-aided impregnation, the researchers systematically investigated the effect of GO on the structure and catalytic performance. When the Cu2Ce molar ratio was set as Ce0.6Cu0.4 (x = 0.4), the Ce0.6Cu0.4O/CNTs showed excellent catalytic activity, wide temperature span of full CO conversion (120–160 °C), and high selectivity especially above 110 °C (until 140 °C). There were some excuses to account for this superior catalytic behavior. In the Ce0.6Cu0.4/CNTs, the binary oxide particles were uniformly dispersed into the channels of CNTs, and the interaction between CuO and CNT inner surface markedly enhanced the reducibility of active
copper species, and more lattice oxygen and oxygen vacancies could be produced on the catalyst surface. To remove and simultaneously absorb the SO\(_2\) and NO from the flue gas, Liu and coworkers proposed a novel ultrasound/Fe\(^{2+}\)/persulfate system to oxidize SO\(_2\) and NO\(_x\), and investigated the influencing factors, active species, products and oxidation mechanism. SO\(_2\) removal was complete in the most catalysis systems except for the absorption in water, while the efficiency of NO removal was condition-controlled because the \(\cdot\text{OH}\) and SO\(_4^{2-}\) \(\cdot\text{OH}\) and SO\(_4^{2-}\) played a key part in NO oxidation (Figure S7). The pH, temperature and Fe\(^{2+}\) concentration had the double effects on NO removal at a low persulfate concentration, but increasing persulfate and Fe\(^{2+}\) concentrations at a high persulfate concentration could improve the efficiency of NO removal. Ultrasound facilitated the NO removal due to the enhancement of mass transfer and chemical reaction, so the efficiency of NO removal increased with the raising of ultrasonic power density, and the facilita-
cation under 28 kHz was more obvious than under 40 kHz. The heating also had a positive effect on the NO oxidation by activating persulfate to produce free radicals, so the ultrasound/Fe\(^{2+}\)/persulfate system at a higher temperature could achieve an increased removal efficiency.

Kwon et al. prepared the composite WC\(_{1-x}\)/Pt/MWNT by the sonochemical synthesis of WC\(_{1-x}\) on Pt-loaded MWNT. Compared with the composite material prepared by simply mixing Pt and WC\(_{1-x}\) nanoparticles, the WC\(_{1-x}\)/Pt/MWNT had an even larger electrochemically active surface area because Pt nanoparticles and WC\(_{1-x}\) nanoparticles were in good contact with each other under ultrasound irradiation. With respect to the electrochemical hydrogen oxidation reaction, the Pt-specific mass activity was enhanced in the presence of WC\(_{1-x}\) nanoparticles, and the H\(^+\)-spillover effect from Pt to WC\(_{1-x}\) was also maximized by the close contact of WC\(_{1-x}\) nanoparticles with Pt nanoparticles, highlighting the synergistic effects between the two nanoparticles. The researchers also prepared amorphous Ni/Fe-alkoxide nanoparticles using a simple sonochemical route by which the Ni and Fe atoms could be controlled in the entire composition range, and the product was readily converted into the corresponding electrocatalytically active Ni/Fe mixed (oxy)hydroxide nanoparticles for oxygen evolution reaction in alkaline media. Through the measurements, the Ni/Fe mixed (oxy) hydroxide electrocatalyst showed a low overpotential and a superior durability.

6. Degradation

6.1. Homogeneous sono-degradation

Most degradation processes are on the base of hydrolysis, reduction or oxidation reactions, and ultrasound irradiation is effective for the degradation of a variety of organics including refractory biomacromolecules and problematic pollutants. Jerome et al. carried out the selective depolymerization of cellulose to glucose in water by using ultrasound irradiation at a high frequency of 525 kHz, which was depend upon the concept that H\(^\cdot\) radicals rather than \(\cdot\text{OH}\) radicals formed by cavitation bubbles would be more likely to induce the cleavage of glycosidic bonds (Fig. 7). Although the current technology required a high-frequency ultrasound, it did not need any catalyst and external heating source, and the depolymerization of cellulose was complete by a selective fashion close to 100% because the radicals transferring on the cellulose surfaces avoided the side degradation of glucose released into the bulk solution. In the context of rising plastic pollution and inefficient plastic recycling technologies, Pandit et al.

Fig. 7. I) Depolymerisation of cellulose to glucose induced by HFUS. II) Maximum yield of glucose as a function of the gaseous atmosphere (60 °C, 525 kHz). III) Influence of H\(^\cdot\) and \(\cdot\text{OH}\) radical scavengers in the HFUS-induced depolymerisation of cellulose. Reproduced with permission. Copyright 2020 the Royal Society of Chemistry.
have used the ultrasound-intensified methanolation reaction to achieve the depolymerization of polycarbonate at room temperature rather than at extreme temperature and pressure conditions.[119] After investigating the effects of various parameters such as ultrasonic input power, solvent composition, temperature, catalyst concentration and the pre-swelling by soaking the polymer, both the significant enhancement in the methanolation rate and the reduction in the reaction time were shown when depolymerizing polycarbonate at 30 °C in a solvent mixture containing NaOH, tetrahydrofuran and methanol (tetrahydrofuran/methanol ratio equal to 3, w/w). Okitsu et al. once studied the sonolysis of C3-C6 alcohols in Au(III) aqueous alcohol solution with a 200 kHz ultrasound irradiation system,[120] focusing on the effects of alcohol type, solution temperature, and dissolved gas on the reduction rate of Au(III). After investigating the gaseous compounds (CO, CO₂, CH₄, C₂H₂, C₂H₆) formed from the 1-hexanol degradation, the changes in the concentrations suggested that CO and pyrolysis radicals acted as reductants in the sonolysis.

### 6.2. Heterogeneous sono-degradation

The combined use of ultrasound irradiation and heterogeneous catalysts will further improve the degree of sonocatalytic degradation because the heterogeneous catalysts can provide additional nuclei to form more radicals. The possibility of combining ultrasound irradiation with heterogeneous catalysis has been studied by Taghizadeh et al., where the complete degradation of chitosan was achieved in the presence of TiO₂ at 24 kHz.[121] Another relevant study about the degradation of cellulose reported by them revealed that the efficiency of catalyst-mediated sonocatalytic degradation was remarkably higher in comparison to the sonocatalytic degradation without catalyst.[122] When the degradation behavior of 2-hydroxyethyl cellulose was carried out in the presence of heterogeneous catalysts (e.g., TiO₂, ZnO, Fe₃O₄ and montmorillonite clay) under ultrasound irradiation (24 kHz), the catalysts could provide a better ability for radical generation through electron transfer between the metal ions and the water molecules during the sonication process. The synergistic effect of Pr-doped ZnO catalyst combined with sonochemistry has been reported by Khataee et al.,[123] where Pr-doped ZnO induced up to 89% degradation of AR17 dye under ultrasound irradiation, and the addition of peroxydisulfate and hydrogen peroxide as an enhancer could improve the degradation efficiency further.

