Specific-Ion Effects Directed Noble Metal Aerogels: Versatile Manipulation for Electrocatalysis and Beyond

Ran Du$^{1}$, Yue Hu$^{2,*}$, René Hübner$^{3}$, Jan-Ole Joswig$^{4}$, Xuelin Fan$^{1}$, Kristian Schneider$^{1}$, and Alexander Eychmüller$^{1,*}$

$^{1}$ Physical Chemistry, Technische Universität Dresden, Bergstr. 66b, 01062 Dresden, Germany.

$^{2}$ College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou, 325000, China.

$^{3}$ Helmholtz-Zentrum Dresden-Rossendorf, Institute of Ion Beam Physics and Materials Research, Bautzner Landstrasse 400, D-01328 Dresden, Germany.

$^{4}$ Theoretische Chemie, Fakultät für Chemie und Lebensmittelchemie, Technische Universität Dresden, 01062 Dresden, Germany.

*e-mail: alexander.eychmueller@chemie.tu-dresden.de (A.E.), and yuehu@wzu.edu.cn (Y.H.).

Summary sentence: Specific-ion effect is demonstrated to create and flexibly manipulate noble metal foams for versatile applications.
Abstract
Noble metal foams (NMFs) are a new class of functional porous materials featuring properties of both noble metals and monolithic porous materials, providing impressive prospects in catalysis, bio-sensing, plasmonic technologies, etc.. Among reported synthetic methods to date, the sol-gel approach manifests overwhelming advantages for versatile synthesis of controlled nanostructured NMFs under mild condition. However, limited gelation methods and insufficient understanding of the underlying mechanism retards structure/composition manipulation of NMFs, hampering on-demand designing for practical applications. Herein highly tunable NMFs are fabricated at room temperature by activating specific-ion effects and regulating ion-nanoparticle interactions, affording various single/alloy NMFs with adjustable compositions (Au, Ag, Pd, Pt), ligament sizes (3.1~142.0 nm), and special morphologies. Their superior performance in programmable self-propulsion devices and electrocatalytic alcohol oxidation are demonstrated. This study provides not only a conceptually new route to fabricate and manipulate functional NMFs, but also an overall picture in understanding the gelation mechanism. It may pave the way for on-target designing versatile NMFs for various applications.

Introduction
Investigation of functional porous materials (FPMs) is an everlasting topic standing at the cutting edge of materials science, because combined porous structures and versatile compositions of FPMs warrant their remarkable performance in widespread fields. (1) Foams, which are equal to aerogels in certain cases, are one type of widely studied FPMs. They feature macroscopically monolithic structures favorable for handling and additional applications, and can be structured from nearly any unit ranging from silica, nanocarbons, polymers, two-dimensional (2D) materials, to inorganic nanocrystals. (2-6) As a rising star in the foam family, noble metal structured foams (NMFs) raised tremendous interest upon their debut. (7-9) Imparting three-dimensional (3D) gel
networks with features of noble metals (e.g. high catalytic activity, high electrical conductivity, plasmonic properties) has endowed NMFs with wide application potentials. However, they are still at the infant stage, where the fabrication strategies are more or less limited and structures/properties cannot be well manipulated.

NMFs are typically fabricated by four classes of methods, i.e., dealloying,(9) templating,(10,11) direct freeze drying,(12,13) and sol-gel process.(14) Since only the sol-gel method obtained great success in producing nanostructured and high-surface-area NMFs at mild condition, it immediately became the most popular synthetic strategy upon advent.(14-19) Because the sol-gel-derived foams are in good agreement with the definition for aerogels, the term noble metal aerogels (NMAs) will be used in this manuscript afterwards. Conventionally, NMAs were prepared by ultracentrifugation and subsequent destabilization of the nanoparticles (NPs) solution to obtain noble metal hydrogels (NMHs) in 1–2 weeks, followed by supercritical drying to afford the corresponding aerogels.(14) Afterwards, considerable efforts were made to enhance the gelation kinetics, modulate the microstructure, and simplify the fabrication procedures. Appropriate destabilizers (e.g. CaCl₂)(15) or elevated temperature (333 K)(16) have been adopted to reduce the gelation time to several minutes or several hours depending on the precursor concentrations (0.3–10 mM). By using Ag nanoshells(17) or PdNi hollow spheres(18) as building blocks, hierarchically structured NMAs with unique optical/electrochemical properties were obtained. To avoid considerable costs incurred by the concentration process, Liu et al.(19) significantly simplified the gelation to one step, directly initiating Pd/Pt gels by using specific amounts of NaBH₄.

