Ultrasound waves at the service of photocatalysis: from sonochemical synthesis to ultrasound-assisted and piezo-enhanced photocatalysis

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Abstract

Sonication induces physical and chemical effects, such as promoting mass transfer and active radical formation, that can be harnessed for process intensification in numerous fields, including photocatalysis. In this perspective, we discuss recent advances in the main domains where photocatalysis and ultrasound technology overlap, namely ultrasound-assisted synthesis of photocatalysts and hybrid technologies combining ultrasound and light irradiation (sonophotocatalysis and piezo-enhanced photocatalysis). The latter, a particular case of external field-enhanced photocatalytic technology, is a relatively new approach that promises to boost photocatalytic efficiency, even though significant challenges remain to be addressed. Finally, we offer some perspectives on the future of ultrasound-assisted photocatalysis, discussing current gaps in knowledge and best practices for data reports.

Keywords

Sonication, sonosynthesis, sonophotocatalysis, piezo-phototronics, piezocatalysts, piezotronic effect

1. Introduction

In a polluted and energy-starving world, photocatalysis is a much-needed technology that has the potential to revolutionize environmental protection, green chemistry, and renewable energy by making use of light to activate reactions of pollutant degradation, selective synthesis, water splitting, and CO_2 reduction. Nevertheless, despite the huge amount of research over the last decades, real-life photocatalysis applications are few and mostly limited to the small-scale treatment of contaminants[1]. Current photocatalytic technologies suffer from limited solar energy utilization, high recombination rate, and low mobility of photo-induced carriers, which curb the process efficiency and result in increased energy costs needed for lamp irradiation.

In this context, ultrasound, *i.e.* sound waves of frequency above 20 kHz, can benefit photocatalysis in multiple ways, from promoting the synthesis of photocatalysts with tailored physicochemical properties to enhancing reaction efficiency via synergisms between ultrasound and light irradiation in sonophotocatalysis[2]. Moreover, piezo-enhanced photocatalysis has recently emerged as a promising external field-enhanced photocatalytic technology[3,4] that can significantly promote the efficiency of both downhill and uphill reactions[5-7].

Ultrasound waves produce both physical and chemical effects in liquid media via acoustic cavitation, *i.e.* the nucleation, growth, and final implosion of gas bubbles within the liquid solvent. The sudden collapse of ultrasound-generated bubbles releases huge energy leading to extreme localized conditions (temperatures of a few thousand K and pressure up to several thousand bars), which result in shock waves within the liquid and in the formation of active species, such as $^{\bullet}OH$ radicals (Fig.1a). However, these phenomena are primarily dependent on experimental parameters like ultrasound frequency and power, medium properties, operating conditions, and reactor geometry[8]. For instance, ultrasound waves with low frequency (20−80 kHz) cause mainly physical effects, whereas chemical effects dominate at high frequencies (150−2000 kHz). Moreover, increasing ultrasound power promotes cavitation activity, with ensuing physical and chemical effects, only up to a certain threshold, due to inefficient sound wave propagation and energy transfer at high power caused by a high density of cavitation bubbles.

Both physical and chemical effects can be put to use in photocatalyst synthesis and photocatalytic reactions. In the following sections, recent advances in these fields will be discussed.

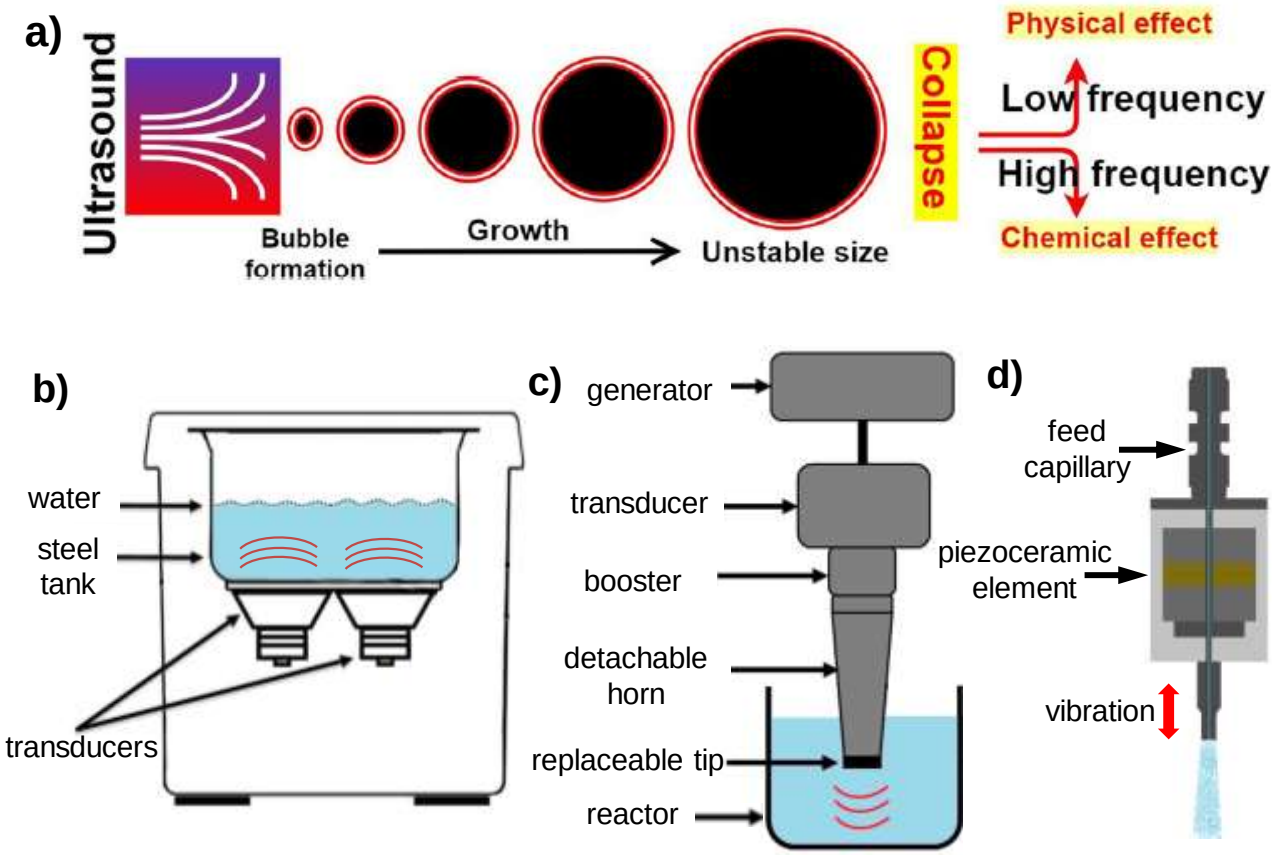

Figure 1 – a) Schematic of the acoustic cavitation phenomenon; reprinted with permission from Ref. [8]. Copyright 2022 American Chemical Society. Different types of sonication equipment: b) sonication bath, c) probe sonicator, d) ultrasonic spray atomizator.

