Building nanoalloy libraries from laser-induced thermionic emission reduction experiments

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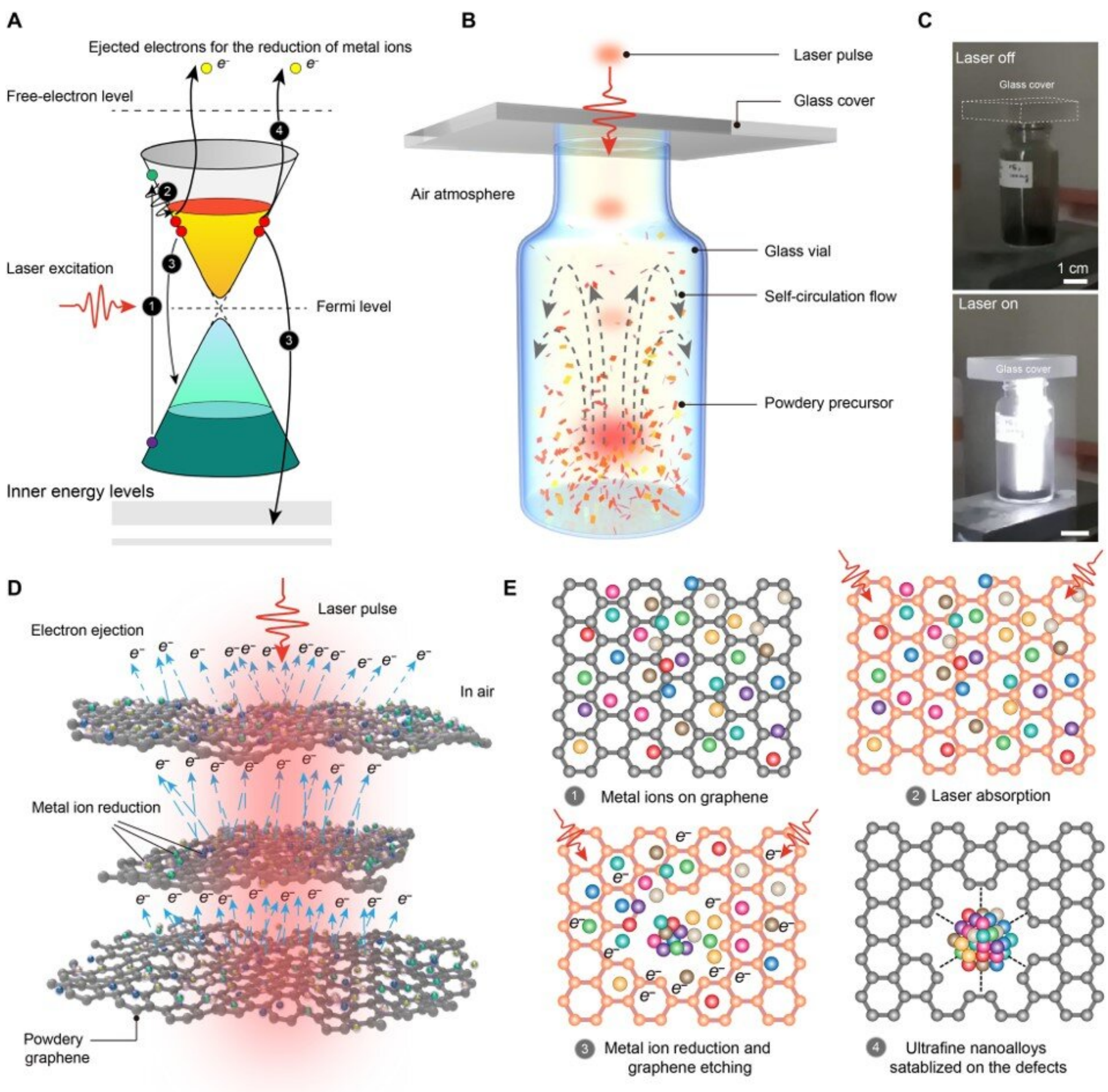
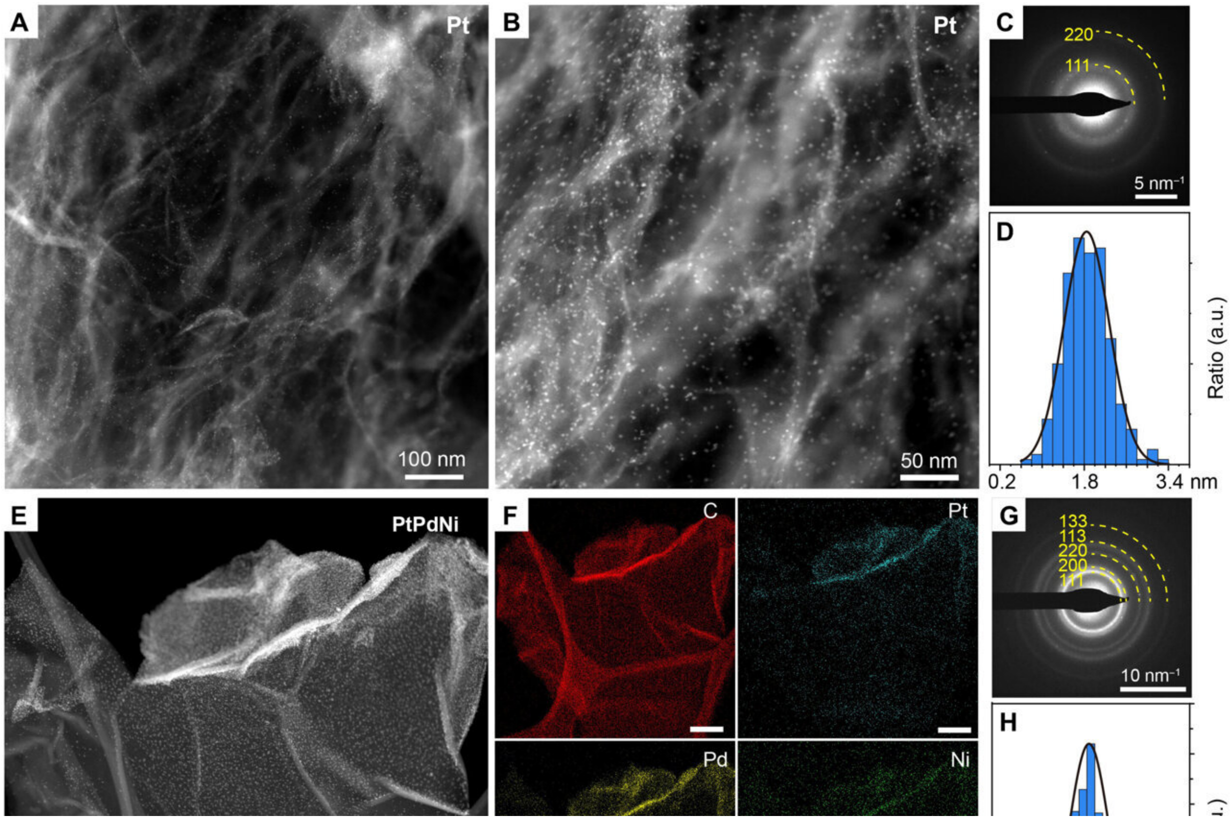