Despite substantial progress being made, the sol-gel method is still at its infant stage and numerous mysteries remain in the complicated sol-gel process, which largely constrains the available systems, impedes the understanding of the gelation mechanism, and blocks the on-
demand manipulation. For example, regardless of the gelation method, the ligament size usually fell into the range of 3~6 nm for Pd/Pt while >100 nm for Au.\textit{(14-16,19,20)} Many strategies work well with the Pd/Pt/alloy systems, but fail in obtaining nanostructured gold gels.\textit{(14-16, 19)} Appealing core-shell structured NMAs were only obtained in form of powders, not to mention the tedious procedures involved.\textit{(21)} Moreover, until now the systematic modulation of the ligament size and corresponding physicochemical properties have not been realized. Additionally, investigations of applications/properties of NMAs are almost only restricted to electrocatalysis. Therefore, from both fundamental and practical considerations, it is high time to develop distinct strategies that could not only fabricate and flexibly manipulate NMAs, but also serve as a platform to study the gelation mechanism.

Salting-out is a long-known method to destabilize colloidal particles from solution. This is usually explained based on the DLVO (Derjaguin-Landau-Vervey-Overbeek) theory, where introduced “undifferentiated” electrolyte ions raise the ionic strength, thus electrostatically screening charged particles and inducing aggregation. However, specific-ion effects emerge with increasing concentration (e.g. \(\geq 100\) mM), and the Hofmeister series was proposed thereafter to arrange ions following their ability to salt-out proteins.\textit{(22-24)} Thus, if the chemical diversity of different ions could be activated, it may provide unprecedented opportunities to engineering the gelation process and the corresponding gels. Although CaCl\(_2\) (\(\leq 1\) mM) and NaCl (8~250 mM) have been used to prepare NMAs,\textit{(15,25)} the adopted concentration is not suitable for unlocking specific-ion effects and the systematic study of the specific-ion effects is in absence. A handful of works discovered the role of specific anions in regulating the gelation behavior of supramolecular and polymer gels,\textit{(26,27)} while the role of cations was scarcely considered. In this study, we present the rapid fabrication and flexible manipulation of NMAs by activating and designing specific-ion effects. By in-depth studying the gelation process experimentally and complementing density-functional calculations, the specific-ion-directed mechanism is proposed and the overall reaction
process is outlined. On this basis, versatile manipulations including compositions (Au, Ag, Pd, Pt, alloys), ligament sizes (6.9~113.7 nm for gold, 3.1~142.0 nm for others), specific surface areas (2.5~29.7 m² g⁻¹ for gold, 3.4~122.7 m² g⁻¹ for others ), and spatial element distribution (e.g. core-shell) are realized. More importantly, the enormous ion library and generality of the presented method will offer unprecedented opportunities for further manipulation of NMAs and extending to diverse colloidal solution systems. Finally, the interesting compression-induced dark-to-shining transition phenomenon, the programmable self-propulsion behavior, and the remarkable activity in electrocatalytic alcohol oxidation of as-prepared NMAs are demonstrated, suggesting their huge potentials in extensive fields.

