

Revealing Dynamic Structural Changes in Platinum-Group-Metal Nanoparticles during the Catalytic Hydrogen Evolution Reaction

Yuto Maruta, * Hirotaka Ashitani, Shogo Kawaguchi, Toshiaki Ina, Osami Sakata, Yoshiki Kubota, Megumi Mukoyoshi, Hiroshi Kitagawa, * Kohei Kusada *

AUTHOR ADDRESS: kusada.kohei.236@m.kyushu-u.ac.jp

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ABSTRACT: Despite the crucial role of structural dynamics in catalytic reactions, the influence of nanoparticle (NP) size and elemental composition on these dynamics under electrochemical conditions is often overlooked. Herein, we present the first systematic operando investigation of the size- and element-dependent structural and electronic dynamics of platinum-group-metal (PGM) NPs (Pt, Pd, Rh, and Ru) during the hydrogen evolution reaction (HER) under both acidic and alkaline conditions. By combining operando powder X-ray diffraction and X-ray absorption spectroscopy, we revealed that the smaller the NPs, the more significant the structural changes, indicating surface adsorbate-induced dynamics. Notably, we also found that the constant lattice expansion in Pt, Pd, and Rh NPs occurred on a slow timescale (several tens of seconds). The electronic states of these NPs were more reductive than their standard zero-valent states owing to interactions with hydrogen. However, the Ru NPs remained oxidized even during the HER, indicating distinct electronic changes in the PGMs. These findings reveal previously unrecognized dynamics, providing a comprehensive understanding of how size and composition influence the structural and electronic changes of PGM NPs in realistic electrochemical reaction environments. This study establishes a foundational framework for operando catalyst investigations and opens new avenues for the rational design of size- and element-optimized HER catalysts.

Water electrolysis technologies play an essential role in a sustainable hydrogen society, where both proton-exchange membrane (PEM) and anion-exchange membrane (AEM) water electrolysis are attracting much attention.^{1–3} The hydrogen evolution reaction (HER) is a key reaction in these systems because it directly determines the efficiency of hydrogen generation.⁴ HER catalysts applied under acidic conditions in PEM systems have been extensively studied, and interest in alkaline conditions for AEM systems has grown rapidly in recent years.⁵ Platinum-group metals (PGMs), including Pt, Pd, Rh, and Ru, are well known for their excellent HER activity, which is often interpreted based on Sabatier's principle, stating that higher catalytic activity is achieved when the interaction between the catalyst surface and intermediates is neither too strong nor too weak.^{6–12} Therefore, PGM catalysts must be comprehensively evaluated under both acidic and alkaline conditions in order to rationally design highly active HER catalysts that are adaptable to a wide range of practical environments.

Despite the recent progress in theoretical calculations and ex situ characterization, understanding the real-time structural and electronic dynamics of catalysts under actual operating conditions remains challenging. Because electrocatalytic reactions occur mainly at the catalyst surface, dynamic changes such as lattice strains and shifts in the oxidation state caused by adsorbates can significantly impact the catalytic performance.^{13,14} In particular, nanoparticles (NPs),

which have a high surface-to-volume ratio, are expected to exhibit size-sensitive structural behavior induced by surface adsorbates; however, this aspect has been frequently overlooked in HER catalysis. Although some operando techniques, such as powder X-ray diffraction (PXRD), X-ray absorption spectroscopy (XAS), and Raman spectroscopy, have revealed important structural and electronic dynamics during catalysis,^{15–18} a systematic understanding of how different metals behave dynamically across a range of particle sizes and pH conditions is lacking.

In this paper, we present a comprehensive investigation of the size- and metal-dependent dynamics of PGM NPs during the acidic and alkaline HER using operando synchrotron PXRD and XAS. We synthesized Pt, Pd, Rh, and Ru NPs with particle sizes of 3 or 5 nm and observed large structural changes in small NPs during the HER. Time-resolved operando PXRD measurements captured the subtle lattice expansion of Pt, Pd, and Rh NPs on a slow time scale. Operando XAS measurements confirmed that the Pt, Pd, and Rh NPs had more reductive states than their standard zero-valence forms and more oxidized states than Ru NPs.