2. Ultrasound-assisted synthesis of photocatalysts

Sonication has long been a key tool for photocatalyst synthesis, enabling morphological control[9], higher crystallinity in mild conditions[10], and promoting heterojunction formation[11]. Besides sonication with ultrasonic baths and probes (Fig.1b,c), techniques like ultrasonic spray atomization (Fig.1d) can be integrated into spray pyrolysis setups to produce well-controlled particle morphologies, as reported by Ji *et al.*[12] for the synthesis of black titania microspheres (Fig.2a,b). Sonication can be adopted for both bottom-up and top-down synthetic approaches. For instance, top-down methods using sonofragmentation to produce comminution of bulk materials have been reported for the synthesis of inorganic and hybrid perovskite nanocrystals[13,14]. Another interesting example was reported by Tang *et al.*[15]: by ultra-sonication of an eutectic Bi-Sn alloy followed by annealing, they produced a nanosized photocatalyst for pollutant remediation.

Bottom-up approaches can rely on chemical as well as on physical effects of cavitation. A classic example is the formation of metal nanoparticles with characteristic structural and morphological properties by volatile organometallic compounds (e.g., metal carbonyls), which tend to concentrate and degrade inside collapsing bubbles (primary sonochemistry[16]). A broader range of nanomaterials can instead be formed by secondary sonochemistry, *i.e.* chemical reactions taking place outside cavitation bubbles, activated by radicals formed inside the bubble that diffuse into the liquid phase[16]. However, most ultrasound-assisted syntheses of photocatalysts harness cavitation physical effects primarily to produce narrower size distributions, higher surface area, and improved phase purity. In this respect, several examples have been recently reported in the case of metal-organic-framework (MOF) photocatalysts[17,18].

Recently, 2D materials like reduced graphene oxide and *g*-C_3N_4 are taking centre stage in photocatalysis. Hence ultrasound-assisted syntheses are becoming increasingly common as indispensable synthetic tools to provide exfoliation[19] and speed up intercalation processes[20,21] by cavitation-induced shear forces. Zhang and coauthors[19] recently compared different exfoliation methods (thermal, chemical, ultrasonic, and one-step exfoliation) to prepare *g*-C_3N_4 for water purification: ultrasonic exfoliation resulted in better performance compared to the chemical method. Exfoliation is beneficial to photocatalytic activity by increasing surface area, porosity, and surface functional groups for attaching co-catalyst[22]. However, the sono-assisted approach showed lower photocatalytic performance than one-step exfoliation, which could be related to a higher degree of structural defects introduced by sonication in the *g*-C_3N_4 nanosheets. Interestingly, Kröger *et al*.[22] used ultrasonication to systematically modulate the particle size and the concentration of surface functional groups of 2D carbon nitride (Fig.2c), demonstrating their role in H_2 evolution. Also, Ruan *et al*.[23] adopted a controlled sonication step to induce electron-trap states associated with N-defects and C−OH terminal groups within n-type *g*-C_3N_4, to cause its transformation from a photoanode material into an efficient photocathode.

The main limit of ultrasound-assisted synthetic approaches lies in their scalability. Most studies report batch syntheses of small amounts of photocatalysts and sonoprocessing is notoriously dependent on reactor geometry[8]. In this respect, Zhu *et al*.[24] reported a continuous flow reactor (Fig.2d) for the deposition of size-controlled Ag nanoparticles on *g*-C_3N_4 for H_2 generation: the particle size, size distribution, and loading content could be varied, changing the residence time, ultrasonic power, and precursor concentration.