**Results and Discussion**

**Overall gelation process**

In brief, the as-prepared gold NP solution was added with specific salts and grounded 4~12 hours to yield the hydrogel, which was further freeze-dried to obtain the corresponding aerogel (Fig. 1A, S1, Movie S1). Notably, the gel forms across wide metal precursor concentrations ($c_M$ of 0.02~2 mM). The lowest concentration ($c_M=0.02$ mM, ~5 days for gelation) was 1~4 order of magnitude lower than that of all reported NMAs to date (0.2 mM to above 100 mM), indicating a robust gelation ability and completely eliminating needs for expensive concentration processes. In contrast, it is impossible to destabilize the gold NP solution (0.2 mM) by frequently used methods (14-16,18) even with prolonged time (e.g., 3 days), such as addition of oxidants or adopting elevated temperature (e.g. 348 K). The long gelation time is a common issue for preparing NMHs. Although it has been cut down to several minutes or several hours,(15,16) the expensive concentration process or the elevated temperature involved can incur high costs or unfavorable structures. Hence our approach displays unique advantages for rapid gelation at simultaneously low $c_M$ and ambient temperature.
More formidable issues remain in regulating multi-scale structures and properties of NMAs. To address them, the gelation process, which is pivotal in determining the as-obtained NMAs, is thoroughly studied. As illustrated in Fig. 1A & S1, the red gold NP solution immediately turned black upon reaction and displayed a vertical color gradient afterwards, finally forming an extremely flexible hydrogel film at the bottom. This phenomenon is in sharp contrast with most systems of other materials,(2,4,5,28) where only the concentrated solution can afford free-standing gels which are of similar size as the original volume. To explain this unconventional phenomenon, a gravity-driven assembly model is proposed. As seen from Fig. 1B, salt-initiated aggregates gradually grow and settle down driven by gravity (see Supplementary Materials), and finally concentrate and evolve into the hydrogel at the bottom. To support the above model, UV-vis absorption spectra of a “half-way” gel system were recorded at different heights (Fig. 1C), unambiguously manifesting a gradient distribution along the gravity direction. Additionally, aggregates are proven to be active during the whole gelation process, which is evident from the spontaneous assembly of several fresh hydrogels into one monolithic gel (Fig. 1D). More intriguingly, hydrogels maintain their activity even after destruction (Fig. S2), displaying promising self-healing properties in diverse environments without external energy input. This remarkable self-healing behavior is discovered for the first time in NMHs, which may account for the observed monolithic structure despite their fragileness.

The holistic picture of the gelation process is further revealed by performing several time-lapse characterizations. In-situ UV-vis absorption spectra show an instant change from the characteristic surface plasmon resonance (SPR) absorption of gold NPs (~514 nm) to broad-band absorption upon reaction (Fig. 1E), indicating fast formation of aggregates with multi-scale microstructures.(29) The following intensity decrease agrees with the proposed gravity-driven sedimentation process. The in-situ dynamic light scattering (DLS) measurement indicated that the hydrodynamic size ($d_h$) of NPs/aggregates rapidly increases from (5.0±0.2) nm to (589±11) nm.
within 2 min and achieve a maximum of (1131±126) nm at ~60 min (Fig. 1F). Due to a positive correlation between the sedimentation speed and the particle size (see Supplementary Materials), larger aggregates fall down quickly and leave smaller ones in the solution phase, resulting in decreasing aggregate sizes with prolonged time. In this way, a volcano-shaped dh-time curve was obtained due to the competition between growth and sedimentation of aggregates. Time-lapse transmission electron microscopy (TEM) and in-situ optical tests further reveal the evolution footprints of 3D networks directly at different scales (Fig. 1G, 1H). Thus far, an overall picture of the sol-gel process is presented by combining multi-scale imaging techniques (10^-9~10^-1 m), spectra analysis, and light scattering measurements.

**Specific-ion effect in gelation**

To manipulate NMAs, the microscale mechanism accounting for the NP growth needs to be studied in depth. In the present system, gelation was induced by high-concentration salts (~10^2 mM) compared to previous reports,(15) satisfying the requirements to activate specific-ion effects dictated by the Hofmeister series.(23) Therefore, 24 salts were selected and arranged according to the Hofmeister series, where the salting-out effect decreased from SO_4^{2-} to SCN^- for anions and from NH_4^+ to Ca^{2+} for cations (Table S1).(22,24) As summarized in Fig. 2A, different ions imposed prominent effects on the color and the form of the final products (Fig. S3, S4), implicating successful activation of specific-ion effects. Generally, products changed from black to brown, from gels to powders induced by salts from the top left to the bottom right, roughly obeying the Hofmeister series. This trend is more evident for cations (along the x axis), which might be due to the enhanced cation-NP interaction resulting from small cation-NP distances which are induced by electrostatic attraction. The partially inversed order for double-charged Mg^{2+} and Ca^{2+} is presumably attributed to quite different surface charge environments of different-valance ions, which is common for the anomalous Hofmeister series presented in specific cases.(24) In contrast, anions may display complicated effects, involving both salting-out
effect and competitive adsorption with citrates, thus leading to the gelation behavior that deviates from the Hofmeister series.\(^{(7)}\)