NPs with an average particle size of 3 nm were synthesized using a one-pot polyol method (Supporting Information) and characterized using transmission electron microscopy (TEM) and PXRD (Figure S1, Table S1). The synthesized 3 nm Pt NPs were supported on carbon (Vulcan XC-

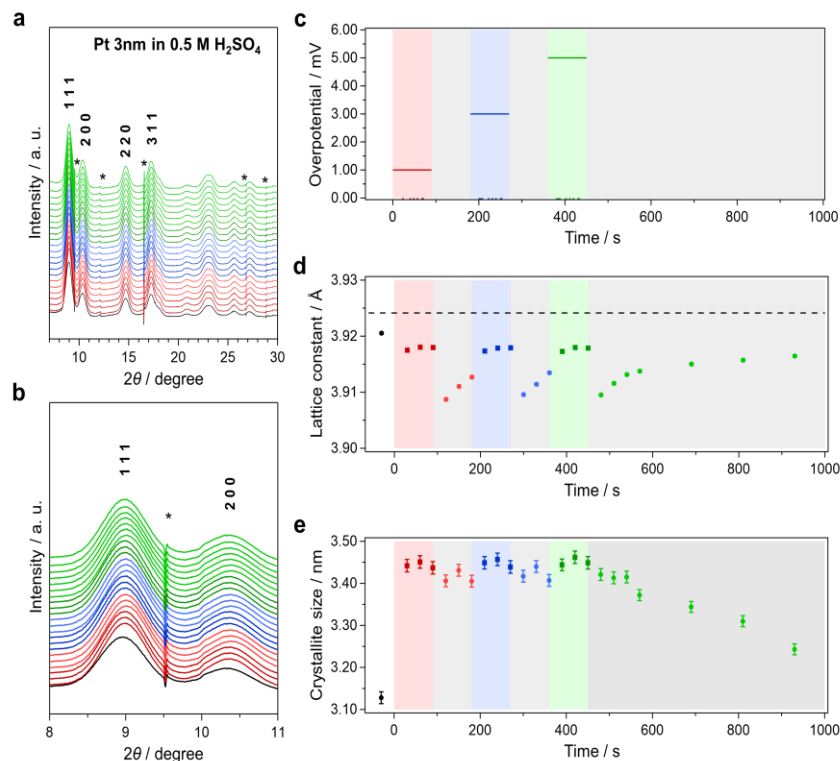


Figure 1. (a) Background-subtracted operando PXRD patterns collected at varying applied potentials (vs. RHE) in 0.5 M H₂SO₄. The black curve represents the measurement at open-circuit potential (OCP) before applying potential. The red, blue, and green curves correspond to measurements at -1, -3, and -5 mV, respectively. The dark-colored curves indicate data acquired during the HER, while the light-colored curves indicate data recorded after returning to OCP. (b) Magnified view of the PXRD patterns in the 2θ range of 8°–11°, highlighting peak shifts during and after HER. (c) Schematic of the operando measurement protocol. The white region indicates the initial OCP condition. The red, blue, and green shaded areas represent applied potentials of -1, -3, and -5 mV, respectively. The gray areas indicate periods at OCP. (d) Time-resolved lattice constants obtained from the Rietveld-refined PXRD data shown in (a), corresponding to the measurement sequence in (c). Error bars are included within the markers. (e) Crystallite sizes obtained from Rietveld refinement.