The discovery of piezoelectric materials opens up a new route to organic degradation in which the deformed piezocatalysts can mediate the transformation between mechanical and electric energies. Xiong et al. used the hydrothermally synthesized tetragonal BaTiO₃ nano/micro-sized particles to degrade a chlorinated pollutant 4-chlorophenol (4-CP) with strong organoleptic effects, where the low-frequency ultrasound irradiation (40 kHz, 110 W) was selected as a vibration energy

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![Fig. 8.](image-url)

**I)** Degradation efficiency of 4-CP with respect to reaction time in different processes (inset: color change in the suspension of 4-CP and t-BaTiO₃ before and after piezo-catalysis). **II)** Piezo-catalysis of 4-CP in the presence of different scavengers (EDTA → hole, NaN₃ → O₂, p-BQ → O₂⁻, TBA → -OH): (a) degradation efficiency of 4-CP, and (b) dichlorination efficiency of 4-CP. **III)** Main pathways for degradation of 4-CP with the t-BaTiO₃-mediated piezo-catalysis process. Reproduced with permission.[124] Copyright 2017 American Chemical Society.
to cause the deformation of piezocatalyst. The results showed that the piezoelectric effect could effectively dechlorinate and degrade 4-chlorophenol or directly degrade to the final products including CO₂, H₂O and Cl⁻ (Fig. 8). In the piezo-catalytic progress, various active species such as h⁺, e⁻, H⁺, OH⁻, O₂ and O₂⁻ were generated from the electron reduction and hole oxidation of O₂/H₂O under ultrasound irradiation, wherein the dechlorination and degradation were mainly attributed to -OH radicals. Bao et al. successfully synthesized Sr-substituted BaTiO₃ (BST) nanostructures with two different morphologies including nanowires and nanoparticles,[125] and thoroughly monitored their piezo-catalytic behavior to degrade the dye molecule methyl orange (MO) in aqueous solution under ultrasonic vibration (80 W, 40 kHz). Compared with pure BaTiO₃ (BT) nanowires, the Sr-substituted nanowires exhibited a superior piezo-catalytic property as a consequence of a lowered phase transition temperature, and the elongated nanowires had a higher piezo-catalytic activity than the nanoparticles due to a higher piezoelectric potential difference between the two polar ends (Figure S8). Similarly, the formation of active species (i.e. hydroxyl radicals and superoxide radicals), played an important role in the decomposition of dye molecules.

The iron catalysts are often used in the combination with ultrasound irradiation because the catalysts can serve as an alternative source of Fe (II) or Fe (III) to produce -OH radicals by Fenton reaction, Fenton-like reaction or others. Zhang et al. have ever synthesized a nanoscale rectorite-supported zero-valent iron (nZVI/R) by the reduction method, where the zero-valent iron was partly oxidized into iron oxide.[126] Compared with rectorite and nZVI, the resultant nZVI/R particles could degrade more methyl orange and metronidazole in the presence of ultrasound within 20 min, and moreover, the degradation ratios under ultrasound were higher than that in the absence of ultrasound. Zhou et al. utilized a novel ultrasound/zero-valent iron/tetraphosphate system (US/ZVI/TPP) to carry out the synergistic degradation of antibiotic norfloxacin (NOR), and the results showed that the US/ZVI/TPP system could effectively degrade NOR with a relatively low dosage of ZVI and ligand as well as in a broad pH range.[127] During the degradation of NOR, there were two radicals (-OH, -O₂) and H₂O₂ to work when the in-situ generation of H₂O₂ occurred via the series of Fe-TPP reactions under the ultrasound. The researchers proposed an integrated catalytic mechanism of US/ZVI/TPP system including the solid-liquid interfacial iron corrosion, bulk homogenous oxygen activation and Fenton reactions, wherein ultrasound would play a mechanically and chemically promotional role in the degradation. The combinative application of ultrasound irradiation with other iron-based catalysts such as Fe₃O₄ catalyst and Fe₃O₄/TiO₂-N-GO catalyst, have been reported in the degradation of organic pollutants (e.g., humic acid, metazachlor).[128,129] Diao and coworkers developed an ultrasound-enhanced sludge biochar iron catalyst/persulfate heterogeneous system for the degradation of bisphenol A in water, and nearly 98% degradation could be reached within 80 min at optimum reaction conditions. In the degradation system, a positively synergistic effect occurred between sonochemistry and catalytic chemistry, and two radicals (SO₄²⁻ and HO⁻) participated in the degradation of bisphenol A, whereas SO₄ radical might be predominant. Moreover, the coexisting Cl⁻, SO₄²⁻ and NO₃ substances had no obvious inhibition on the degradation, but HCO₃ and humic acid had. Hence, A possible degradation pathway was proposed that the radicals attacked the bisphenol A to degrade into some intermediate products with simpler structure through the hydroxylation and demethylation.

Fig. 9. I) The MoS₂ NFs consisted of a great number of nanopetals that were composed of single- and few-layers with the lattice spacing between the two layers being ≈0.64 nm; The HRTEM image of the single-layer MoS₂, where the inset showed the corresponding FFT image. II) The degradation ratio of the RB dye using the MoS₂ NFs, commercial MoS₂, and TiO₂-P25, under different degradation conditions: in the dark (a), ultrasonic wave in the dark (b), the repeatable degradation tests of the MoS₂ NFs under ultrasonic-wave assistance in the dark (c); under ultrasonic-wave assistance with the xenon-lamp illumination using the MoS₂ NFs (d). III) Band structure of MoS₂, no external force acted on the surface (a); Due to the spontaneous polarization in the single-layer MoS₂, the negative end of the polar molecules of the water were preferentially diffused to adsorb on the surface of the semiconductor with the minority free carriers (hole) under the internal electric field, and enhanced the bands bending (upward), forming a space charge region (L) (b); The bands bending downward because the H⁺ (or polar molecules of hydroxyl) accumulated on the semiconductor’s surface with the majority of free carriers (electrons) to generate H₂O₂ (c). H₂O₂ reacted with H⁺ to re-generate water molecules and hydroxyl radicals by receiving one electron under the influence of the electric field (d). The reduction and oxidation process for destroying the organic dye by the spatially spontaneous polarization and the catalyzing process (e). Reproduced with permission.[130] Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA.
MoS$_2$, a kind of transition metal chalcogenide, exhibits on the sheet-like structure, and single and few layered MoS$_2$ piezoelectric property can be used in many potential applications. Recently, Wu et al. have found the ultrahigh degradation activity of single and few layered MoS$_2$ nanoflowers (NFs),\cite{130} where 93% of RhB molecules was degraded within a 60 s ultrasound time (Fig. 9). On the contrary, very less degradation activity was observed with single and few layered MoS$_2$ NFs in the absence of ultrasound, and further, when the reaction was carried out with ultrasound and xenon-lamp illumination (150 W), only 6% enhancement was revealed in degradation. These studies brought on that the ultrasound played an important role in the degradation, where the reaction was caused by the internal polarization-induced piezoelectric field creating the charge carriers from the single and few layered MoS$_2$ NFs. Subsequently, researchers continued the development of dark piezo-catalysts by using MoS$_2$/polydimethylsiloxane nanocomposites.\cite{131} Here, 99% of RhB obliteration was achieved in the first cycle though the catalytic efficiency of MoS$_2$/polydimethylsiloxane was decreased to 67% in the fourth cycle. This efficiency decrement might be ascribed to the peeling of MoS$_2$ sheet from polydimethylsiloxane during the ultrasound irradiation. Similarly, the analog materials including MoSe$_2$ NFs and WS$_2$/polydimethylsiloxane nanocomposites as a dark photocatalyst also have been examined by the degradation of RhB and the inactivation of Escherichia coli (E. coli).\cite{132,133}