Based on the observed phenomenon, the question arises how ions affect the color and form of the products. As dictated by the Hofmeister series, gold NPs should be salted out less effectively following the decreasing salting-out ability from \(\text{NH}_4^+\) to \(\text{H}^+\), presumably leading to gradually incomplete 3D networks, i.e., a gel-to-powder transition. On the other hand, the color could reflect the ligament size to some extent, where the black color often suggests small and hierarchical microstructures.\(^{(29)}\) The reason behind the ligament size evolution will be explained later. The gel status is further correlated with the Zeta potential and the DLS data (Fig. 2B, 2C, S5, S6). The absolute value of the Zeta potential increased and the maximum \(d_h\) decreased following the black gel, black powder, brown gel, and brown powder, suggesting increased solution stability and decreased network development, in line with the analysis discussed before. In addition, the salting-out effectiveness was characterized by the low-threshold gelation concentration \((c_s)\) of salts and proven to follow the Hofmeister series (Fig. 2D, S7). All experiments above suggest that both the form (gel to powder) and color (black to brown) variation trend are strongly correlated to the salting-out effect of specific cations dictated by the Hofmeister series.

Aside from the salting-out function, cations also play a role in removing ligands. It is found that weakly bound citrates leave the NPs during gelation, resulting in negligible residues in the final NPs-fused 3D networks (Fig. S8). This phenomenon can only be caused by the introduction of salts. Considering the opposite charge between cations and citrates, cations may strip citrates away from NPs to allow the development of gel networks. For verification, DFT calculations were performed focusing on the citrate-cation interaction, so as to compare stripping ability of
different cations (see Supplementary Materials). Binding energies ($E_b$) are obtained by calculating the energy change of the following reaction:

$$\text{RCOO}^- + X^+ \rightarrow \text{RCO}X$$  \hspace{1cm} (1)

where RCOO$^-$ and X$^+$ denote citrate and cation, respectively. The solvent effects were considered by using the Conductor-like Screening Model (COSMO) model detailed in the Supplementary Materials. $E_b$ represents the energy decrease of the cation-ligand binding process and reflects the citrate removal efficiency of the different cations. As shown in Fig. S9, the binding energy of single-charged cations exactly followed the Hofmeister series of \(\text{NH}_4^+(0.44 \text{ eV})<\text{K}^+(0.57 \text{ eV})<\text{Na}^+(0.85 \text{ eV})<\text{H}^+(6.59 \text{ eV})\), while the order was inversed for $\text{H}^+$ and double-charged cations ($\text{Mg}^{2+}$ of 2.96 eV, $\text{Ca}^{2+}$ of 2.27 eV) compared to the Hofmeister series. Intriguingly, although the order defined through the calculation of the binding energies partially inversed compared to the Hofmeister series, it well conforms to the order of increasing charge density and suits the experimental phenomenon (Fig. 2A, Table S1). Following the order of $\text{NH}_4^+$, $\text{K}^+$, $\text{Na}^+$, $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, and $\text{H}^+$, the as-prepared products roughly evolved from gels to powders and from black to brown regardless of anions. The plotting of $E_b$ vs. ligament sizes (Fig. S9) further quantifies the trend of size evolution, generally displaying a positive relationship which accords with the trend of color changes. It can be deduced that with increasing $E_b$ from $\text{NH}_4^+$ to $\text{H}^+$, citrates will be more efficiently removed and more active sites would be exposed. In this way, isotropic growth from the enhanced van der Waals attraction\((30)\) between surfaces of gold NPs is promoted and might be responsible for larger ligament sizes. Meanwhile, for high-charge-density cations (e.g., $\text{Mg}^{2+}$, $\text{Ca}^{2+}$, $\text{H}^+$), the very strong cation-citrate interaction may cause high stoichiometry adsorption of cations on the gold NP surface, increasing electrostatic repulsion and thus blocking the development of gel networks. This hypothesis can also be evidenced experimentally, where lower salt concentrations yield gels while higher concentrations do not (e.g., 3.3 vs. 33 mM $\text{MgCl}_2$ or
(CaCl₂). In addition, the concentration of those cations considerably decreased (30~60 at.%) in the supernatant solution after reaction (Table S2). Therefore, increased ligament size and unsupported products are observed with higher \( E_b \).