The LITER for the synthesis of nanoalloys. (A) Illustration of the laser-induced thermionic emission in graphene. Four steps were divided in this process: (1) The laser photons excite electrons from the valence band to the conduction band; (2) a population inversion state is achieved; (3) the Auger-like pathways of electrons; and (4) some hot electrons gain enough energy and eject out as free electrons. (B)The schematic of the laser propulsion of graphene nanoplates across a glass vial that achieved evenly irradiation and reduction of the metal salts loaded on graphene. (C) The optical images of the precursor on the glass vial when the laser is on and off. (D) The illustration of laser-induced electron emission on graphene with metal ions loaded on the surface. (E) The four steps of the LITER process for the formation of ultrafine nanoalloys on carbonaceous supports. Balls with different colors represent different metal ions or atoms. Credit: *Science Advances* (2022). DOI: 10.1126/sciadv.abm6541

High-entropy nanoalloys (HENA) have widespread applications in materials science and applied physics. However, their synthesis is challenging due to slow kinetics that cause phase segregation, sophisticated pretreatment of precursors, and inert conditions. In a new report now published in *Science Advances*, Haoqing Jiang and a team of scientists in industrial engineering, nanotechnology and materials science in the U.S., and China, described a process of converting metal salts to ultrafine HENAs on carbonaceous supports using nanosecond pulse lasers. Based on the unique laser induced thermionic emission and etch on carbon, the team gathered the reduced metal elements of ultrafine HENAs stabilized via the defective carbon support. The resulting process produced a variety of HENAs ranging from 1-to-3 nanometers and metal elements of up to 11 grams per hour, with a productivity reaching 7 grams per hour. The HENAs exhibited excellent catalytic performance during oxygen reduction, with great practical potential.

