Visualization of the Mechanical Wave Effect on Liquid Microphases and Its Application for the Tuning of Dissipative Soft Microreactors

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ABSTRACT: The development of approaches for creation of adaptive and stimuli-responsive chemical systems is particularly important for chemistry, materials science, and biotechnology. The understanding of response mechanisms for various external forces is highly demanded for the rational design of task-specific systems. Here, we report direct liquid-phase scanning electron microscopy (SEM) observations of the high frequency sound-wave-driven restructuring of liquid media on the microlevel, leading to switching of its chemical behavior. We show that under the action of ultrasound, the microstructured ionic liquid/water mixture undergoes rearrangement resulting in formation of separated phases with specific compositions and reactivities. The observed effect was successfully utilized for creation of dissipative soft microreactors formed in ionic liquid/water media during the sonication-driven water transfer. The performance of the microreactors was demonstrated using the example of controlled synthesis of small and uniform gold and palladium nanoparticles. The microsonication stage, designed and used in the present study, opened unique opportunities for direct sonochemical studies with the use of electron microscopy.

KEYWORDS: dissipative systems, soft systems, microreactors, liquid-phase electron microscopy, ultrasound, ionic liquids, metal nanoparticles

INTRODUCTION

The stimuli-responsive chemical systems, which adapt to environmental conditions and can be driven and controlled by external sources of energy, are of particular interest as perspective candidates for the creation of tunable complex and diverse man-made architectures that take advantage of living matter. The development of approaches for the creation of such systems is closely related to the study of dissipative self-assembly processes, the association of molecular building blocks in systems out of equilibrium fueled by different chemicals, electromagnetic, or mechanical energy (Figure 1A).

Among all the types of stimuli, mechanical waves, namely sound/ultrasound, stand out due to the fact that they cannot directly work at a molecular level, but instead are able to interact with the media at microscopic level, initiating uncommon chemical transformations. One of the remarkable features of the ultrasound-assisted reactions is the possibility to achieve extreme conditions within the reaction mixture as a result of acoustic cavitation: formation and collapsing of vacuum bubbles inside the liquid media under sonication conditions, leading to the local emission of huge amounts of energy. The use of sound energy has found a number of applications in organic synthesis, preparation of nanomaterials, processing of crude biomass, and other processes. Along with the cavitation-based approaches, the mechanical standing wave techniques are widely used, for example, in the oil processing, food technology, and biotechnology. To establish which particular sound wave effect is essential for achieving the desired structural changes in the chemical system, mechanistic insight into such challenging systems is needed, and fundamental studies of the mechanical wave-induced phenomena should be carried out.

In the current study, we aimed to get an insight into the mechanism of the influence of mechanical waves on the structure and reactivity of well-known liquid media based on water and ionic liquids (Figure 1A), which are of high importance for chemistry, biology, and energy research. For both theoretical and practical reasons, room-temperature ionic liquids (RTILs) are the best candidates for studies on the effect of mechanical waves in liquid phase. ILs represent a unique type of liquid media, which are able to create different structural patterns in pure form and in their mixtures with...
water\textsuperscript{34−36} and other solvents.\textsuperscript{37,38} Such flexibility of IL-based solutions allows employment of different external stimuli to control their properties, in particular, mechanical waves were employed in a number of ultrasound-assisted processes.\textsuperscript{39−45}

Recently, it was shown that structural and mechanistic studies of ionic liquids can be significantly advanced by application of liquid phase electron microscopy for direct visualization of static structures and dynamic phenomena with high spatial and temporal resolution.\textsuperscript{46,47} The use of such powerful techniques allows taking a fresh look at ionic liquid behavior.

Here, we report direct observations of mechanical standing wave interactions with the liquid phase, leading to alteration of the liquid media structure, composition, and chemical behavior. A fast and convenient method for the visualization of the ultrasound effect with the use of electron microscopy and a special microsonication stage is proposed and was successfully used for a study of microstructured IL/water systems (Figure 1B). With the use of the developed technique, the standing-wave driven transfer of water between different phases of ionic liquid/water mixtures was detected and recorded step-by-step. The observed effect of restructuring of the liquid media under the action of ultrasound waves was subsequently employed to generate soft dissipative ionic liquid/water microreactors, whose performance was demonstrated using the example of controlled gold and palladium nanoparticle synthesis, leading to the formation of highly demanded metal NPs/ionic liquid systems.\textsuperscript{48−51}