In the cases with metal-free catalyst, ultrasound-assisted catalysis facilitated some degradation reactions as well. In Boukherroub’s study,\cite{134} ultrasound was utilized to assist the catalytic degradation of organic pollutants by activating peroxymonosulfate in presence of reduced graphene oxide (rGO). In the metal-free conditions, the results revealed that the combination of peroxymonosulfate, rGO and ultrasound significantly enhanced the degradation rate, arrived the absolute degradation in a relatively short time and removed the exceeding 85% of total organic carbon in the pollutants (e.g., rhodamine B, bisphenol A and tetracycline). However, by using the rGO/ultrasound or peroxymonosulfate/ultrasound condition, the degradation of pollutants was less than 20%. They elucidated that the hydroxyl radicals were the dominant reactive species in the degradation process and the presence of trace manganese in rGO might account for the efficiency to activate peroxymonosulfate.

### 6.3. Indirect sono-degradation

Besides the sono-degradation, the indirect participation of ultrasound irradiation has also been reported in many degradation reactions, that is, more and more catalysts prepared via the sonochemical method are aiming to the degradation reactions. For example, Haghigh et al.\cite{142} have sonochemically coated the transition metal Ni on the precipitated CeO$_2$–ZrO$_2$ support to prepare the Ni/CeO$_2$–ZrO$_2$ nanocatalyst, and applied it in catalytic wet air oxidation of phenol.\cite{135} The removal of phenol was enhanced along with the higher amounts of Ni contents, whereas the excessive nanocatalyst loading could decline the catalytic reactivity in turn. Mastai et al. described a surfactant-free sonochemical method to synthesize CoFe$_2$O$_4$ nanoparticles, and proposed that such cobalt ferrite nanoparticles acted as a catalyst for the degradation of elastomer-based polymers.\cite{136} After the comprehensive study of methylene blue and polybutadiene as an elastomer-based model, the CoFe$_2$O$_4$ nanoparticles were found to be very effective for initiating the radical degradation of methyl ethyl ketone peroxide. Moreover, the detailed study revealed that the radical degradation of polybutadiene involved two parallel processes including polymer crosslinking and polymer scission, and the rate of degradation could be controlled by properly setting the reaction duration and the catalyst concentration. The recycle and reuse of CoFe$_2$O$_4$ nanoparticles without impairing the catalytic efficiency also emphasized their application in the polymer degradation.

6.3.1. Photocatalysis

In recent years, many sonochemistry-synthesized nanomaterials have been applied in the degradation as a photocatalyst.\cite{137} Colmenares et al. once deposition of TiO$_2$ nanoparticles on the inner wall of fluoropolymer microtubes by the ultrasound-based deposition method, where the ultrasound caused the physical changes of polymer surface to create some rough spots and etched surface for the stable immobilization of TiO$_2$ nanoparticles.\cite{138,139} The TiO$_2$-coated microtube showed a good photocatalytic activity under the UV light, since the degradation of phenol in the evaluation had a higher grade than the reported in the conventional batch photoreactor. Towards the removal of environmental pollutant by the photocatalytic approach, Anandan and coworkers used an ultrasonic method to prepare CuO@TiO$_2$ heterojunction nanocomposites.\cite{140} According to the degradation of methyl orange, CuO@TiO$_2$ nanocomposites showed an enhanced photocatalytic activity under the visible light, and its photocurrent was 4.5 folds greater than TiO$_2$ (Fig. 10). Clearly, when doped with CuO, TiO$_2$ still preserved the structural integrity favoring photocatalytic appliances, and meanwhile the dopant extensively increased the mobility of electron via reducing the recombination rate of electron-hole pairs on the TiO$_2$. Bianchi et al. reported the positive effect of ultrasound in both synthesizing Me-doped TiO$_2$ materials (Me = Ag, Cu, Mn) and enhancing the photocatalytic abatement of organic contaminants.\cite{141,142} Where Me-doped TiO$_2$ materials efficiently converted acetone to CO$_2$ under visible light when Ag-TiO$_2$ completely degraded ibuprofen or paracetamol in water by combining UV light and ultrasound. Hunge et al. used the sonochemistry-prepared thin Cu$_2$ZnSnS$_2$ films to carry out the degradation of phthalic acid, and 56% of the sample was removed within 240 min under the sunlight illumination.\cite{143} In the Salavati-Niasari’s study,\cite{144} pristine uniform DyVO$_4$ nanoparticles were fabricated by a sonochemical method (60 W, 18 KHz) to serve as a highly efficient photocatalyst for water treatment. Under visible light, DyVO$_4$ nanoparticles (0.05 g) could remove about 88% of erythrosine at the initial pH 4 after 180 min, and the photocatalytic performance was relatively stable and reusable after five successive cycles.