Developing high-entropy nanoalloys (HENAs)

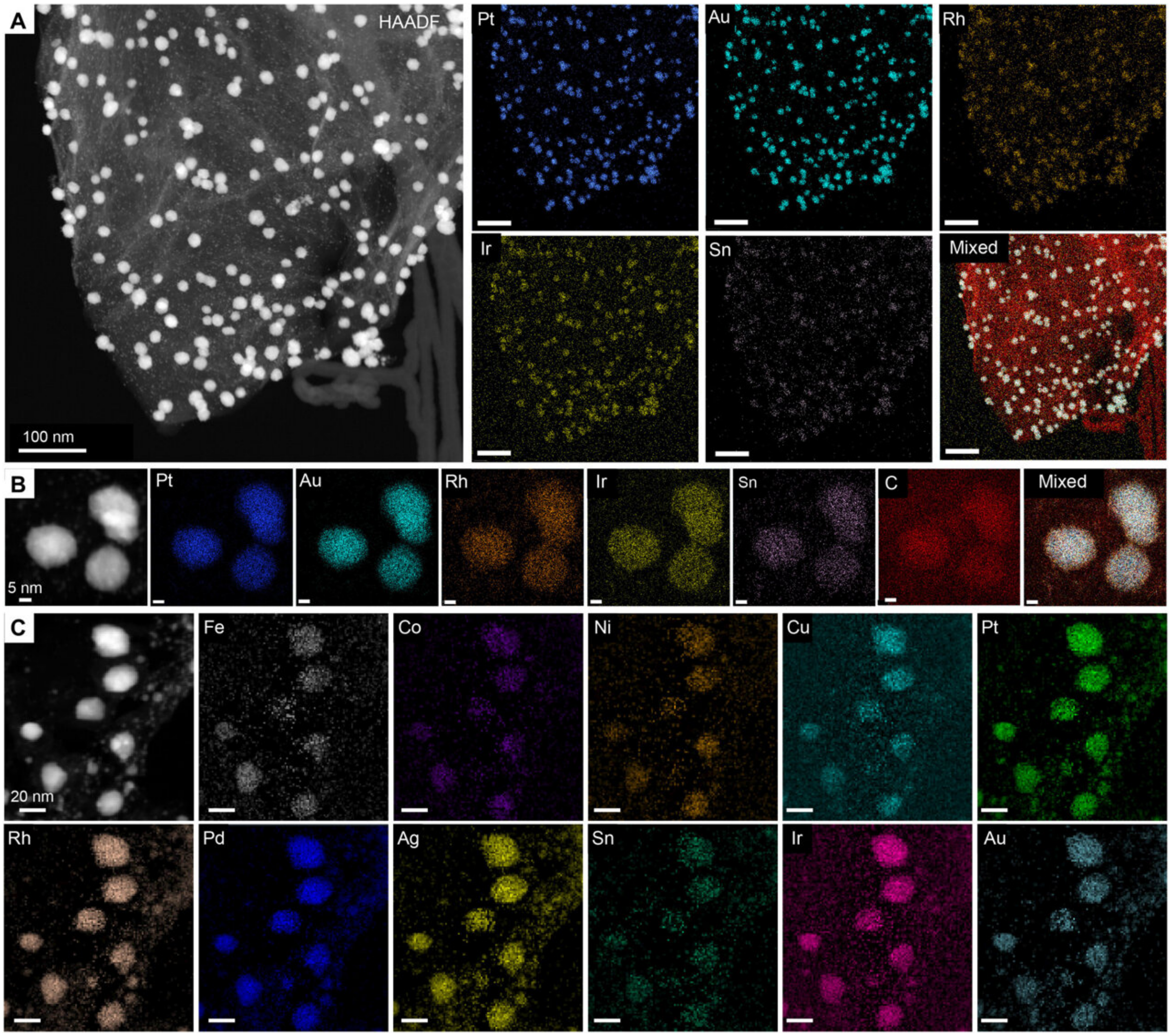
Metal nanoalloys form critical catalysts with widespread applications in chemical reactions across energy fields and environmental science. During conventional bottom-up engineering routes, such as wet chemistry techniques deployed by chemists to synthesize metal nanoalloys, the miscibility of each metallic element in the phase diagram can avoid phase segregation during particle formation. High-entropy nanoalloys (HENAs) with equal stoichiometric ratios of various metals within each particle, have gained much interest due to their unusual physical and chemical properties. These properties make them attractive catalysts for oxygen reduction reactions with ample applications across fields. Materials scientists have shown how slow kinetics in traditional methods challenge the process, leading to phase segregation in nanoalloys, and have developed a range of methods to tackle these challenges. In this work, Jiang et al discussed the direct fabrication of supported ultrafine HENAs based on nanosecond pulsed laser reduction of metal salts on carbonaceous supports. The ultrafast laser reaction preceded the phase separation of alloys, to synthesize libraries of alloys as a straightforward and convenient method, compared to previous experiments.