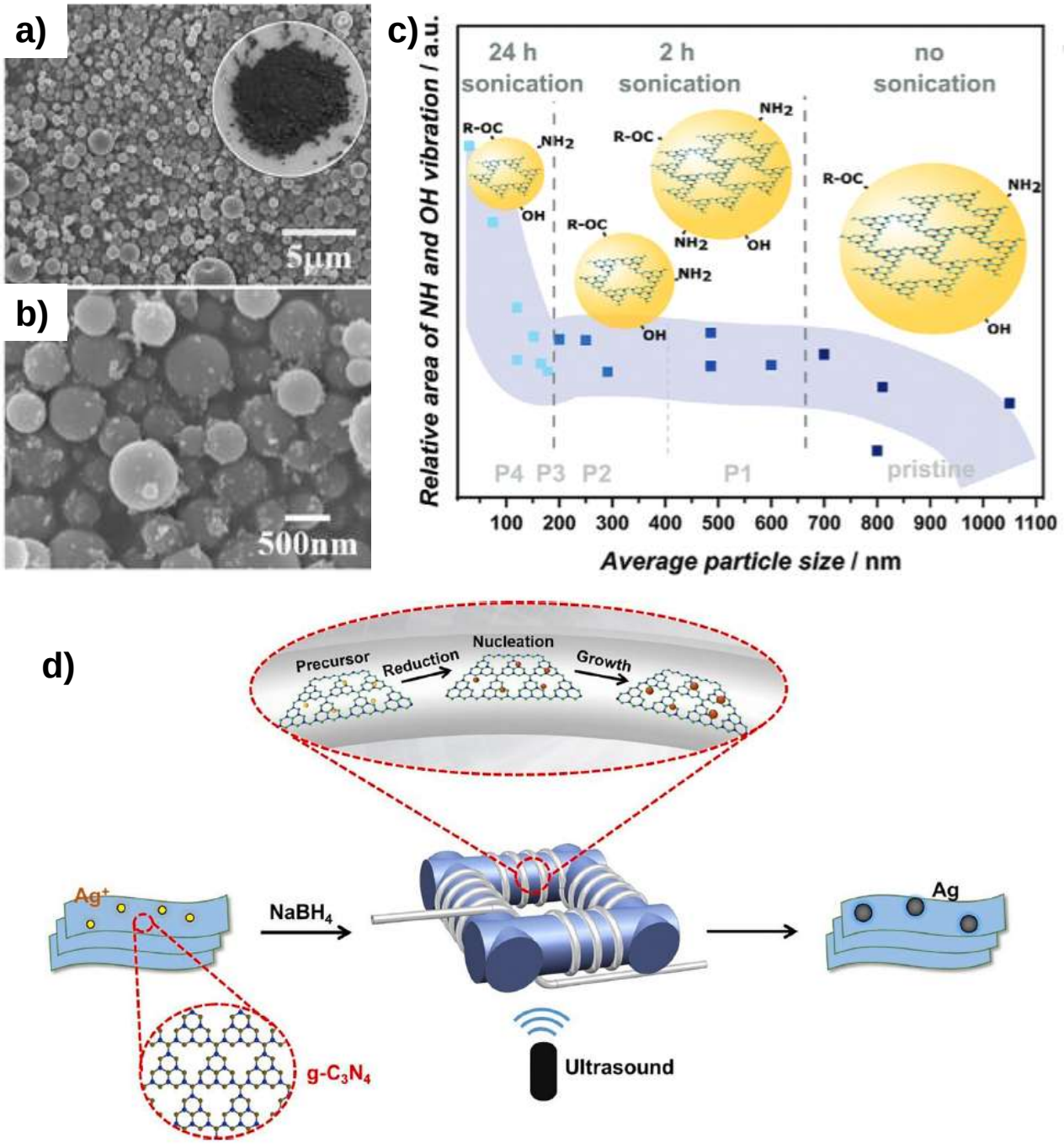

Figure 2 – a,b) Scanning electron micrographs and photo of black TiO_{2-x} microspheres prepared by one-step ultrasonic spray pyrolysis; reprinted with permission from Ref. [12]. Copyright 2021 Elsevier. c) Structural defects in 2D carbon nitride (as relative area of NH and OH vibrations from FTIR analyses) as a function of particle size in samples ultrasonicated for different duration; reprinted with permission from Ref. [22]. Copyright 2021 Wiley. d) Scheme of coiled flow inverter microreactor for the ultrasound-assisted synthesis of Ag/g-C_3N_4 photocatalysts; reprinted with permission from Ref. [24]. Copyright 2022 Elsevier.

3. Sonophotocatalysis

Besides promoting synthesis, the physical and chemical effects of cavitation can also be combined with light irradiation to promote photocatalytic reactions, such as water pollutant degradation. The resulting hybrid advanced oxidation process (AOP), sonophotocatalysis, can benefit from an increased yield of active species due to cavitation-generated radicals, as well as promoted mass transfer between the liquid phase and the photocatalyst surface due to microjets; the latter could also avoid the surface accumulation of intermediates, which can inactivate the photocatalyst[25]. Shear forces also promote the dispersion of the photocatalyst powder, opening the door to innovative microchannel reactors[26] (Fig.3a-c).

The efficiency of the combined process compared to the single treatments can be quantitatively estimated by:

$$\boldsymbol{synergy\ index} = \frac{\boldsymbol{k_{UV+US}}}{\boldsymbol{k_{UV} + k_{US}}}$$

where k_{UV+US}, k_{UV} and k_{US} are the rate constants of the sonophotocatalytic, photocatalytic and sonocatalytic processes, respectively[27]. Synergistic, additive, and antagonistic effects are observed for a synergy index, respectively, larger, equal, and lower than unity. In the literature, observed synergy indexes vary in a relatively broad range, from mostly additive to high synergistic effects, depending on the pollutant molecule, operating parameters (solution pH, temperature, ultrasound power, and frequency), and composition of the medium (e.g., electrolytes)[28]. In particular, the hydrophilicity/hydrophobicity of the pollutant molecule plays a major role: hydrophilic and non-volatile compounds accumulate in the liquid medium, where they are degraded via $^{\bullet}$OH-mediated reactions. Conversely, hydrophobic and volatile compounds migrate at the bubble–liquid interface and inside gas bubbles. Hence they are mainly degraded via pyrolytic reactions and by radicals generated within the bubble. Thus, hydrophobic compounds (i.e., with high octanol-water partition coefficient) generally display a lower synergy index than hydrophilic ones, which instead benefit from promoted radical formation in the liquid medium by photocatalysis[29].

The higher efficiencies of the hybrid treatment translate into lower energy consumption and costs compared to photocatalysis[29] (Fig.3d). However, these values are still one order of magnitude higher than other AOPs, such as UV/H_2O_2[29,30].