The iron-based catalysts prepared by the sonochemical approaches are an alternative of photocatalyst in many degradation reactions. Salavati-Niasari et al. synthesized the pure Zn$_{0.35}$Fe$_{0.65}$O$_4$ nanosheets as a ferrite catalyst material by using a simple sonication, and then purified the murky water containing different pollutants.\cite{145} Under the visible light, Zn$_{0.35}$Fe$_{0.65}$O$_4$ nanosheets could degrade 60.8% of Acid Violet 7, 77.9% of Acid Blue 92, 55.2% of Acid Red 14, and 44.0% of Methyl Orange during 180 min irradiation, and under the UV light, 94.5% of Acid Violet 7, 84.2% of Phenol Red, and 43.0% of Erythrosine would be degraded during 120 min irradiation. Hernández-Uresti et al.\cite{146} synthesized Fe-impregnated BiVO$_4$ photocatalysts through the direct hydrolysis of iron salt with different concentrations after the sonochemical synthesis of BiVO$_4$ nanoparticles. In the Ciprofloxacin degradation under UV–Vis light, the half-time of Fe-impregnated BiVO$_4$ (iron salt, 1 wt%) was 10 times greater than pure BiVO$_4$ and successfully recycled for at least six cycles without the presence of photocorrosion, which suggested that the novel photocatalyst had a high photocatalytic activity probably due to a dual-effect process (photocatalysis and photo-Fenton) irradiation inhibiting the electron-hole pairs recombination. In a mixed solvent (DMF, H$_2$O and Ethanol), Keramati et al.\cite{147} sonochemically synthesized the Fe-benzencarboxylic (Fe-BTC) metal–organic framework (MOF) for the photocatalytic degradation of Ciprofloxacin under UV irradiation. The Fe-BTC showed the highest photocatalytic activity as the volume ratio of DMF, H$_2$O and Ethanol was set as 2:1:2, and the samples had no good photocatalytic performance in the absence of water or ethanol.

The graphitic-like carbon nitride (g-C$_3$N$_4$), acting as a metal-free catalyst, shows an excellent photocatalytic activity in the visible-light range, so the photodegradation of g-C$_3$N$_4$ heterostructures has been carried out in many studies. Hernández-Uresti et al. sonochemically
prepared a WO$_3$/g-C$_3$N$_4$ heterojunction system at 37 kHz, and evaluated its photocatalytic activity by the photodegradation of Orange G dye and antibiotic Ciprofloxacin under solar-like irradiation conditions. [148] The WO$_3$/g-C$_3$N$_4$ composites (especially those containing 5 wt% loading of WO$_3$) exhibited a higher photocatalytic activity than the pure WO$_3$ and g-C$_3$N$_4$ materials, which could be attributed to the heterojunction between WO$_3$ and g-C$_3$N$_4$. The formed heterojunction caused a decrease in the recombination of photogenerated hole-electron pairs prior to an increase in the formation of reactive oxygen species, and thus, both the reactive species and photogenerated holes played a key role in the degradation of pollutants. Furthermore, the WO$_3$/g-C$_3$N$_4$ composites had a sustained photoactive performance, where the photoactive behavior to degrade the Orange G dye was repetitive after three consecutive cycles. By using the similar experimental procedures, a BiPO$_4$/g-C$_3$N$_4$ photoactive system also has been prepared by Hernández-Uresti et al., [149] and the sample with 1 wt% loading of BiPO$_4$ achieved a higher photocatalytic activity for the degradation of Orange G dye and Ciprofloxacin. In the Mahjoub’s study, [150] amine functionalized g-C$_3$N$_4$@MOF nanocomposites (g-C$_3$N$_4$@Ti-MIL125-NH$_2$) were fabricated by a rapid and straightforward sonochemical synthesis route at ambience temperature, where MOF stood for Ti$_4$C$_2$H$_{20}$N$_2$O$_{29}$ metal-organic framework or Ti-MIL125. The solid-phase g-C$_3$N$_4$@Ti-MIL125-NH$_2$ photocatalyst showed a considerable capability to eliminate 4-nitrophenol contaminant from water under the visible light illumination. Compared to the single g-C$_3$N$_4$ and Ti-MIL125-NH$_2$, g-C$_3$N$_4$@Ti-MIL125-NH$_2$ had a better efficiency, because there was much less photoluminescence intensity or a considerable decrease in the photoinduced charge carriers so that the photo-induced electron-hole pairs had a low recombination rate. Moreover, the larger surface area, unique morphology, and better non-agglomerated distribution of nanoparticles in the sonochemical synthesis made the effective mass transfer and separation of photo-generated charge carriers, so the g-C$_3$N$_4$@MOF nanocomposites showed a higher percentage of degradation than those by the hydrothermal technique. In addition, the g-C$_3$N$_4$@MOF nanocomposites displayed an excellent reusability and stability even after four iterations of pollutant degradation.

6.3.2. Sonophotocatalysis

Synergistic effects of sonocatalysis and photocatalysis have been studied widely in the combined degradation process since ultrasound promotes the mechanical disaggregation of photocatalysts enhancing the surface area for the photocatalysis, and the heterogeneity of solid photocatalysts boosts the formation of reactive hydroxyl radicals further contributing to the synergy. [151,152] In the Yesodharan’s study, [153] Zinc oxide was reported to be an active catalyst for the sonophotocatalytic degradation of phenol in water. The synergistic degradation of sonolysis and photocatalysis was higher than the individual sonochemical or photocatalytic degradation, achieving about 89% degradation of phenol. Acidic environment was preferred to implement the sonophotocatalytic degradation due to the enhanced formation of hydroxyl radicals, and in the comparison with TiO$_2$ catalysts, ZnO had a better efficacy possibly attributed to the higher ability to absorb energy
in the ultraviolet spectrum. In another study, Ahmad and coworkers used ZnO-decorated multi-walled carbon nanotubes to degrade Rhodamine B under a low-power ultrasound (35 kHz, 200 W) and natural sunlight. Compared with ZnO nanoparticles and carbon nanotubes, the composite ZnO/CNTs exhibited enhanced catalytic activity including photocatalysis, sonocatalysis and sonophotocatalysis activity, which was attributed to the prevention of electron-hole recombination at the hetero-interface. Within 60 min, the removal efficiency of Rhodamine B was up to 46% under the sunlight irradiation when the maximum value reached 49% under ultrasound irradiation, but the rate constant of sonophotocatalytic degradation was higher than their sum, which pronounced that more reactive radicals and active surface area were produced.