TEM characterization of nanoalloys. (A and B) The TEM images of Pt nanoparticles fabricated by the LITER method. (C) The SAED pattern of Pt nanoparticles on graphene. (D) The particle size distribution of Pt nanoparticles. (E) TEM image of PtPdNi nanoparticles on graphene and the corresponding (F) elemental mappings, (G) SAED pattern, and (H) particle-size distribution plot. (I) High-resolution TEM image of PtPdCoNi nanoalloys on graphene and the corresponding (J) SAED pattern and (K) particle-size distribution plot. (L) High-resolution TEM image of PtPdCoNiCuAuSnFe nanoalloys on graphene and the corresponding (M) SAED pattern and (N) particle-size distribution plot. a.u., arbitrary units. Credit: *Science Advances* (2022). DOI: 10.1126/sciadv.abm6541

Methods: Laser-induced thermionic emission reduction (LITER)

During the experiments, Jiang et al precisely delivered laser packages with a pulse duration of 5 nanoseconds, and a pulse energy of up to 600 mJ to carbonaceous supports to generate an obvious plasma plume with electron jet flow. The scientists implemented a three-step process; during the first step, they facilitated the carbonaceous support to absorb laser photons to generate metal ions and electrons, followed by high-temperature conditions to initiate the reduction and etching of the carbonaceous support. Finally, Jiang et al instantly cooled the reduced metal atoms after laser irradiation for assimilation into ultrafine nanoalloys on the defect site of the carbon support. The process yielded HENAs with uniform sizes and even distribution on the supports. The team named this process the laser-induced thermionic emission reduction, abbreviated as LITER.



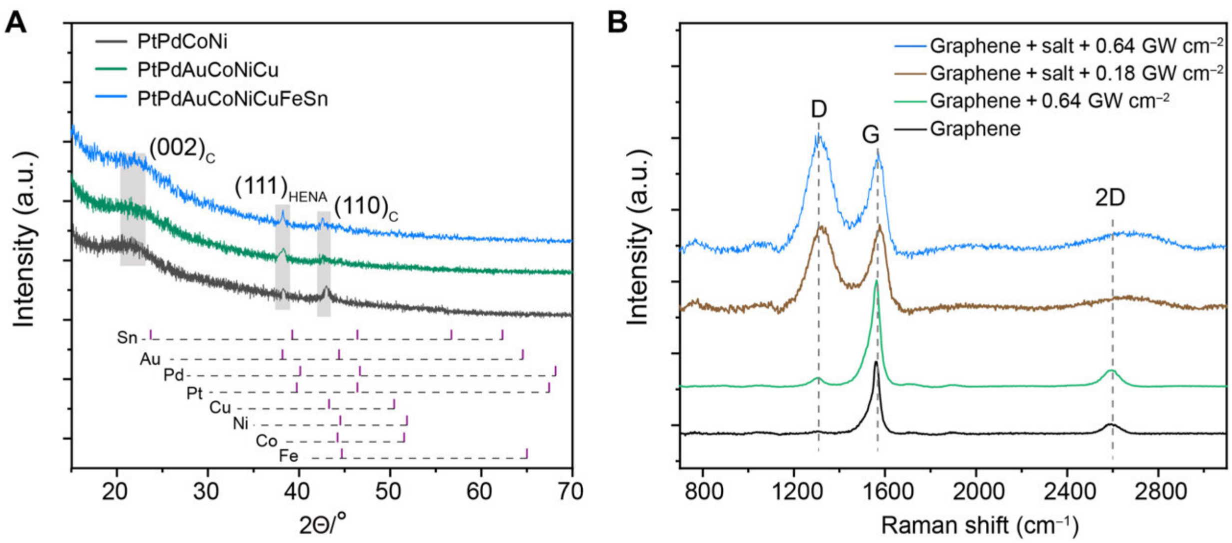
The elemental distribution analysis of the HENAs. (A) The HAADF image of PtAuRhIrSn HENAs on graphene and the corresponding elemental mappings in large area. (B) Well-matched elemental mappings in PtAuRhIrSn HENAs. PXRD patterns of the pristine ZIF-8 nanocrystals laser shock processed ZIF-8 blocks. (C) The HAADF image of HENAs with 11 elements (FeCoNiCuPtRhPdAgSnIrAu) on graphene and the corresponding elemental mappings. Credit: *Science Advances* (2022). DOI: 10.1126/sciadv.abm6541