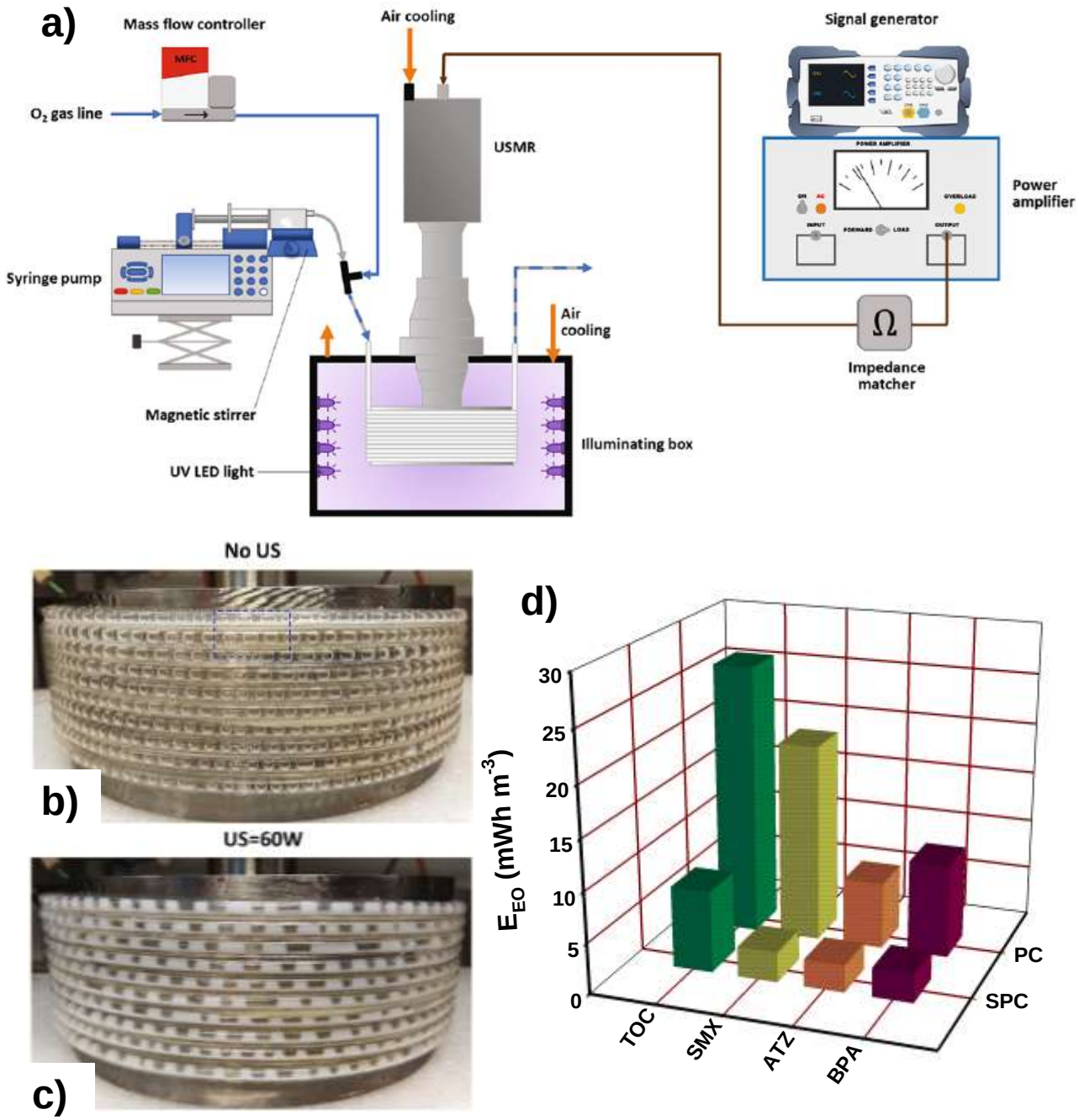

Figure 3 – a) Schematic representation of an ultrasonic milli-reactor for gas–liquid-solid photocatalytic reactions in flow; b-c) Effect of ultrasound on the three-phase flow in the capillary reactor: the photocatalyst powder forms a milky suspension under 60 W ultrasound irradiation (c), whereas no particles are appreciable without sonication (b); reprinted with permission from Ref. [26]. Copyright 2022 Elsevier. d) Electric energy per order, E_{EO}, calculated for the degradation of bisphenol A (BPA), atrazine (ATZ), sulfamethoxazole (SMX) and total organic carbon (TOC) by sonophotocatalysis (SPC) and photocatalysis (PC); reprinted with permission from Ref. [29]. Copyright 2021 Elsevier.

4. Piezo-enhanced photocatalysis

When a photocatalyst displaying piezoelectric properties is irradiated by both ultrasound and light, the mechanical stress caused by ultrasound waves generates a piezo-potential, caused by the deformation of the non-centrosymmetric crystal structure of the piezoelectric[31]. The piezoelectric potential and band bending facilitate the separation of photogenerated charge carriers to opposite surfaces, promoting photocatalytic activity (Fig.4a). Transient photocurrent measurements can demonstrate the piezoelectric promotion of charge separation under synchronous light and ultrasonic irradiation, compared to light irradiation alone.

Piezoelectrics with 1D or 2D structures are more easily deformed by mechanical stress, generating a much greater piezo-potential[31,32]. The piezo-potential, V_P, is related to the width of the piezoelectric material in the *x* dimension, w_x, according to:

$$V_P = \frac{w\, T_k\, d_{kx}}{\varepsilon_0 \varepsilon_r}$$

where T_k is the applied stress in the *k*-dimension, d_{kx} the piezoelectric moduli, ε_0 the vacuum permittivity, and ε_r the relative permittivity in the *x* dimension[6]. Piezoelectric semiconductors include ZnO fibers[32,33], inorganic and organo-halide perovskites[34], ultrathin materials such as 2D transition metal sulfides/selenides[35], g-C_3N_4[36], and layered bismuth-based piezoelectrics like BiOCl[37]. Besides these integrated piezo-photocatalysts, composite piezophotocatalysts consisting of a piezoelectric insulator and a photocatalytic semiconductor have been reported[38].

To boost the piezoelectric potential, besides selecting materials with high piezoelectric coefficient and tailoring their morphology (*e.g.*, longer fibers, single layer materials), a proper selection of operating parameters, in particular the ultrasound frequency[39], should be performed (Fig.4b); the highest activity has been reported to occur at the piezocatalyst resonance frequency[40].

Another strategy widely adopted for promoting piezo-photocatalytic activity is heterojunction formation[41,42]. Indeed, the piezo-potential can effectively tune the carrier migration at the heterojunction interface by modulating the barrier height (piezo-phototronic effect)[3]. Among these systems, composites of noble metals and piezophotocatalysts have recently shown great potential due to the coupling of plasmonic and piezotronic effects[43-47]. On one hand, noble metal nanoparticles provide visible light-response in composites with large bandgap piezophotocatalysts (e.g., inorganic perovskites[43] and ZnO[44,45]) by localized surface plasmon resonance. On the other hand, the Schottky barrier height and the depletion width are altered by the piezoelectric charges gathered at the metal-semiconductor interface (Fig.4c). This can promote the transfer of plasmonic hot carriers, slowing down recombination phenomena. Photocatalytic efficiency can be

promoted even further by combining plasmonic nanoparticles and asymmetric structures[44] (Fig.4d) or by coupling two different noble metals for guided Fermi level alignment[45].

Since the easy recovery of the piezo-photocatalyst is highly desirable, the immobilization of these systems on flexible substrates, such as metal foams and nets[48], is another active area of research (Fig.4e).