In virtue of specific-ion effects analyzed above, the ligament size is controlled from 9.4 nm for NH₄SCN to 199.6 nm for HCl (Fig. 2E). Compared to the Hofmeister series, certain inversions (K⁺ vs. Na⁺) in ligament sizes might be attributed to similarities of certain cations and to possible effects from anions. Statistics from time-lapse TEM imaging further revealed the growth mode of the NPs (Fig. 1G, 2F), where the network development and the ligament size increase occurred simultaneously. Combining the above results, a possible gelation mechanism is proposed (Fig. 2G & S10): (1) the original NPs instantly approach each other upon the addition of salts because of electrostatic screening; (2) the ligands are partially stripped away from the NPs by opposite-charged cations; (3) the NPs fuse together to form aggregates driven by the raised surface energy of uncapped NPs; (4) the aggregates repeat the above process and grow along both the axial and radial directions; (5) the gravity-driven settlement of aggregates facilitates the hydrogel formation at the bottom. During gelation, the cations can not only precipitate the NPs by salting-out effects, but also strip ligands away from the NPs by electrostatic attraction. These combined effects direct the cations to roughly follow the Hofmeister series, changing the products from gels to powders, and from small to large ligament sizes.

**Flexible manipulation of NMA**s

The systematic manipulation of the ligament size and the corresponding physical properties of NMA are the foundation for tailoring their specific applications. After a deep understanding of the gelation process and unlocking of specific-ion effects, the manipulation strategies are devised in several ways. Firstly, specific salts (NH₄SCN, NH₄NO₃, and KCl) were deliberately selected as initiators based on the previous results (Fig. S11, S12), adjusting the ligament size from 8.9±2.5
nm (for NH₄SCN) to 80.3±9.2 nm (for KCl) as characterized by TEM, SEM (scanning electron microscopy), and XRD. In addition, an even larger ligament size of 113.7±16.2 nm was achieved by MgCl₂-induced gels. The change of the ligament size further tunes their density, specific surface area, and pore volume from 83.0 to 212.8 mg cm⁻³, 29.7 to 2.5 m² g⁻¹ (5843.4 to 492.5 m² mol⁻¹), and 0.218 to 0.010 cm³ g⁻¹, respectively. Secondly, a double-salt system was employed to continuously adjust the ligament size between the values given by the two single-salt systems. As shown in Fig. 3A, NaCl/NaOH hybrid salts quasi-continuously modulate the ligament size from 64.0±13.3 to 8.9±1.8 nm. Instead of a linear variation, the ligament size changed sharply by introducing a small amount of the second salt (2~10%) while keeping nearly unchanged in the broad middle region (NaOH%=20~80%). Thirdly, the ligament size was modulated by altering the concentrations of the employed salts (NH₄F was taken as example) or gold precursors, ranging from (8.0±1.1) to (17.2±4.6) nm and 6.9±1.5 to 17.2±3.9 nm, respectively (Fig. S13). In virtue of the above strategies, the ligament sizes of the gold gels could be designed from 6.9 to 113.7 nm, covering a wide region not realized in previous reports (Fig. 3B). Moreover, there is still ample space to extend the current systems and devise the gel parameters by elaborately selecting appropriate ions from the enormous ions library. Interestingly, we found that the employed ligand, i.e. trisodium citrate, displayed – beyond its old role as only ligand or reductant – a new face as the gelation agent when its concentration is sufficiently high (Fig. S14).