Laser exposure

The LITER (laser-induced thermionic emission reduction) method predominantly included two steps: loading metal salts on carbonaceous supports to form the precursor and laser treatment on the precursor. Jiang et al used four-layered graphene supported HENAs as examples to demonstrate the method. At first, they dispersed a few-layered graphene powder in the ethanol solvent with chloride metal salts under stirring. After evaporating the ethanol solvent under vacuum, they obtained the graphene-supported metal precursor, then loaded it into a glass vial to subject the metal precursor to nanosecond laser pulses in air. The spot size of the laser pulses was 5 nm with laser pulse energy of 620 mJ. During laser pulse interactions, they formed high density plasma plumes to propel the graphene flakes across the whole container. Upon laser irradiation, the graphene layer absorbed the laser pulse for heat conversion to form a high-temperature local environment suited for metal salt pyrolysis. After laser exposure, the metal salts decomposed rapidly to form metal atoms to facilitate the formation of HENAs without phase separation.

Precursor synthesis and metal salt reduction

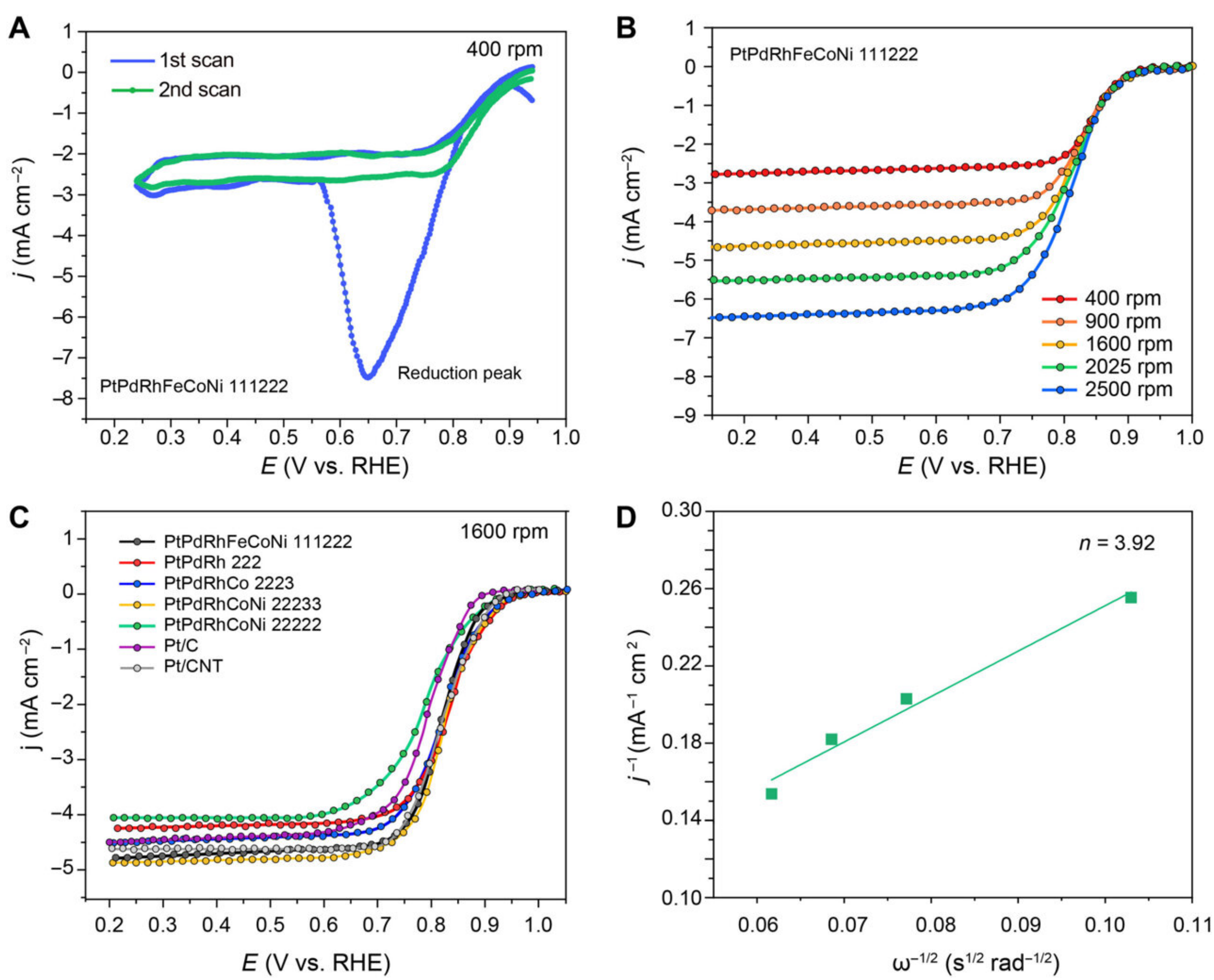
Before HENA (high-entropy nanoalloy) synthesis, Jiang et al developed ultrafine platinum nanoparticles on few-layered graphene using LITER to investigate laser reduction under atmospheric conditions. To prepare the precursor, they wet impregnated platinum tetrachloride ($PtCl_4$) salt on the surface of few-layered graphene and dried the sample under vacuum to obtain a black powder. The team loaded this precursor into a glass vial for laser treatment of the product. The laser pulse produced an energy pulse of 620 mJ at a pulse duration of 5 ns, with a spot size of 5 mm and wavelength of 1,064 nm to initiate the reduction of metal salts via laser pulse, and generated a plasma plume. After laser irradiation, they soaked the black powder to dissolve unreacted salts under vacuum drying.