\section*{RESULTS AND DISCUSSION}

For the electron microscopy study of the high-frequency sound wave effect on the soft liquid systems, ionic liquids with relatively small amounts of water additives were chosen as a medium. In our previous studies, we showed that self-organized structures can be easily generated in ionic liquids with the use of 5−20 vol % of water additives. Morphology and dynamic behavior of these structures can be effectively monitored by liquid-phase SEM.\textsuperscript{46,52−54} The unique possibility to observe microstructures created by water in ionic liquid with the use of SEM opened the way for the study of their behavior under different stimuli for creation of efficient methodologies.

On the first step of the study, microstructured liquid media was prepared by mixing of $[\text{C}_4\text{mim}][\text{BF}_4]$ ionic liquid ([$\text{C}_4\text{mim}][\text{BF}_4]$: 1-butyl-3-methyl imidazolium tetrafluoroborate) with 10 vol % of water. The prepared mixture appeared as a colorless transparent solution without any notable heterogeneity. The use of optical microscopy for initial mixture analysis confirmed its homogeneous nature. No inclusions were detected in the sample film on an ordinary microscope glass slide (Figure 2A).

The picture was completely different in the case of SEM imaging. A number of liquid microdroplets were detected within the sample (Figure 2B). It is worth mentioning that no special sample preparation procedure was used, as in the case of optical microscopy, the droplet of the sample was applied on a standard microscope holder: a metal grid or metal stub. Due to the obvious benefits of the method, such as availability of specific pronounced contrast between two liquid phases, SEM was used for further studies devoted to exploring the effect of mechanical waves in ionic liquid/water media.

For the accurate electron microscopy studies of the effect of ultrasound waves in liquid phase, we designed a special source...
of ultrasound based on a compact piezoelectric element. A photograph and a scheme of the assembled device are given in Figure 3. The piezoelectric element is fixed on a SEM holder for bulk specimens and connected to function generator, which provides the alternating signal with a frequency of 30–40 kHz. A sample is applied on a copper TEM grid placed in the center

Figure 3. SEM study of the effect of mechanical waves on the [C₄mim][BF₄]/water system. Photograph (A) and scheme (B) of the designed microsonication stage developed for electron microscopy measurements. (C) SEM images of the [C₄mim][BF₄]/water system after ultrasonic treatment for certain amounts of time (droplets of water-containing phase are colored in green, and large water-containing films and channels are colored in orange; scale bar 50 μm).

Figure 4. Quantitative analysis of the ultrasound effect on the [C₄mim][BF₄]/water system. Morphological analysis based on the obtained SEM images (A). Analysis of the sample mass loss (decrease in water concentration in the inset plot) during sonication (B). IR (C) and ¹H NMR (D) spectra of the [C₄mim][BF₄]/water system after sonication for certain amounts of time.
of the piezoelectric element working surface (Figures 3A and B, also see Figures S1 and S2 in the Supporting Information for enlarged images). Also, a small droplet of sample may be put directly on the surface of the device without a grid, if grid-style sample localization is not required.

With the use of the microsonication stage, the effect of sonication on the \([\text{C}_4\text{mim}][\text{OTf}]\)/water system was studied with the use of electron microscopy. The microscopy images were taken after treatment of the sample with ultrasound for a certain amount of time. In total, 10 points were recorded for each sample (see Movie S1 and Movie S2 for animated presentation of the sample behavior under the sonication conditions and Figures S3−S12 and S13−S22 for frozen frames). The most representative images are summarized in Figure 3C. At small sonication times of less than 60 s, formation of small droplets (colored green in Figure 3C) within a broad size range of 1−15 μm was observed. The further expansion of this microphase led to formation of large perforated droplets reaching 50 μm in size, as well as channels and films (colored orange in Figure 3C). After 600 s of sonication, the film covered the major part of the sample surface. On the basis of previously reported observations,52−54 the microdroplets, channels, and films on the sample surface were attributed to the water-rich phase, whereas the rest of the surface was associated with the ionic liquid-rich phase.