Sivasankar et al. studied Fe-doped TiO$_2$ catalysts (Fe-TiO$_2$) with various iron loading for the sonophotocatalytic degradation of Naphthol-blue-black dye, and 96% removal was achieved for the 2.2 g/L Fe-TiO$_2$ (1:7) catalyst. For real textile wastewater, the sonophotocatalytic degradation with Fe-TiO$_2$ (1:7) could remove 91% of total organic carbon. To improve the photocatalytic property of semiconductor photocatalysts, Liu et al. synthesized Ag$_2$O-BaTiO$_3$ hybrid nanostructure by assembling Ag$_2$O nanoparticles on BaTiO$_3$ nanocrystals. In response to the periodic ultrasonic driving, BaTiO$_3$ displayed a spontaneous polarization potential which acted as an alternating built-in electric field to incessantly enhance photo-induced charge carrier separation, significantly improving the photocatalytic activity and cyclic performance of Ag$_2$O-BaTiO$_3$. In the sonophotocatalytic degradation of Rhodamine B (Rh B) under UV light/ultrasound irradiation (Fig. 11), the degradation rate was 90% in 2 h for Ag$_2$O but reached 100% for Ag$_2$O-BaTiO$_3$, though both catalysts could directly mineralize the dye without any byproducts. The degradation activity for Ag$_2$O decreased about 50% after five sonophotocatalytic cycles, but there was less than a 10% decrease in activity for Ag$_2$O-BaTiO$_3$, suggesting that the built-in field in the hybrid nanostructure could improve the cyclic sonophotocatalytic property by maintaining the photoinduced carrier separation and even prohibiting the electrons to react with Ag$^+$. 

7. Polymerization

Polymerization can be implemented either by the chain growth re-action of the monomers with reactive double bonds after a free radical initiation process, or by a two-step procedure including polymer degradation and radical polymerization where polymer degradation generates some macro-radicals to copolymerize with the monomers. On the basis, ultrasound irradiation will be a good initiating source for some polymerization reactions since the primary radicals or secondary radicals can be produced during the acoustic cavitation.

7.1. Catalyst-free sono-polymerization

In the Grieser’s study, the miniemulsion polymerization of n-butyl methacrylate was successfully performed in organic liquid/water...
mixtures with aliphatic or aromatic hydrocarbons under 20 kHz ultrasound and ambient condition. In another work, they sonochemically copolymerized methyl methacrylate and butyl acrylate in different proportions without chemical initiators,[158] and the analysis indicated that the microstructure and composition of copolymers were consistent with the terminal model by the classical copolymerization processes. Moholkar et al. gained a physical insight into the sonochemical copolymerization,[159] and found the moderately alternating behavior of copolymerization since the reactivity ratio of both monomers was less than 1, wherein methyl methacrylate had a higher reactivity. By the surfactant-free aqueous emulsion polymerization, Yan et al. synthesized a copolymer of hydrophilic acrylamide and hydrophobic styrene in a high yield with the assistance of ultrasound, and the copolymer was amphiphilic but its hydrophobicity exhibited a little stronger than hydrophilicity.[160] Huets et al. has used a facile sonochemical strategy to successfully complete the in situ self-assembly of polymer molecules, where the macro-radicals were produced from the mid-chain cleavage of poly(vinyl alcohol) and were employed directly as initiating species to combinate with methyl methacrylate or butyl acrylate.[161]

Recently, the catalyst-free sono-polymerization process become a promising strategy for the reconstruction of biocompatible molecules. Alkylpolyglycosides has mostly important applications in cosmetic, food, pharmaceutical and detergent industries for its bio-based hydrotropes or surfactants depending on the nature of alkyl alcohol. In the report by Jerome et al.,[162] the concentrated feeds of carbohydrates including unprotected mannose, glucose or xylose could be activated at only 40 °C by high-frequency ultrasound (550 kHz) in an alcoholic solution, inducing the selective formation of alkylpolyglycosides (Fig. 12). This technology showed a possibility to convert the highly concentrated feeds of carbohydrates (up to 80 wt% conversion) even though it did not involve any catalyst or activating agent. Conversely to the popular Fischer glycosylation, the obtained alkylpolyglycosides had an average degree of polymerization in a window of 2–7 which addressed significant unmet needs, because the ultrasound-based polymerization at only 40 °C avoided the degradation of carbohydrates. Hao et al. reported the catalyst-free sono-polymerization process of poly(ethylene glycol)-based nanoparticles for drug delivery,[163] where three different macromonomers (i.e. acrylate-terminal methoxy poly(ethylene glycol), cyclic peptides containing RGD-modified acrylate-terminal methoxy poly(ethylene glycol), 2-aminoethyl methacrylate hydrochloride) were able to be quickly polymerized to form the engineering functional nanoparticles in a one-pot process under the optimized ultrasound frequency (412 kHz), ultrasound power (40 W) and polymerization temperature (40 °C). The poly(ethylene glycol)-based nanoparticles not only could be freeze-dried into a powder form but also could be redispersed into an aqueous solution without any aggregation after the freeze-drying, which might boost the storage and transportation as a nanomedicine system.

7.2. Catalyst-mediated sono-polymerization

7.2.1. Homogeneous catalysts

Foreseeably, the application of catalysts is able to subsidize the sono-polymerization. In the Pinjari’s study,[164] the cardanol-cased novolac resin was synthesized by a step-growth polymerization, where the ultrasound-assisted condensation reaction between cardanol and formaldehyde occurred in the presence of an acid catalyst (e.g., adipic acid, citric acid, oxalic acid, sulphuric acid, hydrochloric acid). By the research into free formaldehyde content, pH and viscosity values after the reaction, it found that the species and amount of acid catalyst had a nonnegligible effect on the conversion. Some phase transfer catalysts combined with the ultrasound irradiation also show many diverse applications in synthesizing various organic and polymeric materials. Murugesan et al. employed cetyltrimethylammonium bromide as a phase transfer catalyst to polymerize the monomer acrylonitrile in an ethyl acetate/water system under ultrasound (25 kHz/300 W).[165] In

Fig. 12. I) Contribution of the present work: case of glucose. II) Monitoring of the reaction progress by HPLC-SEC (40 wt% of mannose in methanol, 40 °C, 550 kHz): (i) Standard mannose, (ii) t = 1 h, (iii) t = 2 h, and (iv) t = 3 h. III) Relative proportions of the substitution patterns in linear regions of the product obtained after high-frequency ultrasound (HFUS) irradiation of d-mannopyranose in methanol. For the sake of clarity, only the pyranoside form was represented except for the 1,5 linkage, which implied the furanoside form. Reproduced with permission.[162] Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA.
the case, the reactive radical was powerfully produced with the aid of ultrasound, and then the anion was extracted from aqueous phase by cetyltrimethylammonium bromide and transferred to organic phase, so the polymerization rate was highly enhanced compared to the silent condition. As well, they completed the polymerization of N-vinyl carbazole under ultrasound by using a multi-site phase transfer catalyst (i.e. 1,4-bis (triethyl methyl ammonium) benzene dibromide).[166] Umapathy et al. used three different phase transfer catalysts (e.g., 1,4-bis(dimethylhexyl) ethylene diammonium bromide, 1,4-bis(dimethylheptyl) ethylene diammonium bromide, 1,4-bis(dime thyloctyl) ethylene diammonium bromide) to facilitate the synthesis of poly (methyl methacrylate) in an oxygen-free atmosphere under the ultrasound radiation,[167] where K$_2$S$_2$O$_8$ acted as a water-soluble initiator.