On the basis of the proposed gelation mechanism, the current system could be easily expanded to diverse noble metals (Ag, Pd, Pt) and their alloys (Fig. S15, Table S3, S4). It is interesting that introducing a second metal to the gold system always leads to a reduction of the ligament size, enabling a fine manipulation from e.g. (10.3±2.1) to (3.7±0.5) nm for the Au/Pd system (Fig. 3C, S16). Further investigations showed that the Au, Ag, and Au/M (M=Pd, Pt) systems with higher Au content give relatively large ligament sizes and are easier to be modulated, while Pd and alloy systems with lower Au ratios resulted in small-sized gels (Fig. 3D, S16). This phenomenon may
partially result from the cohesive energy difference of metals which positively correlates with their enthalpy of vaporization ($\Delta H_v$/kJ mol$^{-1}$), following Ag(258)<Au(324)<Pd(362)<Pt(469). A lower $\Delta H_v$ (Ag, Au) indicates weaker NP interactions, so that the NPs may need more coordinating neighbors to stabilize the structure, which leads to large ligament sizes, and vice versa. Summarizing the data from all prepared NMAs, ligament sizes from 3.1 to 142.0 nm, densities from (44.0±3.6) to (212.8±9.6) mg cm$^{-3}$, BET surface areas from 122.7 to 2.5 m$^2$ g$^{-1}$ (15918.8 to 492.5 m$^2$ mol$^{-1}$), and BJH pore volumes from 0.704 to 0.013 cm$^3$ g$^{-1}$ are obtained, demonstrating the superior manipulation capacity of the current strategy. Correlating the ligament size with diverse parameters/properties showed that, generally the density/mechanical bending strength increase with increasing ligament size, while the BET surface area/pore volume decrease (Fig. 3E, 3F). This provides certain guidelines to engineer the physical parameters of NMAs.

Among various NMAs, alloy aerogels always display a large application potential because of synergistic effects endowed by the multiple components, especially when deliberately designed secondary structures, e.g. hollow or core-shell architectures are included. As seen from energy-dispersive X-ray spectroscopy (EDXS) analysis in the TEM, the spatial element distributions are either homogeneous (Pd-Pt (Fig. 3G)), inhomogeneous (Au-Pd (Fig. S17B), Au-Pd-Pt (Fig. S17D)) or show an imperfect core-shell structure (Au-Ag (Fig. S17A)). To control the spatial distribution of elements, a straightforward dynamic shelling approach (DSA) is developed in the frame work of the presented strategy. By simply introducing the second metal precursor during the initial gelation stage of the first metal, the second metal can nucleate and grow on the as-formed partially-developed networks owing to the reduced energy cost by the heterogeneous nucleation process, eventually resulting in core-shell-structured gels. This approach can not only yield various bi-/trimetallic gels with well-defined core-shell structures (e.g., Au-Ag, Au-Pd, Au-Pt, Au-Pd-Pt), but also modulate the shell thickness (0.5~2.5 nm) by simply adjusting the ratios of the different components (Fig. 3H, 3I, S18). In comparison with previously reported core-shell-
structured NMAs fabricated via either the underpotential deposition followed by a galvanic replacement reaction (Pd₈Au-Pt)\(^{(21)}\) or via one-pot synthesis by using a special reductant (PdPb-Pd)\(^{(34)}\) the presented approach not only provides intact NMAs with well-defined and tunable core-shell structures, but manifests its considerable generality and simplicity owing to its straightforward mechanism.

**Properties and applications of NMAs**

Certain properties and potential applications of as-prepared NMAs are studied to unravel their practical values. Most bulk metals appear lustrous and white. In contrast, nanostructured NMAs appear black which has been explained to be due to light trapping in hierarchical microstructures because of multiple absorption and scattering by nearby grains\(^{(29)}\). On the other hand, most metals exhibit remarkable ductility (i.e., the plasticity), which is explained by their strong dislocation emission ability\(^{(35)}\). Therefore, it might be possible to induce a dark-to-shining transition by rearranging NMAs manually. As illustrated in **Fig. 4A-C, 19, and Movie S2**, various NMAs could be easily pressed from a height of millimeters to micrometers and thereby to regain metallic gloss via compacted nanostructured “mirror surfaces”. Additionally, different aerogels could be welded together to form macroscopic hetero-structures. Due to the extraordinary plasticity, NMAs could be arbitrarily shaped and encased in elastomers (e.g., polydimethylsiloxane) for potential use as flexible conductors.