To quantify the morphological changes in the sample, we calculated the relative sample area covered with the water-rich phase of diverse morphology or the IL-rich phase for each sonication time (Figure 4A). The area covered by the water-containing phase increased evenly. The isolated droplets dominated in the phase morphology for the first minutes of ultrasonic treatment, whereas at higher sonication times, liquid films and channels prevailed over other microstructures (Figure 4A). In the case of another microstructured system, \([\text{C}_2\text{mim}][\text{OTf}]/\text{water}\) ([\(\text{C}_2\text{mim}][\text{OTf}]: 1\text{-ethyl-3-methyl imidazolium trifluoromethanesulfonate}]), the same process of the water-containing phase growth was detected, but the microphase had a solid form (possibly IL hydrate), and its formation rate was much higher compared to that of \([\text{C}_4\text{mim}][\text{OTf}]\) (see Movie S3 for an animated presentation of the sample behavior under sonication conditions and Figures S23−S34 for frozen frames). For the homogeneous \([\text{C}_2\text{mim}][\text{OTf}]/\text{water}\) ([\(\text{C}_2\text{mim}][\text{OTf}]: 1\text{-butyl-3-methyl imidazolium trifluoromethanesulfonate}) system, no changes in morphology associated with the mechanical wave effect were detected (see Movie S4 for animated presentation of the sample behavior under sonication conditions and Figures S35−S43 for frozen frames).

The main effect of ultrasound waves observed by electron microscopy was the accumulation of the water-containing phase on the surface, accompanied by formation and growth of the droplets followed by their aggregation. On the basis of detected morphological changes, one can conclude that ultrasound treatment of the IL-water system leads to the transfer of water between different phases of the system and its accumulation near the surface layer with establishment of nonequilibrium conditions.

To verify these conclusions, we carried out a series of experiments, in which a number of parameters were measured for bulk samples after sonication. First of all, direct temperature measurements showed the absence of noticeable macroscopic sample heating during the ultrasonic treatment. At the next step, weighing experiments indicated a decrease in the sample mass under the influence of ultrasound. The total mass loss was about 5 mass% after sonication for 900 s (Figure 4B). This value corresponds to 50% loss of water, assuming that the ionic liquid does not evaporate. This conclusion was further supported by IR and \(^1\text{H} \text{NMR spectroscopy measurements (Figures 4C and 4D).}

IR spectra of the \([\text{C}_2\text{mim}][\text{BF}_4]/\text{water system before and after treatment with ultrasound are given in Figure 4C. Spectroscopic data for the [\(\text{C}_2\text{mim}][\text{BF}_4]/\text{water system are thoroughly described in the literature, so the obtained spectra can be analyzed on the basis of previously published results.55−57 It can be clearly seen that the amount of water notably decreases with the increase in ultrasonic treatment time. The relative intensity of OH valence bands at 3300−3700 cm\(^{-1}\) continuously decreases during sonication (the intensity of CH valence bands at 2800−3200 cm\(^{-1}\) was set as a reference). Analysis of the structure of OH valence bands shows the presence of two types of water with different consumption rates: slowly evaporating water (bands at 3500−3700 cm\(^{-1}\)), which can be considered as water bonded to ionic liquid, and rapidly evaporating bulk water (shoulder at 3300−3500 cm\(^{-1}\)). Therefore, taking into account results of electron microscopy observations, under the mechanical wave treatment conditions, the preferable ways of water transfer are the specific bounding to ionic liquid or irreversible removal from the liquid system. Decrease in the water content of the sample
was additionally demonstrated by $^1$H NMR spectroscopy (Figure 4D). The ratio between the integral intensities of water OH groups signals and ionic liquid CH$_3$ group signals decreased 5-fold after 600 s of sonication. The small additional peak in the water region detected at high sonication time was attributed to the HDO impurities in the deuterated solvent used for the sample preparation and was excluded from the calculations.

Additionally, IR and NMR spectroscopy data clearly demonstrated the stability of ionic liquid during the sonication.

**Figure 6.** Effect of ultrasound waves on the synthesis of metal nanoparticles. Schematic representation of the strategy (A) and methods (B) for the preparation of the metal NPs in ionic liquids or the supported metal NPs. SEM images of the reaction mixtures for gold (C) or palladium (D) nanoparticle synthesis in the IL/water mixture under UV irradiation in the absence of ultrasound or under the ultrasonic treatment. TEM images of the supported palladium nanoparticles obtained in the absence of ultrasound or under the ultrasonic treatment (E). Scale bars: 5 μm (C, D), 50 nm (E). Also see Figures S50−S64.
No products of ionic liquid decomposition (hydrolysis, for example) were detected in the spectra (see Figures S44–S45 for the full-range NMR spectra of the [C4mim][BF4]/water system before and after sonication). This observation confirmed that the ultrasound-driven alteration of the system morphology was not caused by deep chemical modification of the solution.