72R), and the catalyst was dispersed in a mixture of isopropanol and 5 wt% Nafion. The catalyst ink was uniformly deposited on carbon paper (Supporting Information). Operando PXRD measurements were conducted using a custom-designed electrochemical cell at BL13XU SPring-8 (Supporting Information and Figures S2–S4).¹⁹ PXRD patterns were measured first under an open-circuit potential (OCP) and then every 30 s to monitor structural changes in a sequence of applied potentials. Varying potentials (-1, -3, and -5 mV vs. RHE) were sequentially applied for 90 s each at 90 s intervals at OCP (Figure 1c). The measurements were stopped at ~10 min after the final potential step (-5 mV) to observe the structural relaxation after HER. The background signals were subtracted to extract structural changes in the catalyst (Supporting Information). Figures 1a and 1b show the background-subtracted PXRD patterns of 3 nm Pt NPs in 0.5 M H₂SO₄ during and after the HER. The PXRD patterns were Rietveld refined to quantify the dynamic changes in the lattice constants and crystallite sizes (Figures S5 and S6). Figure 1d indicates that the lattice constant of the 3 nm Pt NPs repeatedly changed during the HER under all applied potentials and continued to change after the potential was turned off. The lattice contraction of the 3 nm Pt NPs reached a steady value within 60 s during the HER and gradually returned to the initial state at the OCP. Simultaneously, the

crystallite size increased under the HER conditions, likely owing to surface reduction, and subsequently decreased to its original size after returning to the OCP (Figure 1e). These changes in the lattice constants and crystallite sizes were accompanied by a sequence of applied potentials, indicating that we successfully tracked the HER-induced dynamic structural changes of the catalyst.

To confirm whether these structural changes were actually induced by the HER, we investigated Pt NPs of different sizes (5 nm and commercial Pt black, Supporting Information). The 5 nm Pt NPs were characterized using TEM and PXRD (Figure S7). Operando PXRD measurements were performed in both acidic (0.5 M H₂SO₄) and alkaline (1 M KOH) solutions (Figures S8–S10). Figures 2b and 2d show the relative changes in the lattice constants from the initial values at the OCP used to evaluate the size-dependent behavior. The 3 nm Pt NPs exhibited the most pronounced variations under HER conditions in both electrolytes. These results confirm that our operando PXRD approach is capable of capturing subtle surface-induced structural dynamics during the HER, which have likely been overlooked in previous studies owing to the high surface-to-volume ratio of small NPs. We also investigated black Rh and Pd NPs with sizes of 3 nm and 5 nm (Supporting Information and Figures S12–S21). While 3 nm Rh NPs changed the most, 5 nm Pd NPs exhibited more pronounced structural variations than

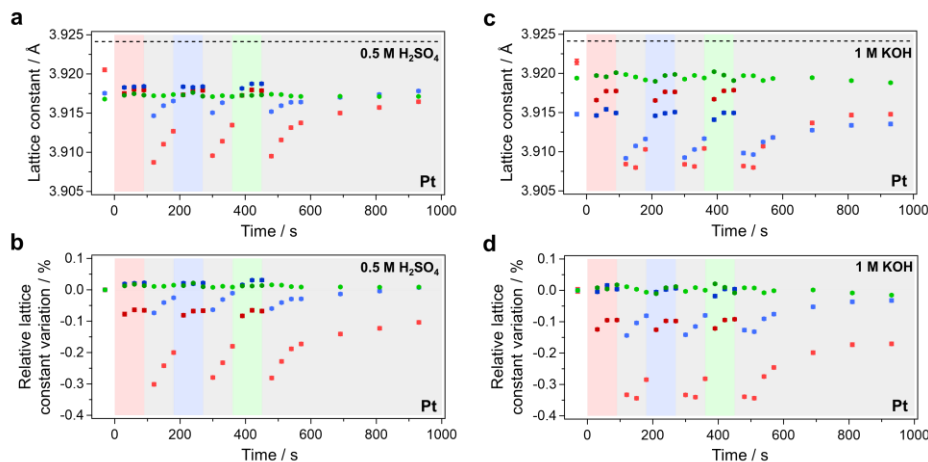


Figure 2. (a, c) Time-resolved lattice constants of Pt NPs during and after HER, measured in (a) 0.5 M H_2SO_4 and (c) 1 M KOH. (b, d) Relative changes in lattice constants, referenced to the initial value obtained at OCP before electrochemical measurement, in (b) 0.5 M H_2SO_4 and (d) 1 M KOH. The timing of applied potentials corresponds to the measurement sequence shown in Fig. 1c. The data represent 3 nm particles (red), 5 nm particles (blue), and commercial Pt black (green). The dark-colored markers indicate values recorded during the HER, while the light-colored markers represent measurements taken after returning to OCP. The error bars are included within the markers.