The synergic efficacy of ultrasound and phase transfer catalysts accelerated drastically the polymerization rate, and the efficiency of catalysts increased with the increase in the chain length, which might be associated in the polar group attaching to the carbon chain.

Sometimes, the trapping agents can serve as a catalyst to assist the effects of ultrasound irradiation on the polymerization. Nitroxide-mediated atom transfer radical polymerization (ATRP) under ultrasound has been reported in many studies because various nitroxides can quickly react with carbon-centered active species as stable radicals. [168] When two non-equivalent macro-radical species are produced through the mid-chain cleavage from the ultrasonic degradation of polymers, the nitroxides in the initial reaction mixture will trap the macro-radicals creating the dormant macro-initiators, and by a thermal procedure, the nitroxide moiety of macro-initiators can in turn undergo the homolytic dissociation to generate the active macro-radicals reversibly, initiating the vinyl polymerization. Copper halide-mediated polymerization routes are similar to the concept that the combination of ultrasound with atom transfer radical polymerization because the copper halide and nitroxides have one thing in common to act as a trapping agent (Figure 59).[9] In the approach, it is not the mechanical agitation of low-frequency ultrasound but the sonochemical effects of high-frequency ultrasound to apply in the atom transfer radical polymerization, where the hydroxyl radicals produced by the sonochemical reactions in aqueous solution serve as a reducing agent to convert Cu(II) halide to Cu(I) halide. The follow-up identical procedure is performed that the radical polymerization is catalyzed by the active Cu(I) form in the presence of initiators and polymerizable monomers. While the ultrasound irradiation is turned off, the Cu(II) species will build up rapidly with declining the active Cu(I) so that the propagation of polymer stands at a dominant deactivation to halt the growth of chains. As a result, such ultrasound-induced atom transfer radical polymerization reaction can

Fig. 13. I) Poly(HEA) prepared via sonoATRP: Conversion vs. sonication time for sonoATRP reactions with varying amounts of Cu (50–1000 ppm) (Left); GPC molecular weight characterisation of poly(HEA) prepared via sonoATRP with 250 ppm Cu (Right). II) Different target DPs of poly(HEA) prepared via sonoATRP; (b) monomer conversion with alternating ON/OFF periods of applied US; (c) GPC traces of the chain extension of poly(HEA) (orange dashed trace = homopolymer, blue solid trace = pseudo block co-polymer). All sonoATRP procedures were performed at frequency = 490 kHz, power = 40 W, [HEA] = 0.75 M. Reproduced with permission. [169] Copyright 2018 The Royal Society of Chemistry. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
be in temporal control.

Qiao et al. applied high frequency ultrasound (490 kHz, 40 W) for the controlled polymerization of 2-hydroxyethyl acrylate with the help of a pre-catalyst Cu(II)Br₂ complex.[169] Under the ultrasound treatment (Fig. 13), the radicals from the cavitation of aqueous solutions reduced Cu(II) to Cu(I) and initiated the atom transfer radical polymerization of water-soluble 2-hydroxyethyl acrylate (HEA). The conversion of monomers reached higher than 90% in a short time (less than 60 min), and the obtained poly(2-hydroxyethyl acrylate) had an excellent molecular weight distribution with a polymerization degree of 100–800, suggesting a remarkable chemical fidelity at a faster polymerization rate. Luo et al. carried out the similar work that the methyl acrylate monomers were sonochemically polymerized in the presence of Cu(II) Br₂ complex and tris(2-dimethylaminoethyl) amine, except for a significant distinction on the mechanism.[170] In the controlled radical polymerization, the sonochemically induced electron transfer mediated the synthesis rather than the atom transfer, where the dimethylsulfoxide-derived radicals formed under ultrasound irradiation combined with the tris(2-dimethylaminoethyl) amine allowing the generation of Cu(I) activator by an electron transfer process. Unfortunately, no conversion was observed for the polymerization of styrene, implying that the sonochemically induced electron transfer had a partial monomer scope.

The sonochemically induced atom transfer radical polymerization may allow to produce the block copolymers in the presence of different species of monomers even if the synthesis efficiency is limited by the ultrasound-induced incomplete degradation of polymer precursor. Yaci et al. have used the combination of ultrasound irradiation with the copper halide-mediated atom transfer radical polymerization to synthesize the block copolymers of poly(methyl methacrylate) and poly-styrene.[171] Under a low-frequency ultrasound, the activating macro-radicals were produced from the effective cleavage of poly(methyl methacrylate) and poly-styrene.[171] In a heated surrounding, the chain extension of atom transfer radical polymerization was activated after the styrene monomer was added directly, where the as-synthesized CuCl acted as a copper catalyst. The analysis results from the gel permeation chromatography showed a relatively good blocking efficiency and monomodal polymer peaks even though the residual homopolymer chains or broadly dispersed products might be caused by using the combination approach. Xiang et al. developed a new process with the ppm level of CuBr₂ catalyst for the sonochemically induced atom transfer radical polymerization in aqueous media.[172] Various diblock polymers were yielded via the polymerizations of oligo(ethylene oxide) methyl ether methacrylate and 2-hydroxyethyl acrylate with poly(ethylene oxide)-bromo phenylacetate with the assistance of Cu catalyst and tris(2-pyridylmethyl) amine when exposed to ultrasonication (40 kHz, 110 W) at room temperature. Likewise, they used an alkyl halide-functionalized DNA fragment to carry out the conjugation of DNA and polymer, and as the results showed, the molecular weight of products clearly shifted to a higher range than the original DNA macroinitiator, proposing a DNA-polymer biohybrid. The case indicated that the ultrasound-induced atom transfer radical polymerization at ambient temperatures had the potential for bio-conjugation reactions in aqueous conditions.

7.2.2. Heterogeneous catalysts

Alternatively, a cocatalyst is able to facilitate the copper-mediated polymerization reaction in a certain condition.[173] Esser-Kahn et al. have ever used the mechano-chemically active BaTiO₃ nanoparticles and copper bromide to conduct the controlled radical polymerization under a low-frequency ultrasound,[174] where BaTiO₃ had a high electrochemical potential capable of reducing Cu(II) bromide to Cu(I) bromide prior to activating the atom transfer radical polymerization at ambient temperature. The innovative co-catalyst system resulted in the smooth polymerization of n-butyl acrylate, in which the molecular weights increased with the monomer conversion and the polydispersity was consistently low throughout. However, the resulting molecular weight was lower than expected because the strong shear gradients generated under ultrasonic conditions gave rise to polymer degradation.