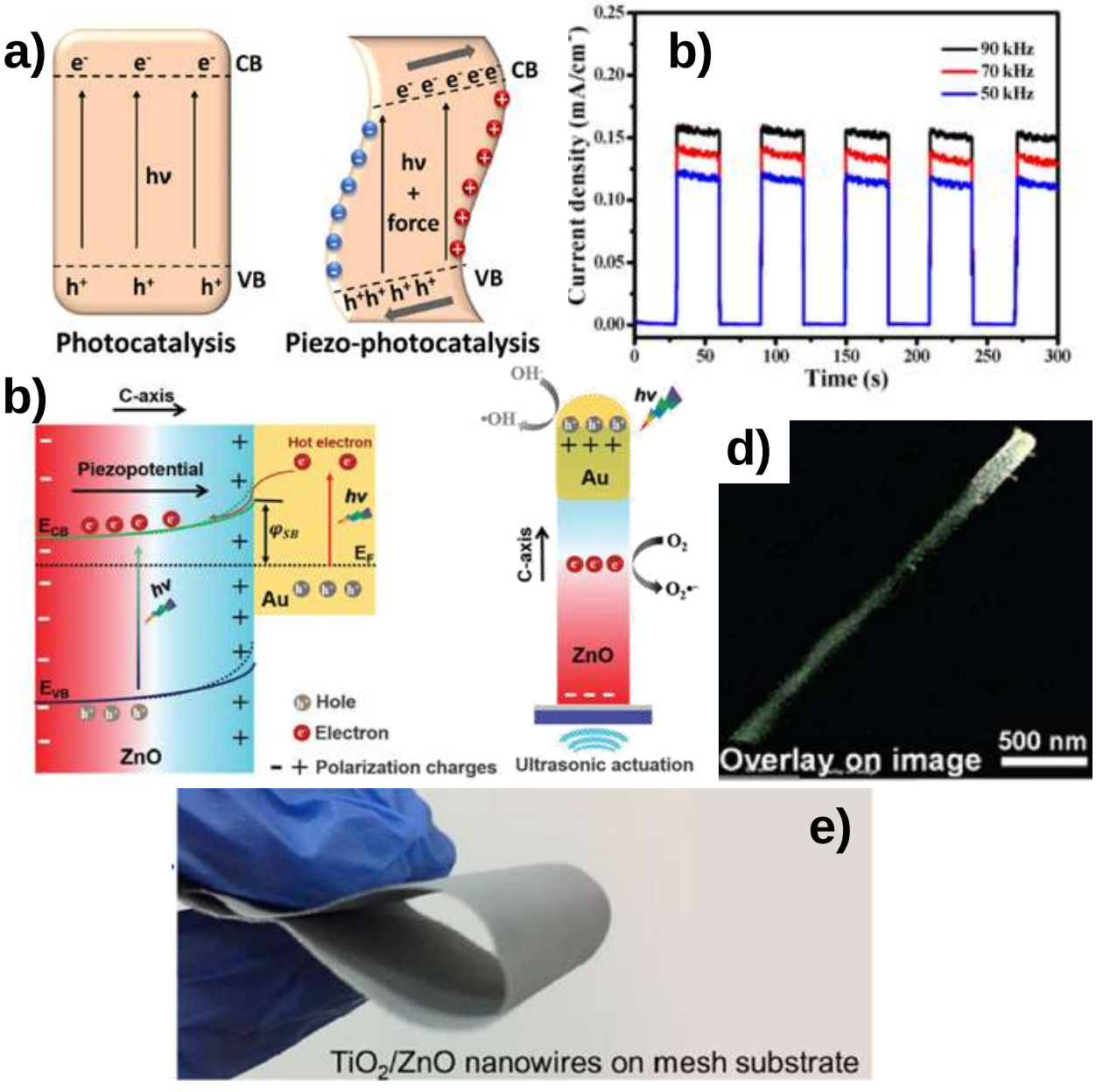

Figure 4 – a) Schematic illustration of the mechanisms of piezo-enhanced photocatalysis compared to photocatalysis; reprinted with permission from Ref. [5]. Copyright 2022 Elsevier. b) Current vs. time curves of ZnO nanorods under various ultrasonic frequencies; reprinted with permission from Ref. [39]. Copyright 2020 Elsevier. c,d) Asymmetric Au−ZnO nanorods: c) schematic (c) and SEM image (d) of the system, along with the mechanism of

piezo-photocatalytic enhancement (ϕ_{SB}, E_F, E_{CB} and E_{VB} stand for Schottky Barrier, Fermi level, conduction and valence band energies, respectively); reprinted with permission from Ref. [44]. Copyright 2020 Wiley. e) Images of flexible stainless steel mesh substrate coated with TiO_2/ZnO nanowire arrays; reprinted with permission from Ref. [48]. Copyright 2018 American Chemical Society.

5. Conclusions and perspectives

Ultrasound has proven an indispensable ally in the quest for better photocatalysts and more efficient photocatalytic processes. However, sonoprocessing has some intrinsic limitations that need to be carefully considered.

First of all, operating costs related to energy consumption, as well as to the periodic replacement of transducer and tip materials, can represent obstacles to the real-life applicability of these technologies. In this respect, the final application crucially affects the affordable cost of the technology. So far, combined sonophotocatalytic approaches have mainly been applied to pollutant degradation, with much higher costs compared to other AOPs such as Fenton and UV/H_2O_2, and most piezo-photocatalytic studies focused on the degradation of dyes. While there is a growing number of reports about H_2 production by water splitting, hybrid processes still have limited application to other uphill photocatalytic reactions such as CO_2 reduction, N_2 fixation, and H_2O_2 generation.

Another issue when probe sonicators are used is tip erosion, as it causes contamination of synthesized materials and treated effluents: indirect sonication schemes, such as cup-horn sonoreactors, can be used to solve this issue.

Notably, sonoprocessing suffers from scale-up issues related to the heterogeneous distribution of cavitation activity within the reactor. In this context, more studies pertaining to continuous and pilot-scale reactors are encouraged. Also, at the lab scale, operating parameters and reactor geometry play a key role in determining the reproducibility of experiments. Unfortunately, numerous literature studies provide insufficient experimental details: indispensable parameters include frequency, actual power, sonicator type, sonication mode and duration, solution temperature, reactor geometry, probe type, and tip immersion depth for probe sonicators.

Among the different ultrasound applications, piezo-enhanced photocatalytic technologies are arguably the most promising. However, they are still in the early stages of development, as the first pioneering studies were reported in the first decade of this century[49]. There are still numerous gaps in our knowledge, such as how far the piezo-potential can influence the coupled

semiconductor photocatalysts or the effect of temperature on the piezo-photocatalytic material. In this respect, we need experimental techniques and advanced simulation tools to characterize the phenomenon *in situ* and *in-operando* conditions.