their smaller counterparts (Figures S22 and S23). This trend for Pd is in line with previous studies on the size dependence of hydrogen absorption in Pd NPs, which found that hydrogen storage capacity decreased with decreasing particle size.²⁰ Accordingly, the structural changes observed for Pd NPs are likely dominated by hydrogen absorption in their lattice rather than surface interactions. Insignificant changes in the lattice constants of Pd black during the HER were observed at lower potentials because Pd black showed lower activity in both electrolytes (Figure S23). These findings indicate that smaller NPs are ideal model systems for clarifying the surface-induced structural dynamics during electrochemical catalytic reactions.

To investigate the element dependence, 3 nm Ru NPs were also measured (Supporting Information and Figures S26 and S27). Figure 3 shows the time variation of the lattice constants and current of 3 nm Pt, Rh, Pd, and Ru NPs at -5 mV. The current–time (i – t) curves show that the current rapidly increased and then stabilized for all metals. Notably, the lattice constants of the 3 nm Pt, Pd, and Rh NPs also changed in a similar time-dependent manner: they increased until 60 s and did not significantly change after 60 s under both conditions. By contrast, the

lattice constant of the Ru NPs decreased slightly under acidic conditions, whereas under alkaline conditions, it continued to increase throughout the measurement period. These behaviors indicate that Ru responds differently to the electrochemical environment than the other PGM NPs.

To further investigate the elemental dependence of the structural changes during the HER, operando XAS measurements were conducted for 3 nm Pt, Rh, Pd, and Ru NPs under both conditions (Supporting Information and Figure S28). The Pt- L_{3} edge was measured for 3 nm Pt NPs, and the K-edge was measured for 3 nm Rh, Pd, and Ru NPs. XAS spectra were obtained at the OCP before electrochemical measurements. After pretreatment, operando XAS measurements were also performed at -5 mV. All NPs were found to be reduced during the HER (Figure 4). To evaluate the electronic states of the NPs, the Pt- L_{3} white line intensity and the K-edge positions of Rh, Pd, and Ru were compared (Figure 5).^{21,22} Notably, the 3 nm Pt, Rh, and Pd NPs showed lower valence states than their reference foil samples in both acidic and alkaline environments (Figures 5a, 5b, and 5c).