In another study, they used the piezochemical reduction of copper-based catalyst under ultrasound to synthesize a linear polytriazole via the Cu(I)-catalyzed cycloaddition reaction of multivalent azides and alkyne (Figure S10).[175] Matyiaszewski et al. dwelled on the piezoelectric catalysis of BaTiO₃ nanoparticles in the combination with atom transfer radical polymerization in the condition of 40 kHz ultrasound and low-ppm Cu catalyst,[176] and found that the different crystal structures and particle sizes of BaTiO₃ catalyst had the effects on the piezoelectric property, leading to a variation in the reaction kinetics. A poly(methyl methacrylate) layer cladding BaTiO₃ nanoparticles would enhance the effectiveness of catalyst by increasing the solubility and potentially and avoiding the aggregation events in the reaction system.

Additionally, the piezoelectric ZnO catalyst was also developed to apply in the sonochemically controlled atom transfer radical polymerization. In the Xia’s report,[177] a robust mechanically controlled atom transfer radical polymerization was developed in the presence of low-loading ZnO particles, where the enhanced interfacial interactions between piezoelectric ZnO nanoparticles and deactivated Cu(II) triflate complex enabled the formation of activator Cu(I) complex and resulted in 90% polymerization conversion after an 8 h ultrasonic agitation (Fig. 14I). Although the ultrasound-driving atom transfer radical polymerizations have been mediated by using copper-based catalyst complex in water or by the addition of piezoelectric materials in organic solvents, the procedures slowly proceeded and easily yielded the contaminated polymers due to new initiated chains and residual piezoelectrics. To solve the problem, Xia et al. introduced sodium carbonate into the atom transfer radical polymerization, and achieved 80% conversion of methyl acrylate in dimethylysulfoxide within 2 h.[178] In the presence of carbonate anions, the (CO₃)₂Cu(II) complex would be in situ formed prior to the conversion of Cu(II) activators to Cu(I) activators, and then the homolytic cleavage occurred to generate the Cu(I) species and carbonate radical anions, where the former acted as activators for atom transfer radical polymerizations while the latter were scavenged by dimethylysulfoxide (Fig. 14II). This approach promised the synthesis of well-defined and pure polymers or polymer-based hybrids.

7.2.3. Other catalysts

As well, there are some other vibrant catalysts to synergize the polymerization under the ultrasound irradiation. In the ring opening polymerization of lactide, Dubey et al. employed stannous octoate Sn(Oct)₂ and tri-phenyl phosphine as the organic catalysts in a suitable solvent to produce polylactic acid,[179] in which ultrasound was used to activate and/or boost the polymerization as an alternative energy source. In the Zhou’s report,[180] the eutectic gallium-iumdium as a liquid alloy, was designed to mediate the controlled mechanochemical polymerization of water-soluble monomers in the presence of external ultrasound stimulus. In the polymerization, a bulk liquid metal was disrupted into micro- and nano-droplets with reactive surface during ultrasound irradiation, and simultaneously the monomers combined into polymers. Because the pristine surface of liquid metal was continuously produced by ultrasound consuming the dissolved oxygen, this polymerization avoided oxygen inhibition effect, showing high reaction rate and excellent ability to produce polymers with high molecular weight, whilst these could be also potentially controlled by the applied sonication power. Thus, researchers applied the liquid metal-mediated mechanochemical method to complete the polymerization of a wide variety of water-soluble monomers such as acrylamide (AAM), N,N-dimethylacrylamide, 2-hydroxyethyl acrylate, N-acryloyl morpholine, 2-(dimethylamino)ethyl methacrylate, and 2-hydroxyethyl acrylate.
methacrylate (Fig. 15). In addition, liquid metal droplets were readily reclaimed and reused for polymerization. When adding 10 wt% NaOH aqueous solution, the recycling rate of liquid metal was around 80% independent on the recycling cycle number, and the polymerization performed with recycled catalyst had little influence on the conversion even after four recycling cycles.

Pourayoubi et al. prepared the six keggin-type polyoxometalate nanoparticles based on [PW_{12}O_{40}]^{3-} and [SiW_{12}O_{40}]^{3-} with Ag⁺ and (ZrO)²⁺ cations under ultrasound irradiation,\(^\text{[181]}\) and commandeered them to catalyze the synthesis of poly (amido-ester) at room temperature. The polyoxometalate nanoparticles could lead to the improvement by at least 22% in the polymerization yield, even though the molecular weight of polymers was decreased owing to the restrictive effect of heterogeneous nanocatalysts on the mobility of reactive groups at the end of growing polymer chains. Recently, Gedanken and coworkers have found that the CDs produced by the sonication of PEG-400 could act as an initiator in the synthesis of polypyrrole and its copolymers,\(^\text{[182]}\) overcoming some organ dangers (e.g., skin irritation, asthmatic symptoms) brought by using other initiators (e.g., ferric chloride, silver nitrate) and would undergo a subsequent proton transfer leading to the formation of amide bond as well as the water elimination. The whole process could be enhanced by the high acid capacity of catalyst and the effect of ultrasound, and the reusable cycle of sulfonated-RGO was even significantly reduced sonication time by using an increased catalyst amount and sonication power. As well, the sulfonated-RGO was applied in other reactions or chemical processes. In the Naemi’s report,\(^\text{[183]}\) aminomodified GO was treated with Isoatoic Anhydride (IA) and then combined with copper iodide in acetonitrile in order to form a GO-NH-IA-Cu(I) catalyst. The sonication of alkenes, alkyl halides and NaN_3 in ethanol was subjected to the catalysis of the GO-NH-IA-Cu(I) successfully producing various 1,2,3-triazole derivatives, during which the reaction rate was accelerated with the high yield and purity of product by ultrasound irradiation. The sulfonated reduced GO (sulfonated-RGO) synthesized by the ultrasonic treatment have ever been used to efficiently catalyze the direct amination of carboxylic acid with amines under ultrasound irradiation at room temperature,\(^\text{[184]}\) and the high yield of amide products was obtained from the reaction between amine and various aromatic or aliphatic carboxylic acid within a short time. In the case, the ammonium carbonate salt formed by the reaction of ammonium salt and carboxylic acid, was an intermediate needed in the amination reaction, and would undergo a subsequent proton transfer leading to the formation of amide bond as well as the water elimination. The whole process could be enhanced by the high acid capacity of catalyst and the effect of ultrasound, and the reusable cycle of sulfonated-RGO was even up to 7. In another Naemi’s study, researchers used the sulfonated-RGO catalyst in the heterogeneous system for the preparation of bisphenolic compounds in the presence of ultrasound irradiation,\(^\text{[185]}\) namely the sonochemical reaction of 2,4-diacylphenol with various aromatic/aliphatic aldehydes, and the synthesis yield was exceedingly high with a significantly reduced sonication time by using an increased catalyst amount and sonication power. As well, the sulfonated-RGO was applied in the ester-exchange and etherification of glycerol with isobutene reaction.\(^\text{[186,187]}\)