A better understanding of the process mechanisms could help design piezo-photocatalysts more efficient at collecting mechanical energy: powerful mechanical excitation is needed due to poor mechanical energy collection, such as mechanical-to-chemical energy conversion efficiency for ZnO fibers was calculated to be 18%[50].

Finally, another crucial issue for the real-life applicability of these systems is the lifetime and cost of piezo-photocatalysts. The most promising systems are currently elongated/thin structures, often with heterojunctions. The mechanical stress due to prolonged sonication can limit the long-term stability and recyclability of these materials. Piezocatalysts based on polymers could better withstand deformation due to their flexibility under strain. However, while a broad range of polymers exhibits piezoelectric properties, they usually present reduced piezoelectric coefficients compared to inorganic materials and require costly procedures to promote their piezoelectric response[51].

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Declaration of interest:

None

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References

[1] E. Pargoletti, D. Meroni, G. Cappelletti, **Photocatalytic removal of gaseous ethanol, acetaldehyde and acetic acid: from a fundamental approach to real cases**, Int. Mater. Rev. (2022) DOI:10.1080/09506608.2021.2017390.

[2] J. Theerthagiri, S. J. Lee, K. Karuppasamy, S. Arulmani, S. Veeralakshmi, M. Ashokkumar, M. Y. Choi, **Application of advanced materials in sonophotocatalytic processes for the remediation of environmental pollutants**. J. Hazard. Mater. 412 (2021) 125245.

[3] C. Hu, S. Tu, N. Tian, T. Ma, Y. Zhang, H. Huang, **Photocatalysis Enhanced by External Fields.** Angew. Chem. Int. Ed. 60 (2021) 16309–16328.

[4] X Li, W Wang, F Dong, Z Zhang, L Han, X Luo, J. Huang, Z. Feng, Z. Chen, G. Jia, T. Zhang, **Recent Advances in Noncontact External-Field-Assisted Photocatalysis: From Fundamentals to Applications**. ACS Catal. 11 (2021) 4739−4769.

[5] Z. Jiang, X. Tan, Y. Huang, **Piezoelectric effect enhanced photocatalysis in environmental remediation: State-of-the-art techniques and future scenarios**. Sci. Total Environ. 806 (2022) 150924.

[6] S Tu, Y Guo, Y Zhang, C Hu, T Zhang, T. Ma, H. Huang, **Piezocatalysis and Piezo-Photocatalysis: Catalysts Classification and Modification Strategy, Reaction Mechanism, and Practical Application**. Adv. Funct. Mater. 30 (2020) 2005158.

[7] R. Mohanty, S. Mansingh, K. Parida, K. Parida, **Boosting sluggish photocatalytic hydrogen evolution through piezo-stimulated polarization: a critical review**. Mater Horizon (2022), DOI:10.1039/d1mh01899j.

[8] * D. Meroni, R. Djellabi, M. Ashokkumar, C.L. Bianchi, D.C. Boffito, **Sonoprocessing: From Concepts to Large-Scale Reactors.** Chem. Rev. 122 (2022) 3, 3219–3258.
* This article provides a comprehensive and updated overview of the role of operating parameters and reactor geometry on ultrasound-assisted processes. Available sonoreactor geometries are also presented.

[9] D. Meroni, C. Gasparini, A. Di Michele, S. Ardizzone, C.L. Bianchi, **Ultrasound-assisted synthesis of ZnO photocatalysts for gas phase pollutant remediation: Role of the synthetic parameters and of promotion with WO_3.** Ultrason. Sonochem. 66 (2020) 105119.

[10] D.A. Giannakoudakis, A. Qayyum, D. Łomot, M. O. Besenhard, D. Lisovytskiy, T. J. Bandosz, J. C. Colmenares, **Boosting the Photoactivity of Grafted Titania: Ultrasound-Driven Synthesis of a Multi-Phase Heterogeneous Nano-Architected Photocatalyst.** Adv. Funct. Mater. 31 (2021**)** 2007115.

[11] D. Kong, H. Fan, D. Yin, D. Zhang, X. Pu, S. Yao, C. Su, **$AgFeO_2$ Nanoparticle/$ZnIn_2S_4$ Microsphere p−n Heterojunctions with Hierarchical Nanostructures for Efficient Visible-Light-Driven H_2 Evolution**. ACS Sustainable Chem. Eng., 9 (2021) 2673−2683.

[12] M. Ji, Y.H. Choa, Y.I. Lee, **One-step synthesis of black TiO_{2-x} microspheres by ultrasonic spray pyrolysis process and their visible-light-driven photocatalytic activities.** Ultrason. Sonochem.74 (2021) 105557.

[13] S.S. Bhosale, A.K. Kharade, E. Jokar, A. Fathi, S.-M. Chang, E. W.-G. Diau, **Mechanism of Photocatalytic CO_2 Reduction by Bismuth-Based Perovskite Nanocrystals at the Gas−Solid Interface**. J. Am. Chem. Soc. 141 (2019) 20434−20442.

[14] H. Huang, Q. Xue, B. Chen, Y. Xiong, J. Schneider, C. Zhi, H. Zhong, A. L. Rogach, **Top-Down Fabrication of Stable Methylammonium Lead Halide Perovskite Nanocrystals by Employing a Mixture of Ligands as Coordinating Solvents.** 129 (2017), 32, 9699-9704.

[15] J Tang, R Daiyan, MB Ghasemian, S.A. Idrus-Saidi, A. Zavabeti, T. Daeneke, J. Yang, P. Koshy, S. Cheong, R. D. Tilley, R. B. Kaner, R. Amal, K. Kalantar-Zadeh, **Advantages of eutectic alloys for creating catalysts in the realm of nanotechnology-enabled metallurgy**. Nat. Commun. 10 (2019) 4645.

[16] N. Pokhrel, P. K. Vabbina, N. Pala, **Sonochemistry: science and engineering**. Ultrason. Sonochem. 29 (2016) 104–128.

[17] R. Abazari, A. R. Mahjoub, G. Salehi, **Preparation of amine functionalized g-C_3N_4@H/SMOF NCs with visible light photocatalytic characteristic for 4-nitrophenol degradation from aqueous solution**. J. Hazard. Mater. 365 (2019) 921–931.