Results of electron microscopy observations supported with spectral measurements revealed the key processes occurring at sonication of the IL/water mixture: restructuring of the water-rich droplets in the IL/water system, accumulation of water in microphase near the surface of the ionic liquid, and partial evaporation of bulk water from the sample. Graphical representations of the system morphology evolution and stepwise sonication mechanism are summarized in Figure 5. Initially, the addition of water to ionic liquid media leads to the spread of water with formation of water-rich microphase. After a short time, the microstructure of the system stabilizes when water concentration in microdomains reaches the equilibrium value. Before the sonication, the water exists as a microphase consisting of water-enriched droplets and some solid inclusions within the droplets, which may be attributed to ice or solid ionic liquid hydrates. Interaction of ultrasound with IL/water media leads to the appearance of standing waves within the liquid, which create the driving force for the water transfer between different phases. The directed movement of the formed water-rich structures at sonication causes accumulation of the water in microstructured form accompanied by partial evaporation of bulk water, which is not strongly embedded in IL media. Additional pumping of the water into the microdroplets causes growth of the water-rich phase, resulting in formation of large droplets, channels, and films. The films on the sample surface remain stable under further sonication.

The carried-out complex structural study has shown that sonication of the IL/water systems under mild conditions results in restructuring of the water-containing phase and intensive transfer of water between different phases, which can lead to the appearance of useful properties, for instance, enhanced chemical reactivity in the system. The ability to tune the properties of the IL/water mixture on the microlevel by the pro-

To test this hypothesis, we employed the synthesis of metallic nanoparticles from the water-soluble metal salts in the IL/water mixture as a model and practically important process. The treatment with intense ultraviolet (UV) radiation leading to photolysis of the water and direct reduction of the metal salts was used for the metal particle formation, and sonication with ultrasound was employed to control the microstructure of the reaction mixture (Figure 6A). To evaluate the effect of ultrasound on the morphology of gold particles prepared from HAuCl₄ in the [C₄mim][BF₄]/water environment, a series of experiments with different sonication times was carried out. Reaction mixtures were treated with UV for 15 min either in the absence of ultrasound or under the short (for the first 5 min) or prolonged (for the entire 15 min) action of ultrasound. Morphology of the resulting mixtures was analyzed directly in solution with the use of electron microscopy (Figure 6C). UV irradiation of the reaction mixtures, which initially contained only a minor amount of solid species (see Figures S46–S47), successfully led to the formation of nanosized gold particles. Particles obtained in the absence of ultrasound treatment had sizes of about 20–50 nm and were dispersed in the sample in the form of aggregates with sizes from several hundreds of nanometers to several dozens of micrometers and a variety of shapes only slightly reflecting the initial morphology of the IL/water system. Application of ultrasound at the initial steps of the gold nanoparticle synthesis (5 min of sonication) resulted in dramatic changes in the morphology of the prepared system. The size of the individual particles decreased to less than 20 nm, and the degree of aggregation was significantly lower compared to the synthesis under silent conditions. Moreover, gold nanoparticles were concentrated inside clearly visible microdroplets. This observation allowed us to conclude that ultrasound created specific zones with high concentration of the reacting solution consisting mainly of water and water-soluble metal salt. As in the case of pure IL/water solution (see Figure 3C), phase composition of the multicomponent mixture changed under the action of ultrasound. Increase in sonication time resulted in formation of wide areas in the reaction mixture saturated with the gold precursor. In these areas, the reduction of the gold salt led to the appearance of large zones densely and uniformly filled with gold nanoparticles with the sizes of about 20–50 nm.

To exclude the influence of the UV irradiation on the microlevel properties of the ionic liquid/water mixture, the control experiment was carried out. The [C₄mim][BF₄]/water system was treated with ultraviolet light for 15 min and then analyzed by SEM. The microstructure of the liquid was completely preserved (see Figures S48 and S49), so the factor of the media structural property alteration with UV irradiation can be neglected.