The characterization of the HENAs and graphene support. (A) The PXRD patterns of different HENAs obtained by LITER method. (B) The Raman spectra of graphene, laser-treated graphene, and laser-treated graphene with metal salt precursors on them. Credit: *Science Advances* (2022). DOI: 10.1126/sciadv.abm6541

Materials characterization and applications of HENA

They characterized the product via microscopy to reveal its structure, using scanning electron microscopy to show how the product identified to pristine few-layered graphene and using transmission electron microscopy and high-angle annular dark field images, they revealed the morphology of the product with uniform and even distribution. The uniform nanoparticles formed on graphene also exhibited identical selected-area electron diffraction patterns. Jiang et al. showed that LITER (laser-induced thermionic emission reduction) can be generalized to develop a large variety of nanoalloys on graphene by loading designated metal salts on the precursors as identified using elemental mappings from energy dispersive spectroscopy. The team further studied the stoichiometric ratio and chemical state of the elements in HENAs (high-entropy nanoalloys) using the same technique, as well as X-ray photoelectron spectroscopy to reveal the chemical states of the elements. Jiang et al next conducted electrochemical performance analysis to understand the function of HENAs by fabricating them on carbon nanotubes. They setup a conventional rotating disk electrode to evaluate catalytic performance using linear sweep voltammetry measurements. The team believe that rational screening of HENAs by computer or other methods can lead to the discovery of advanced catalysts with better performance.



The electrocatalytic performance of the HENAs in ORR. (A) The CV curves and (B) the ORR polarization plots under different rotation speeds of HENA catalyst of PtPdRhFeCoNi on CNTs. (C) ORR polarization plots of different catalysts measured at speed of 1600 rpm. (D) The electron transfer number of PtPdRhFeCoNi on CNTs derived from Koutecky-Levich plots at a potential of 0.4 V versus RHE. Credit: *Science Advances* (2022). DOI: 10.1126/sciadv.abm6541

Outlook

In this way, Haoqing Jiang and colleagues described the refinement of uniform high-entropy nanoalloys (HENAs) via the corresponding metal salt precursors under direct laser-induced thermionic emission on graphene, and on carbon nanotubes in nanoseconds. The resulting HENA nanostructures delivered remarkable catalytic performance in oxygen reduction reactions. The laser-induced thermionic emission reduction (LITER) method introduced in this work is an advanced method to mix a variety of elements into ultra-small alloys in a scalable and energy-efficient manner. The scientists envision integrating the rich combination of elements, the ultrafast laser technology and nanoscale features to produce alloy libraries with a variety of properties for widespread applications.

More information: Haoqing Jiang et al, Nanoalloy libraries from laser-induced thermionic emission reduction, *Science Advances* (2022). DOI: 10.1126/sciadv.abm6541

Zhiming Li et al, Metastable high-entropy dual-phase alloys overcome the strength–ductility trade-off, *Nature* (2016). DOI: 10.1038/nature17981

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