[18] M. Zhang, Q. Shang, Y. Wan, Q. Cheng, G. Liao, Z. Pan, **Self-template synthesis of double-shell TiO_2@ZIF-8 hollow nanospheres via sonocrystallization with enhanced photocatalytic activities in hydrogen generation**. Appl. Catal. B-Environ. 241 (2019) 149–158.

[19] M. Zhang, Y. Yang, X. An, J. Zhao, Y. Bao, L. Hou, **Exfoliation method matters: The microstructure-dependent photoactivity of g-C3N4 nanosheets for water purification**. J. Hazard. Mater. 424 (2022) 127424.

[20] D. A. Giannakoudakis, N. Farahmand, D. Łomot, K. Sobczak, T. J. Bandosz, J. C. Colmenares, **Ultrasound-activated TiO_2/GO-based bifunctional photoreactive adsorbents for detoxification of chemical warfare agent surrogate vapors**. Chem. Eng. J. 395 (2020) 125099.

[21] DA Giannakoudakis, K Vikrant, AP LaGrow, D. Lisovytskiy, K.-H. Kim, T. J. Bandosz, J. C. Colmenares, **Scrolled titanate nanosheet composites with reduced graphite oxide for photocatalytic and adsorptive removal of toxic vapors.** Chem. Eng. J. 415 (2021) 128907.

[22] ** J Kröger, A Jiménez-Solano, G Savasci, V. W. H. Lau, V. Duppel, I. Moudrakovski, K. Küster, T. Scholz, A. Gouder, M.-L. Schreiber, F. Podjaski, C. Ochsenfeld, B. V. Lotsch, **Morphology Control in 2D Carbon Nitrides: Impact of Particle Size on Optoelectronic Properties and Photocatalysis**. Adv. Funct. Mater. 31 (2021) 2102468.
** This research work demonstrates that sonication can tailor the H_2 evolution performance of 2D carbon nitride by acting on both the particle size and concentration of surface functional groups. An optimal amount of defects created shallow trap states in the optical band gap, promoting charge percolation and photocatalytic activity, whereas excessive amounts of terminal defects decreased H_2 evolution by acting as recombination centers.

[23] Q. Ruan, T. Miao, H. Wang, J. Tang, **Insight on Shallow Trap States-Introduced Photocathodic Performance in n-Type Polymer Photocatalysts**. J. Am. Chem. Soc. 142 (2020) 2795−2802.

[24] H. Zhu, K. J. Wu, C. H. He, **Ultrasound-assisted synthesis of visible-light-driven Ag/g-C_3N_4 catalysts in a continuous flow reactor.** Chem. Eng. J. 429 (2022) 132412.

[25] P. Liu, Z. Wu, A. V. Abramova, G. Cravotto, **Sonochemical processes for the degradation of antibiotics in aqueous solutions: A review**. Ultrason. Sonochem. 74 (2021) 105566.

[26] * Z. Dong, S.D.A. Zondag, M. Schmid, Z. Wen, T. Nöel, **A *meso*-scale ultrasonic milli-reactor enables gas–liquid-solid photocatalytic reactions in flow**, Chem. Eng. J. 428 (2022) 130968.
* This work addresses the issue of clogging of continuous-flow micro- and milli-reactors due to suspended photocatalyst particles. Ultrasound irradiation is used to promote liquid mixing, gas–liquid mass transfer and resuspension of the settled particles during the photocatalytic selective oxidation of benzyl alcohol by TiO_2.

[27] D. Meroni, M. Jiménez-Salcedo, E. Falletta, B.M. Bresolin, C.F. Kait, D.C. Boffito, C.L. Bianchi, C. Pirola, **Sonophotocatalytic degradation of sodium diclofenac using low power ultrasound and micro sized TiO_2.** Ultrason. Sonochem. 67 (2020) 105123.

[28] F.V. de Andrade, R. Augusti, G.M. de Lima, **Ultrasound for the remediation of contaminated waters with persistent organic pollutants: A short review**. Ultrason. Sonochem. 78 (2021) 105719.

[29] * B. Ryu, K. T. Wong, C. E. Choong, J. R. Kim, H. Kim, S.-H. Kim, B.-H. Jeon, Y. Yoon, S. A. Snyder, M. Jang, **Degradation synergism between sonolysis and photocatalysis for organic pollutants with different hydrophobicity: A perspective of mechanism and application for high mineralization efficiency.** J. Hazard. Mater. 416 (2021) 125787.
* This work shed light on the synergistic effects occurring in the sonophotocatalytic degradation of pollutants of different hydrophobic/hydrophilic character; the high sinergy index observed for hydrophilic compounds was attributed to $^{\bullet}OH$ radical formation in the bulk liquid by splitting of cavitation-related H_2O_2 initiated by photogenerated electrons. Moreover, the energy consumption and treatment costs of the sonophotocatalytic process were calculated and compared to the purely photocatalytic approach.

[30] N. N. Mahamuni, Y. G. Adewuyi, **Advanced oxidation processes (AOPs) involving ultrasound for waste water treatment: A review with emphasis on cost estimation.** Ultrason. Sonochem. 17 (2010) 990–1003.

[31] L. Pan, S. Sun, Y. Chen, P. Wang, J. Wang, X. Zhang, J.-J. Zou, Z. L. Wang, **Advances in Piezo-Phototronic Effect Enhanced Photocatalysis and Photoelectrocatalysis.** Adv. Energy Mater. 10 (2020) 2000214.

[32] D. Meroni, C.L. Bianchi, D.C. Boffito, G. Cerrato, A. Bruni, M. Sartirana, E. Falletta, **Piezo-enhanced photocatalytic diclofenac mineralization over ZnO.** Ultrason. Sonochem. 75 (2021) 105615.

[33] Y. Zhang, S. Wang, Y. Zhao, Y. Ding, Z. Zhang, T. Jiang, Z.L. Wang, L. Li, **Piezo-phototronic effect boosted catalysis in plasmonic bimetallic ZnO heterostructure with guided fermi level alignment**. Mater. Today Nano 18 (2022) 100177.