The detected behavior of the reaction mixture under the action of ultrasound totally reflects the regularities observed in the case of IL/water systems (see Figure 3C). At short sonication times (5 min), the reaction was localized in microsized droplets, whereas continuous sonication (15 min) resulted in formation of large film-like reactive phases. Summarizing the points stated above, one can conclude that in a microsized system based on ionic liquid and small amounts of cosolvent (water), ultrasound can actually create zones with specific reactivity due to the effect of cosolvent pumping to certain points inside the ionic liquid media probably defined by the profile of standing ultrasound waves in liquid.

To access another type of industrially relevant nanomaterials, a water-soluble palladium complex (NH₄)₂PdCl₂ was used instead of the gold salt. Palladium particle synthesis was carried out with the use of UV irradiation under silent or sonication conditions. The morphology of the formed mixtures was analyzed by SEM in solution (Figure 6D). In the absence of ultrasound, the reduction of palladium complex resulted in formation of large aggregates of particles. The sizes of individual particles varied in a wide range: 20–30 nm for small particles, 50–100 nm for middle-sized particles, and several hundreds of nanometers for large ones, which made them not suitable for practical applications. Interestingly, some microdroplets enriched with aqueous phase were detected at the same time, but the absence of metal particles within the droplets clearly indicated the lack of specific reactivity inside the microphase under silent conditions. By contrast, the microdroplets formed under the action of ultrasound served as microreactors for the synthesis of practically relevant palladium
particles. Under sonication conditions, Pd nanoparticles appeared exclusively inside the microdroplets. Their average size did not exceed 20 nm, and the degree of aggregation was low. Thus, the microcompartment-controlled synthesis was successfully performed for gold and palladium nanoparticles and revealed a general character for both metals.

At the last step, the possibility of palladium nanoparticle capture on the solid supports from the ionic liquid/water media during the synthesis was evaluated. The influence of sonication on the morphology of resulting materials was also tested. To reach the goal, a solid support was added to the reaction mixture before the reaction. After the synthesis, the solid phase was separated from the mixture, washed, and dried. The structure of supported palladium particles was established with the use of transmission electron microscopy (TEM). A number of supports, namely graphite, multivalien carbon nanotubes (MWCNTs), TiO$_2$ (anatase), gamma-Al$_2$O$_3$, and SiO$_2$ (silica gel), were employed for the deposition of nanoparticles. Carbon materials, graphite (Figure 6E) and MWCNTs (see Figures S65 and S66), demonstrated excellent performance due to the high affinity of metallic nanoparticles to conjugated carbon moieties. The application of ultrasound allowed reduction of the average size of the particles from 10 to 5 nm for graphite (see Figures S67 and S68 for histograms of particle size distribution) and from 9 to 5 nm for MWCNTs. Using the developed method, palladium catalysts, highly demanded in industry and academic research, could be prepared without any chemical reducing/stabilizing agents. Dynamic stabilization was achieved by ultrasound-driven microcompartment-controlled synthesis, which is a powerful catalyst preparation approach. It is noteworthy that amount of the reaction mixture used for supported catalyst preparation exceeded by an order of magnitude the typical amount of sample in the in situ electron microscopy experiments. The obtained results correlated well with each other, which showed the reproducibility and scalability of the employed synthetic method.

For more clear understanding of the ultrasound effect in a microcompartment-controlled synthesis, a number of additional experiments were carried out. To verify that the simultaneous action of ultraviolet and ultrasound was essential we performed control experiments with consequent treatment of the palladium salt-containing reaction mixture with UV irradiation and with ultrasound (and vice versa). In both cases, polydisperse palladium particles were obtained, but the system initially treated with ultrasound (see Figures S69–S71) contained the higher amount of individual microdroplets filled with small palladium particles compared to the mixture initially treated with UV radiation (see Figures S72–S74). This observation allowed one to conclude that the formation of the microcompartments was more important for the control of metallic particle synthesis than destruction of particle aggregates by ultrasound after the synthesis, which may be initially proposed as a main effect of sonication. Interestingly, the carried out experiments demonstrated only partial stability of the created microcompartments under the reaction conditions, so to get the total control over the synthesis, the sonication should be performed until the end of the process.

Summarizing the results of electron microscopy observations, one can conclude that for microstructured IL-based media, the sonication-driven modification of the reaction mixture structure can be considered as the main effect responsible for the synthesis of well-dispersed metallic particles. At the same time, the effect of aggregate destruction under the action of ultrasound cannot be totally eliminated; however, its contribution to the overall reaction mechanism is not significant.