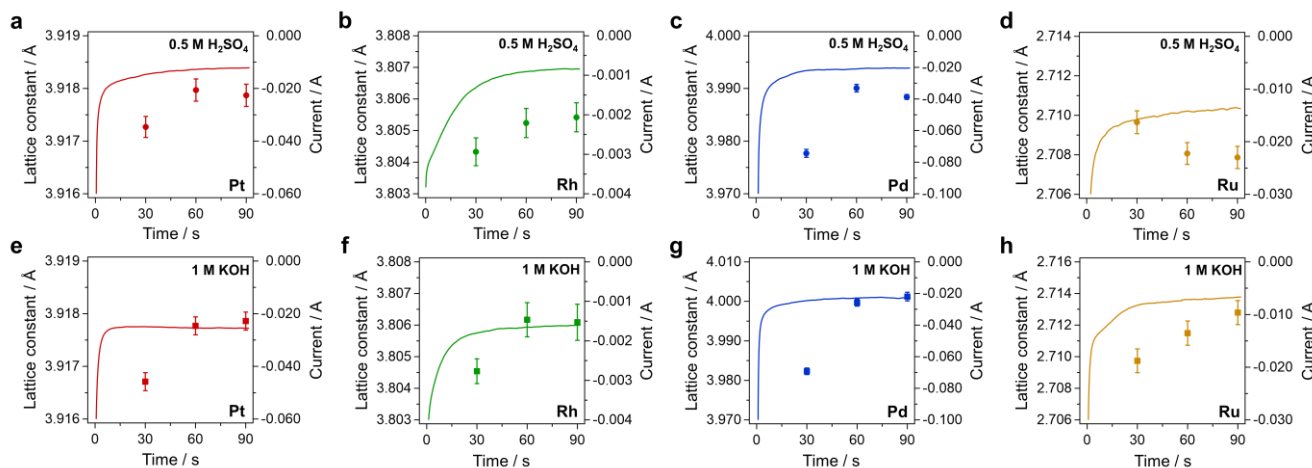


Figure 3. Time-dependent lattice constant variations and current at -5 mV (a–d) in 0.5 M H_2SO_4 and (e–h) in 1 M KOH. (a, e) Results for 3 nm Pt NPs, (b, f) Rh NPs, (c, g) Pd NPs, and (d, h) Ru NPs. The markers represent the lattice constants.

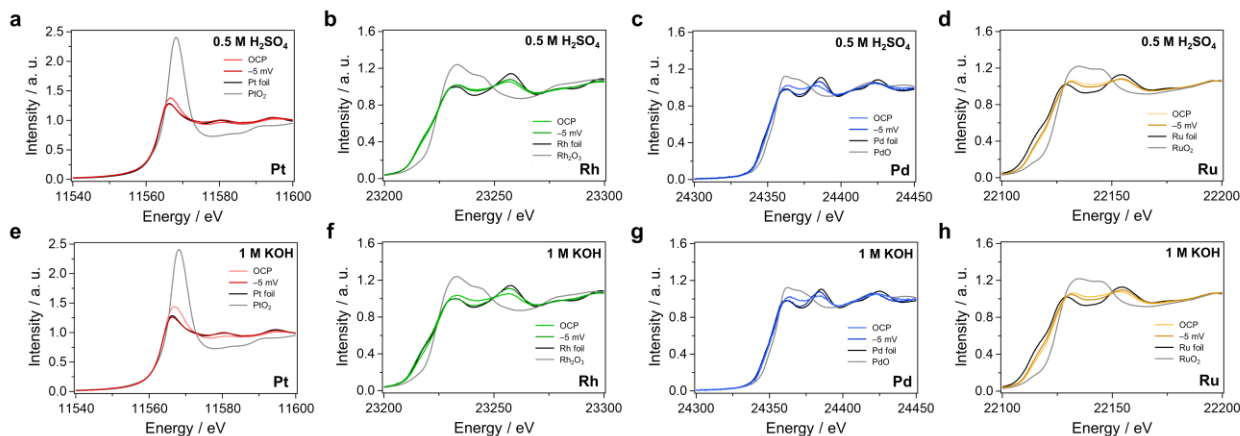


Figure 4. (a–d) Operando XAS spectra obtained at OCP before electrochemical measurement and at -5 mV in 0.5 M H_2SO_4 and (e–h) 1 M KOH . (a, e) Pt NPs (b, f) Pd NPs, (c, g) Rh NPs, and (d, h) Ru NPs. Reference samples, including bulk and oxide forms, are shown in all graphs for comparison.

These results can be attributed to the metal–hydrogen interaction of the NPs.^{23,24} By contrast, the oxidation states of the 3 nm Ru NPs were higher than those of the Ru foil (Figure 5d), indicating that the Ru NPs were not fully reduced during the HER.

By combining the operando PXRD and XAS results, the element-dependent structural and electronic dynamics of PGM NPs under HER conditions were systematically clarified. The time-dependent subtle increase in lattice constants of less than 0.1% is likely attributed to the interaction between the NP surface and adsorbed hydrogen, as doping electrons into metals weakens the metallic bond and may lead to slight lattice expansion. In the case of the Pd NPs, the over 0.1% lattice expansion is due not only to surface adsorption but also to hydrogen absorption within the particles. Operando XAS revealed that the Ru NPs were not fully reduced at the HER potentials in this experiment, unlike the other PGM NPs. This observation is consistent with theoretical predictions showing that Ru has the largest difference in adsorption energies between H and O among the four PGMs studied²⁵, indicating that Ru remains partially oxidized under HER conditions. The lattice constant variation observed for the Ru NPs likely reflects the complex interplay between the incomplete reduction, hydrogen adsorption, and surface oxidation. Further investigation is required to fully elucidate the origin of this behavior. Operando XAS revealed that Pt, Rh, and Ru NPs exhibited more reduced electronic states under alkaline conditions than under acidic conditions. This may be attributed to the difference in hydrogen coverage between acidic and alkaline media²⁶. This phenomenon is consistent with the operando PXRD data, which showed that the