Utilizing the catalytic oxygen evolution by decomposing H₂O₂\(^{(36)}\) high-surface-area silver aerogel is made to a powerful self-propulsion device as an alternative to expensive Pt-based materials (**Fig. 4D**). The intensive catalytic reaction enables a maximum speed of 1.2 cm s\(^{-1}\) in 1.5 wt.% H₂O₂ solution, comparable to that of Ag micromotors (>0.1 cm s\(^{-1}\)) and bioelectrochemical self-propulsion devices (~1 cm s\(^{-1}\))\(^{(36,37)}\). Intriguingly, the motion form could be programmed by utilizing a heterostructured Au-Ag gel (**Fig. 4E, Movie 3**). Upon reaction, it rotated
automatically and displayed an angular speed of up to 168 rpm, which is due to its non-symmetrical structure where only the Ag part can catalyze \( \text{H}_2\text{O}_2 \) for propulsion.

Finally, the potential of NMAs in electrocatalysis is tested by the alcohol electro-oxidation reactions. Cyclic voltammograms (CV) were performed in the presence of ethanol, where the forward peak (i.e., the anodic peak) represents the oxidation of freshly adsorbed ethanol, while the backward peak indicates the removal of carbonaceous intermediates produced in the forward scan.\(^{(20,38)}\) Hence, the peak current density of the forward scan \( (I_f) \), and the ratio of the peak current densities of forward/backward scans \( (I_f/I_b) \) can serve as indicators to evaluate the catalytic performance. As seen from Fig. 4F & 4G, it is surprising that high-surface-area Pd and Pd-Pt aerogels (122.7 and 58.0 m\(^2\) g\(^{-1}\), respectively) show a lower performance compared to that of commercial Pd/C and Pt/C catalysts, presumably due to their less-continuous networks (Fig. S15B). In contrast, Au-Pd and Au-Pd-Pt aerogels showed substantially higher performance with \( I_f \) of 2.65 and 4.82 A mg\(^{-1}\) Pd+Pt, which are 2.8–6.1 times higher than that of commercial Pd/C or Pt/C catalysts and higher than most reported NMAs such as Pd-Cu, Pd-Ni, and Au-Ag-Pd aerogels (ca. 2.0–5.6 times compared to Pd/C).\(^{(16,18,20,38)}\) Also, a \( I_f/I_b \) of 1.37 is achieved for Au-Pd-Pt aerogels, displaying advantage over that of commercial (0.9–1.15) and most reported NMAs catalysts (0.9–1.28).\(^{(16,18,20)}\) Moreover, the excellent long-term activity (up to 10000 seconds) is observed for both Au-Pd and Au-Pd-Pt catalysts (Fig. 4H, S20). Additionally, Au-Pd and Au-Pd-Pt aerogels delivered superior electrocatalytic performance for the methanol oxidation reaction (MOR, see Fig. S20), displaying high \( I_f \) of 1.22 and 2.06 mg\(^{-1}\) Pd+Pt compared to that of Pd/C and Pt/C (<0.5 mg\(^{-1}\) Pd+Pt). This may enable their possible use as anodic catalysts for various fuel cells. Aside from abundant active sites provided by the large specific surface area, the exceptional performance of NMAs may also rely on their intact and highly conductive 3D networks endowed by the gold component, which can enhance the electrical conductivity, and thus facilitating efficient electron transfer in electrocatalysis.
To sum up, a specific-ion directed gelation strategy was developed to rapidly fabricate and flexibly manipulate noble metal foams at room temperature from their NP solution. By activating specific-ion effects and subtly regulating the NP-ion interactions, diverse single-/multi- NMFs with widely tunable compositions (Au, Ag, Pd, Pt), ligament sizes (3.1~142.0 nm), specific surface areas (2.5~122.7 m² g⁻¹), and spatial element distribution (e.g. core-shell) are obtained. Combining experimental results and DFT calculations, the gel status is found to strongly depend on cation-ligand interactions, roughly following the Hofmeister series. On this basis, an overall picture of the sol-gel process is proposed, comprising electrostatic-screening-induced aggregation, ligands-stripping-directed NPs fusion, and gravity-driven sedimentation and gelation process. Finally, several intriguing properties/applications of NMFs are demonstrated, including compression-induced dark-to-shining transition, devisable self-propulsion behavior, and high electrocatalytic activity towards ethanol/methanol oxidation. This study provides not only a conceptual-new and general route to fabricate and on-demand manipulate noble metal foams, but also certain perspectives in understanding the gelation process and underlying mechanism, therefore paving the way for on-target designing versatile NMFs for various applications. Due to the enormous ion library and the generality of the gelation mechanism, the presented method may also adapt to versatile colloidal solution systems for on-demand manipulation towards desirable applications.
MATERIALS AND METHODS