## CONCLUSIONS

In conclusion, the effect of the mechanical standing waves on the structural and chemical properties of mixtures of various ionic liquids with water was detected by using a combination of liquid phase electron microscopy and spectroscopy studies. The mechanism of high-frequency sound wave interactions with microstructures in liquid media was revealed. The results indicate that multistep water transfer between different phases of the studied IL/water mixtures takes place under sonication conditions. The migration of water leads to the formation of different morphologies, namely, water-rich microdroplets, films, and solid inclusions and to the partial removal of water from the liquid media. The employment of a specially designed microsonication stage for SEM measurements demonstrated excellent results in sonication of small amounts of sample with high degree of localization.

The observed high-frequency sound wave effect on the IL/water mixtures was successfully used for the control of chemical reactivity of the liquid media in metal nanoparticle syntheses. The results indicate that sonication of the reaction mixture containing ionic liquid, water, and a water-soluble metal salt leads to formation of soft dissipative microreactors that effectively promote the formation of small and uniform gold and palladium nanoparticles.

The microsonication stage developed in the present study opens flexible opportunities for the direct sonochemical mechanistic studies and for connection of ultrasound technique with nanotechnology, and we expect the growth of interest to the use of the proposed technique for applications in different areas of chemistry and materials science.

## EXPERIMENTAL SECTION

### General Considerations

Ionic liquids (1-butyl-3-methyl imidazolium tetrafluoroborate, [C$_{4}$mim][BF$_4$]; 1-butyl-3-methyl imidazolium trifluoromethanesulfonate, [C$_{4}$mim][OTf]; 1-ethyl-3-methyl imidazolium trifluoromethanesulfonate, [C$_{4}$mim][OTf]), deionized water, metal salts, oxide materials (TiO$_2$, SiO$_2$, γ-Al$_2$O$_3$), and carbon materials (graphite, multivalien carbon nanotubes) were purchased from commercial sources. 1H NMR spectra were collected with the use of a Fourier 300 HD spectrometer operating at 300.1 MHz for 1H nuclei. The NMR chemical shifts are given relative to the corresponding deuterated solvent signals. The spectra were processed using the Bruker Topspin 2.1 software package (Bruker). Scanning electron microscopy measurements were performed on a Hitachi SU8000 field-emission scanning electron microscope (FE-SEM). Images were acquired in the secondary electron mode at 1 or 2 kV accelerating voltage. Transmission electron microscopy measurements were carried out with the use of a Hitachi HT7700 instrument operating in the bright-field mode at 100 kV accelerating voltage. IR spectra were registered with a Bruker ALPHA FT-IR spectrometer. Leica DM4 B upright digital microscope was employed for optical microscopy analysis.

### Design of Microsonication Stage for Electron Microscopy

For the electron microscopy observations of the ultrasound effect with a high degree of sample localization, a special microsonication stage was developed. A compact (1 cm in diameter) piezo ultrasound transducer KPUS–40FS–10TR–650 (Ningbo Kepo Electronics Co., Ltd.) was used as the source of ultrasound. The ultrasound transducer...
was fixed on a SEM holder for bulk samples and connected to a function generator (GZCh-KL, Russia) operating at frequencies up to 100 kHz and 12 W power. For each particular experiment, the frequency of the generator was adjusted for the maximal piezo ultrasound transducer performance with the use of a 20–30 μL water droplet as a control sample. The optimal frequencies were within the range 35 ± 3 kHz. See Figures 3A and 3B for a photograph and a principal scheme of the reactor and Figures S1 and S2 for the enlarged images.

**SEM Observation of the Sonication Effect with the Use of a Microsonication Stage**

One-hundred microliters of ionic liquid and 10 μL of water were placed into a standard 1.5 mL plastic tube and vigorously stirred for 1 min using a vortex shaker. The resulting solution was applied to a copper TEM grid (200 mesh) using a micropipette. The excess of solution was removed from the grid surface by a scalpel blade. The resulting sample was placed on the working surface of the piezo ultrasound transducer fixed on the holder (see the description above). The sample of water solution in ionic liquid was treated with ultrasound in the air for a certain amount of time and then transferred to the electron microscope chamber for FE-SEM measurements. Ten successive points corresponding to 0, 5, 15, 30, 60, 120, 240, 360, and 900 s of sonication for [C4mim][BF4], 9 successive points corresponding to 0, 5, 10, 15, 20, 25, 30, 60, 120, 240, 360, and 900 s of sonication for [C4mim][OTf], and 12 successive points corresponding to 0, 5, 10, 15, 20, 25, 30, 60, 120, 240, 360, and 900 s for [C4mim][BF4] were collected. FE-SEM data were processed using Digimizer v4.3.0 software.