lattice constants were slightly larger in alkaline solution. These findings demonstrate that subtle structural dynamics were captured using our combined operando PXRD–XAS approach. In summary, we systematically investigated, for the first time, the size- and metal-dependent structural and electronic dynamics of PGM NPs during the HER in acidic and alkaline environments. Operando PXRD revealed that smaller Pt and Rh NPs exhibited more pronounced lattice changes, which were attributed to surface hydrogen adsorption, whereas larger Pd NPs changed more substantially owing to hydrogen absorption inside the particles. Time-resolved measurements showed gradual lattice expansion for the Pt, Pd, and Rh NPs under both pH conditions, whereas the Ru NPs expanded only in alkaline media. Operando XAS revealed that the electronic states of Pt, Rh, and Ru NPs were more reduced under alkaline conditions than under acidic conditions, which likely contributed to the larger lattice expansion in alkaline media. For Ru, partial reduction can account for its unique structural response. Importantly, the combination of operando PXRD and XAS enabled the detection of previously overlooked subtle dynamic changes in both the structure and electronic states during electrochemical reactions. These findings reveal new insights into element-specific catalytic behavior. This study opens a new avenue for catalyst discovery by incorporating dynamic structural behavior into design strategies.

AUTHOR INFORMATION

Corresponding Author

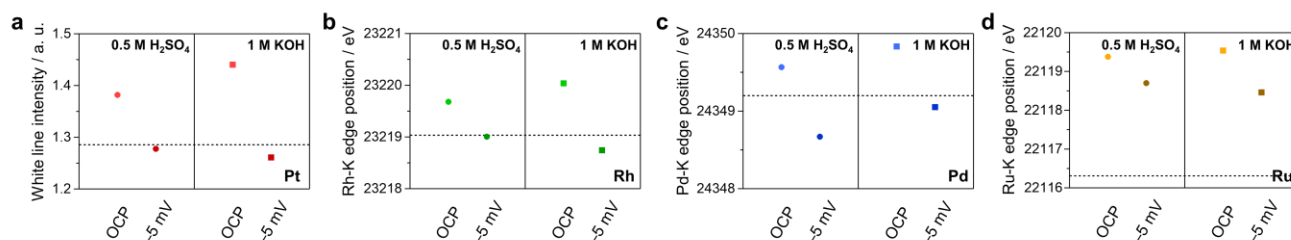


Figure 5. (a) White line intensity of XAS spectra for Pt NPs obtained at OCP before electrochemical measurement and at -5 mV in both 0.5 M H_2SO_4 and 1 M KOH . (b–d) Peak positions of XAS spectra for (b) Pd NPs, (c) Rh NPs, and (d) Ru NPs at OCP before electrochemical measurements and at -5 mV in 0.5 M H_2SO_4 and 1 M KOH . The black dashed line indicates the values for the foil reference samples.

Yuto Maruta-Division of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan

Hiroshi Kitagawa-Division of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan

Kohei Kusada-Division of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan; The HAKUBI Center for Advanced Research, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan; Institute of Advanced Study, Kyushu University, 6-1, Kasugakōen, Kasuga-shi, Fukuoka, 816-8580, Japan; Faculty of Engineering Sciences, Kyushu University, 6-1, Kasugakōen, Kasuga-shi, Fukuoka, 816-8580, Japan

Authors

Hirofumi Ashitani- Japan Synchrotron Radiation Research Institute (JASRI), 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan

Shogo Kawaguchi- Japan Synchrotron Radiation Research Institute (JASRI), 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan

Toshiaki Ina- Japan Synchrotron Radiation Research Institute (JASRI), 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan

Osami Sakata- Japan Synchrotron Radiation Research Institute (JASRI), 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan

Yoshiki Kubota- Department of Physics, Graduate School of Science, Osaka Metropolitan University, 3-3-138 Sugimoto-cho, Sumiyoshi-ku, Osaka, 558-8585, Japan

Megumi Mukoyoshi- Division of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan

Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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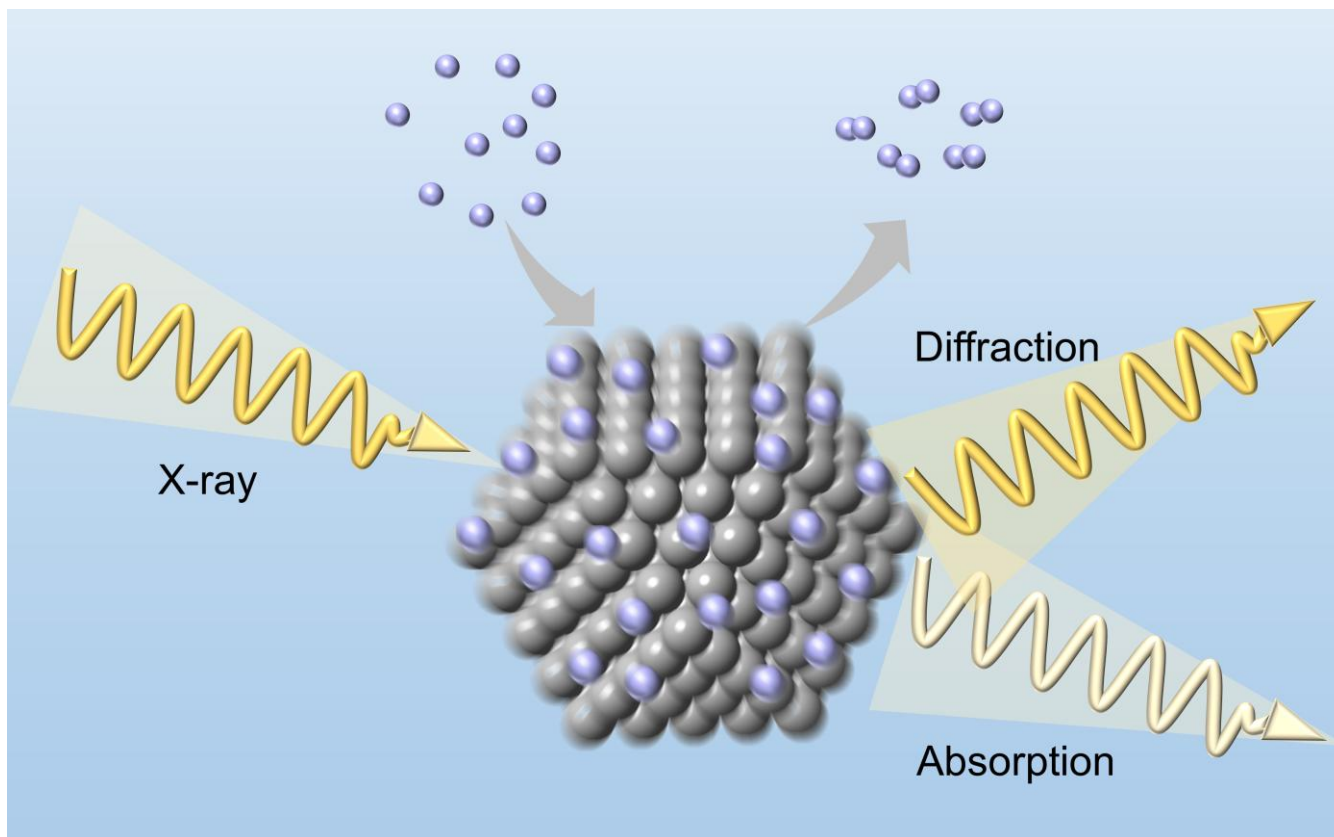
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