Binder et al. synthesized a series of polymeric bis(N-heterocyclic carbene) copper(I) complexes (e.g., poly(isobutylene)-based, poly(styrene)-based, and poly(tetra-hydrofuran)-based Cu(I)-biscarbene...
LMMMP conducted at the presence of oxygen (O\textsubscript{2}) complexes by N-methylimidazolium-telechelic polymers coordinating after polymerization of AAm by LMMMP at a sonication time of 240 min; Conversion of AAm dependent on the sonication time (d), where the red triangles denoted LMMMP conducted at the presence of oxygen (O\textsubscript{2}) while yellow circles and blue squares denoted sonicating of the deoxygenated solution of AAm with or without LM, respectively; Molecular weight distribution of PAAm synthesized by LMMMP and by sonicating the deoxygenated solution with or without LM at the sonication time of 240 min (e); Conversion of AAm versus the number of recycling steps (f); Recycling process of LM after LMMMP (g). Reproduced with permission.[180] Copyright 2019 Wiley-VCH Verlag GmbH & Co. KGaA. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 15. Schematic illustration of liquid–metal-mediated mechanochemical polymerization (LMMMP). Air-saturated aqueous solution of monomers was sonicated at the presence of LM. During sonication, bulk LM was dispersed into micro- and nanodroplets and monomers were converted into high molecular weight polymer. In addition, the LM could be reclaimed by treating with NaOH aqueous solution. SEM images (a, b) and EDS mapping (c) of the resulting LM micro- and nanodroplets after polymerization of AAm by LMMMP at a sonication time of 240 min; Conversion of AAm dependent on the sonication time (d), where the red triangles denoted sonicating of the deoxygenated solution of AAm with or without LM, respectively; Molecular weight distribution of PAAm synthesized by LMMMP and by sonicating the deoxygenated solution with or without LM at the sonication time of 240 min (e); Conversion of AAm versus the number of recycling steps (f); Recycling process of LM after LMMMP (g). Reproduced with permission.[180] Copyright 2019 Wiley-VCH Verlag GmbH & Co. KGaA. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

complexes) by N-methylimidazolium-telechelic polymers coordinating to tetrakis(acetonitrile)copper(I) hexafluorophosphate.[188] With the aid of ultrasound, the polymeric copper(I) bis(N-heterocyclic carbene) complexes were activated to generate the catalytic active copper(I) monocarbene complexes by a cleavage of one sterically shielding bis(N-heterocyclic carbene) ligand, monitoring the copper(I)-catalyzed azide/alkyne cycloaddition. By the copper(I)-catalyzed cycloaddition of benzyl azide and phenylacetylene, the conversion of such “click” reaction was suggested to be up to 97%. For the efficient synthesis of various 1,4-dihydropyridine derivatives, the pyrimidine-2,4-diamine-functionalized silica-coated magnetic nanoparticles (Fe\textsubscript{3}O\textsubscript{4}/SiO\textsubscript{2}-PDA) were prepared as a co-catalyst in the Maleki’s report.[189] Via the co-catalyzing by the prepared Fe\textsubscript{3}O\textsubscript{4}/SiO\textsubscript{2}-PDA and ultrasound irradiation, the high reaction yield (89%) for the 1,4-DHP derivatives was obtained in a short time (10 min) and disclosed a substantial catalytic activity executed between Fe\textsubscript{3}O\textsubscript{4}/SiO\textsubscript{2}-PDA and ultrasound, which was up to one probable thing that ultrasound irradiation could provide more appropriate conditions to activate the catalytic sites of co-catalyst.

Mahjoub et al. successfully synthesized GO-amide-functionalized MOF nanocomposites at room temperature and atmospheric pressure by using a simple and large-scale sonochemical method.[190] In comparison with the parent materials, the obtained nanocomposites exhibited a higher adsorption efficiency toward cationic Methylene Blue, and the 90% dye was removed reaching the equilibrium status within 2 min. Although the main driving force for the adsorption of Methylene Blue came from the strong interaction between the cationic dye and the amide groups in the nanocomposites, GO combining with MOF provided a favorable pathway to utilize their unique properties, improving the performance for dye removal. Tadjarodi et al. have used the GO complex to function as an effective Hg(II) ion adsorbent under ultrasonication at room temperature,[191] where 2-pyridinycarboxaldehyde thiosemicarbazone (2-PTSC) was selected as a tridentate-coordination ligand to modify GO surface so that GO could possess a strong coordination capacity with Hg(II) ions. The ultrasound irradiation could increase the diffusion coefficient to mix GO-PTSC with Hg(II) ions more quickly, in turn enhancing the interparticle collision and chemical reactivity of adsorbents and adsorbates. Prolonging the sonication time could improve the Hg(II) removal because the adsorbents had a better dispersion into the solution and/or increased contact sites for Hg(II) ions. In the research, the adsorption capacity of Hg(II) ions found was to be 302 mg/g, which was exceedingly high compared with other conventional mercury removers. Besides Hg(II) ions, other heavy metals such as Pd(II), Ni(II), Cd(II) and Cu(II) also could be adsorbed effectively by the GO complex. In Zare-Dorabei’s study,[192] GO was chemically modified with 2,2-dipyridyldiamine (DPA) to form a GO-DPA complex with DPA grafted on the surface and edges of GO. In the adsorbent, the DPA served as a strong bidentate ligand that provided a specific binding capability towards most of heavy metals and formed the complex with understudy ions by chelation. Like the adsorption for Hg(II) ions, the improved mass transfer under ultrasonication took place as well as augmented mixing, dispersion and interparticle collisions, which accelerated the adsorption process of heavy metal.[193,194] The research results found that almost 20 mg/L heavy metal ions were removed successfully within a 4 min sonication.

9. Conclusion

Ultrasound, responsible for many physical and chemical effects, is
appealing and conducive to the preparation or modification of nano-materials, and also can be directly used for the catalysis processes owing to its high-frequency mechanical property. This review simply describes the basic principles or mechanisms about the sonochemistry including primary sonochemical process and secondary sonochemical process, and roughly summarizes the ultrasound-assistant synthesis of nano-structured inorganic materials. The emphasis is highly put on the applications of sonochemically prepared products in the catalysis reactions such as hydrogenation, oxidation, degradation, esterification, etc. By such review, we hope to provide a more comprehensive understanding of sonochemistry and inorganic materials synthesis, and broaden the updated applications of ultrasound irradiation in the catalysis or other fields.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ulsoch.2020.105384.

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