**Measurements of the Sample Weight Changing during Sonication**

Four-hundred microliters of [C4mim][BF4] ionic liquid and 40 μL of water were placed into a standard 1.5 mL plastic tube and vigorously stirred for 1 min using a vortex shaker. Thirty microliters of the resulting solution was placed on the working surface of the piezo ultrasound transducer fixed on the holder (see the description above). The sample weight was measured using an Ohaus Discovery semi-micro analytical balance after 0, 5, 15, 30, 60, 120, 240, 360, 600, and 900 s of sonication. The results were averaged for three successive experiments.

**IR Spectroscopy Monitoring of the Sonication Effect**

Four-hundred microliters of [C4mim][BF4] ionic liquid and 40 μL of water were placed into a standard 1.5 mL plastic tube and vigorously stirred for 1 min using a vortex shaker. Thirty microliters of the resulting solution was placed on the working surface of the piezo ultrasound transducer fixed on the holder (see the description above). The droplet of the sample was treated with ultrasound for a certain amount of time. In total, 8 samples corresponding to 0, 30, 60, 120, 240, 360, 600, and 900 s of sonication were obtained. The samples were studied as a thin layer of neat liquid between two CaF2 windows.

**1H NMR Spectroscopy Monitoring of the Sonication Effect**

Four-hundred microliters of [C4mim][BF4] ionic liquid and 40 μL of water were placed into a standard 1.5 mL plastic tube and vigorously stirred for 1 min using a vortex shaker. Thirty microliters of the resulting solution was placed on the working surface of the piezo ultrasound transducer fixed on the holder (see the description above). The droplet of the sample was treated with ultrasound for a certain amount of time. In total, 4 samples corresponding to 0, 120, 360, and 600 s of sonication were obtained. The samples were studied as solutions in 600 μL of acetone-d6.

**Synthesis of Gold Nanoparticles in Ionic Liquid Media**

HAuCl4·3H2O (3.9 mg, 0.01 mmol) was dissolved in 500 μL of deionized water. Ten microliters of the resulting gold salt solution and 100 μL of [C4mim][BF4] ionic liquid were placed into a standard 1.5 mL plastic tube and vigorously stirred for 1 min using a vortex shaker. A 1 μL droplet of the resulting solution was placed on the working surface of the piezo ultrasound transducer fixed on the holder (see the description above). The droplet was covered with a titanium TEM grid (200 mesh). The whole setup was placed under a DRT-220 mercury-vapor ultraviolet lamp (Russia) for 15 min. The UV irradiation was carried out without additional sonication or under simultaneous treatment with ultrasound for 5 or 15 min starting from the beginning of the UV irradiation. After the reaction, the setup was transferred to the electron microscope chamber, and the morphology of the reaction mixture was analyzed by FE-SEM.

**UV Irradiation of the IL/Water Mixture**

One-hundred microliters of [C4mim][BF4] ionic liquid and 10 μL of water were placed into a standard 1.5 mL plastic tube and vigorously stirred for 1 min using a vortex shaker. A 1 μL droplet of the resulting solution was placed on the surface of aluminum specimen stub and covered with a titanium TEM grid (200 mesh). The prepared sample was placed under a DRT-220 mercury-vapor ultraviolet lamp (Russia) for 15 min. Morphology of the resulting liquid was analyzed by FE-SEM.