[34] Z. Zhao, L. Wei, S. Li, L. Zhu, Y. Su, Y. Liu, Y. Bu, Y. Lin, W. Liu, Z. Zhang, **Exclusive enhancement of catalytic activity in $Bi_{0.5}Na_{0.5}TiO_3$ nanostructures: new insights into the design of efficient piezocatalysts and piezophotocatalysts**. J. Mater. Chem. A 8 (2020) 16238.

[35] Y. Zhao, X. Huang, F. Gao, L. Zhang, Q. Tian, Z.-B. Fang, P. Liu, **Study on water splitting characteristics of CdS nanosheets driven by the coupling effect between photocatalysis and piezoelectricity**, Nanoscale 11 (2019) 9085.

[36] C. Hu, F. Chen, Y. Wang, N. Tian, T. Ma, Y. Zhang, H. Huang, **Exceptional Cocatalyst-Free Photo-Enhanced Piezocatalytic Hydrogen Evolution of Carbon Nitride Nanosheets from Strong In-Plane Polarization.** Adv. Mater. 33 (2021) 2101751.

[37] X. Zhou, F. Yan, S. Wu, B. Shen, H. Zeng, J. Zhai, **Remarkable Piezophoto Coupling Catalysis Behavior of $BiOX/BaTiO_3$ (X = Cl, Br, $Cl_{0.166}Br_{0.834}$) Piezoelectric Composites.** Small 16 (2020) 2001573.

[38] S. Jia, Y. Su, B. Zhang, Z. Zhao, S. Li, Y. Zhang, P. Li, M. Xu, R. Ren, **Few-layer MoS_2 nanosheet-coated $KNbO_3$ nanowire heterostructures: piezo-photocatalytic effect enhanced hydrogen production and organic pollutant degradation.** Nanoscale 11 (2019) 7690.

[39] S. Zhang, Z. Liu, M. Ruan, Z. Guo, L. E, W. Zhao, D. Zhao, X. Wu, D. Chen, **Enhanced piezoelectric-effect-assisted photoelectrochemical performance in ZnO modified with dual co-catalysts.** Appl. Catal. B – Environ. 262 (2020) 118279.

[40] W. Feng, J. Yuan, L. Zhang, W. Hu, Z. Wu, X. Wang, X. Huang, P. Liu, S. Zhang, **Atomically thin ZnS nanosheets: Facile synthesis and superior piezocatalytic H_2 production from pure H_2O.** Appl. Catal. B – Environ. *277 (2020) 119250.*

[41] X. Liu, X. Shen, B. Sa, Y. Zhang, X. Li, H. Xue, **Piezotronic-enhanced photocatalytic performance of heterostructured $BaTiO_3/SrTiO_3$ nanofibers**. Nano Energy 89 (2021) 106391.

[42] J. Wu, W. Wang, Y. Tian, C. Song, H. Qiu, H. Xue, **Piezotronic effect boosted photocatalytic performance of heterostructured BaTiO3/TiO2 nanofibers for degradation of organic pollutants.** Nano Energy 77 (2020) 105122.

[43] Y. Fu, Z. Ren, L. Guo, X. Li, Y. Li, W. Liu, P. Li, J. Wu, J. Ma, **Piezotronics boosted plasmonic localization and hot electron injection of coralline-like $Ag/BaTiO_3$ nanoarrays for photocatalytic application.** *J. Mater. Chem. C* 9 (2021) 12596.

[44] ** D. Xiang, Z. Liu, M. Wu, H. Liu, X. Zhang, Z. Wang, Z. L. Wang, L. Li, **Enhanced Piezo-Photoelectric Catalysis with Oriented Carrier Migration in Asymmetric Au−ZnO Nanorod Array.** Small 16 (2020) 1907603.

** In this work, a highly asymmetric structure, coupling a 1D piezoelectric material and plasmonic nanoparticles, was adopted to generate high piezoelectric potential as well as to optimize the spatial distribution and migration of charge carriers. High aspect ratio ZnO nanorods were decorated with Au nanoparticles only at the ends of the nanorod to create the asymmetric piezo-photocatalytic architecture.

[45] ** Y. Zhang, S. Wang, Y. Zhao, Y. Ding, Z. Zhang, T. Jiang, Z.L. Wang, L. Li, **Piezo-phototronic effect boosted catalysis in plasmonic bimetallic ZnO heterostructure with guided Fermi level alignment**. Mater. Today Nano 18 (2022) 100177.

** This study demonstrates the use of guided Fermi level alignment to further boost piezo-phototronic effect by plasmonics. A bimetallic ZnO array was prepared with Pt nanoparticles evenly distributed on the ZnO nanorods and Au nanoparticles on the nanorods top. Charge separation and

migration was promoted by the efficient transfer of hot electrons, generated from the plasmonic excitation of Au nanoparticles, to Pt nanoparticles via ZnO, promoted by the piezo-phototronic effect. The piezo-potential induces the ZnO band bending with opposite directions at the Au/ZnO and Pt/ZnO Schottky junctions, thus promoting the separation of photo-generated carriers along the guided Fermi level alignment.

[47] S. Li, Z. Zhao, M. Liu, X. Liu, W. Huang, S. Sun, Y. Jiang, Y. Liu, J. Zhang, Z. Zhang, **Remarkably enhanced photocatalytic performance of Au/$AgNbO_3$ heterostructures by coupling piezotronic with plasmonic effects.** Nano Energy 95 (2022) 107031.

[48] Z. Wang, T. Hu, H. He, Y. Fu, X. Zhang, J. Sun, L. Xing, B. Liu, Y. Zhang, X. Xue, **Enhanced H_2 Production of TiO_2/ZnO Nanowires Co-Using Solar and Mechanical Energy through Piezo-Photocatalytic Effect**. ACS Sustainable Chem. Eng. 6 (2018) 10162−10172.

[49] Y.F. Hu, Y.L. Chang, P. Fei, R.L. Snyder, Z.L. Wang, **Designing the Electric Transport Characteristics of ZnO Micro/Nanowire Devices by Coupling Piezoelectric and Photoexcitation Effects**. ACS Nano 4 (2010) 1234–1240.

[50] K.S. Hong, H. Xu, H. Konishi, X. Li, **Direct Water Splitting Through Vibrating Piezoelectric Microfibers in Water.** J. Phys. Chem. Lett. 1 (2010) 6, 997–1002.

[51] M. Smith, S. Kar-Narayan, **Piezoelectric polymers: theory, challenges and opportunities.** Int. Mater. Rev. 67 (2022) 1, 65-88.