**Synthesis of Palladium Nanoparticles in Ionic Liquid Media**

(NH4)2PdCl6 (3.6 mg, 0.01 mmol) was dissolved in 500 μL of deionized water. Ten microliters of the resulting palladium salt solution and 100 μL of [C4mim][BF4] ionic liquid were placed into a standard 1.5 mL plastic tube and vigorously stirred for 1 min using a vortex shaker. A 1 μL droplet of the resulting solution was placed on the working surface of the piezo ultrasound transducer fixed on the holder (see the description above). The droplet was covered with a titanium TEM grid (200 mesh). The whole setup was placed under a DRT-220 mercury-vapor ultraviolet lamp (Russia) for 15 min. The UV irradiation was carried out without additional sonication or under simultaneous treatment with ultrasound for 15 min starting from the beginning of the UV irradiation. After the reaction, the setup was transferred to the electron microscope chamber, and the morphology of the reaction mixture was analyzed by FE-SEM.

**Synthesis of Supported Palladium Nanoparticles**

(NH4)2PdCl6 (3.6 mg, 0.01 mmol) was dissolved in 500 μL of deionized water. Fifty microliters of the resulting palladium salt solution and 500 μL of [C4mim][BF4] ionic liquid were placed into a standard 1.5 mL plastic tube and vigorously stirred for 1 min using a vortex shaker. Thirty microliters of the resulting solution and 2 mg of the support (graphite, multiwalled carbon nanotubes (MWCNTs), TiO2 (anatase), gamma-Al2O3, and SiO2 (silica gel)) were placed on the working surface of the piezo ultrasound transducer fixed on the holder (see the description above). The droplet was covered with a titanium TEM grid (200 mesh). The whole setup was placed under a DRT-220 mercury-vapor ultraviolet lamp (Russia) for 15 min. The UV irradiation was carried out without additional sonication or under simultaneous treatment with ultrasound for 15 min starting from the beginning of the UV irradiation. After the reaction, the resulting mixture was analyzed by TEM. Before TEM measurements, the samples were deposited on the carbon-coated copper TEM grids (200 mesh) from suspension in isopropanol.

**Synthesis of Palladium Nanoparticles with Sequential UV/Ultrasound Treatment**

(NH4)2PdCl6 (3.6 mg 0.01 mmol) was dissolved in 500 μL of deionized water. Ten microliters of the resulting palladium salt solution and 100 μL of [C4mim][BF4] ionic liquid were placed into a standard 1.5 mL plastic tube and vigorously stirred for 1 min using a vortex shaker. A 1 μL droplet of the resulting solution was placed on the working surface of the piezo ultrasound transducer fixed on the holder (see the description above). The droplet was covered with a titanium TEM grid (200 mesh). The whole setup was placed under a DRT-220 mercury-vapor ultraviolet lamp (Russia) for 15 min. After UV irradiation, the reaction mixture was treated with ultrasound for 15 min under the same experimental conditions. After the reaction, the setup was transferred to the electron microscope chamber, and the morphology of the reaction mixture was analyzed by FE-SEM.
microscope chamber, and the morphology of the reaction mixture was analyzed by FE-SEM. Another sample was prepared and analyzed by a similar method but with initial treatment with ultrasound for 15 min followed by UV irradiation for another 15 min.

### ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.0c00024.

Additional electron microscopy data for experiments with mini-source of ultrasound, SEM and TEM images for experiments with metal particles, results of the particles size distribution analysis, NMR spectra for IL/water systems, and enlarged scheme and photograph of the ultrasonic microreactor (PDF)

Animated set of successive FE-SEM images of the [C₄mim][BF₄]-water mixture before sonication and after sonication for 5, 15, 30, 60, 120, 240, 360, 600, and 900 s with images recorded at 250× magnification (AVI)

Animated set of successive FE-SEM images of the [C₄mim][OTf]-water mixture before sonication and after sonication for 5, 15, 30, 60, 120, 240, 360, 600, and 900 s with images recorded at 400× magnification (AVI)

Animated set of successive FE-SEM images of the [C₄mim][OTf]-water mixture before sonication and after sonication for 5, 10, 15, 20, 25, 30, 60, 120, 240, 360, and 600 s with images recorded at 250× magnification (AVI)

Animated set of successive FE-SEM images of the [C₄mim][OTf]-water mixture before sonication and after sonication for 5, 15, 30, 60, 120, 360, 600, and 900 s with images recorded at 250× magnification (AVI)

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**Author Contributions**

A.S.K. designed electron microscopy techniques, performed the experimental work, and measured and analyzed the data. E.S.D. carried out the studies on metal nanoparticles synthesis. V.P.A. created the idea and supervised the whole project. All authors discussed the results, contributed to writing the manuscript, and approved the final version of the manuscript for submission.

**Notes**

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