Fabrication of Noble Metal Hydrogels and Aerogels

Hydrogels were synthesized by the two-step method at ambient temperature (~293 K), i.e. the preparation of nanoparticle solutions and the following gelation. As an example, the aqueous solution of trisodium citrate dehydrate (400 mM, 25 μL), HAuCl₄·3H₂O (32.5 mM, 30.8 μL), and NaBH₄ (200 mM, 20 μL) were added successively to 4.93 mL water and stirred for 30~60 minutes. After aging for ~1 day, NH₄F (1 M, 555 μL) solution was added and the mixture was subsequently grounded for 4~12 h to acquire the hydrogel. After washing with water and exchanging with tert-butanol, the corresponding aerogel was obtained by freeze drying for ~24 h.

Electrochemical Measurements

All electrochemical tests were performed with a three-electrode system. The catalyst ink was prepared by dispersing a specific amount of catalyst in 2-propanol by sonication, the accurate concentration of active components (Pd and Pt) was determined by ICP-OES. For electrocatalysis of ethanol and methanol oxidation, the loading of active components was ~20 μg cm⁻², and electrochemical tests were performed in N₂ saturated 1 M KOH aqueous solution containing 1 M ethanol or methanol.
References and Notes


47. Y. Marcus, Thermodynamics of Solvation of Ions. Part 5.—Gibbs Free Energy of

48. A.-K. Herrmann, P. Formanek, L. Borchardt, M. Klose, L. Giebeler, J. r. Eckert, S.
    Kaskel, N. Gaponik, A. Eychmüller, Multimetallic Aerogels by Template-Free Self-

49. Q. Shi, C. Zhu, D. Du, C. Bi, H. Xia, S. Feng, M. H. Engelhard, Y. Lin, Kinetically
    Controlled Synthesis of Aupt Bi-Metallic Aerogels and Their Enhanced Electrocatalytic

50. S. Naskar, A. Freytag, J. Deutsch, N. Wendt, P. Behrens, A. Köckritz, N. C. Bigall,
    Porous Aerogels from Shape-Controlled Metal Nanoparticles Directly from Nonpolar

**Acknowledgments**

**General:** R.D. acknowledges the support from the Alexander von Humboldt Foundation. X.F.
acknowledges the financial supported by the Chinese Scholarship Council. We thank Minghao
Yu and Irena Senkovska for gas adsorption tests, Minghao Yu for FT-IR tests, Susanne
Goldberg, Christine Damm, and Prof. Kornelius Nielsch for SEM and TEM measurements or
training, Linlin Wang and Dr. Juliane Simmchen for optical imaging, Xin Gao for XPS
measurements, Dr. Bin Cai, Dr. Jinying Wang, Dr. Nannan Mao, Dr. Shibin Deng, Dr. Wei
Liu, Dr. Yabin Chen, and Ying Jiang for helpful discussions. Furthermore, the use of HZDR
Ion Beam Center TEM facilities and the funding of TEM Talos by the German Federal
Ministry of Education of Research (BMBF), Grant No. 03SF0451 in the framework of HEMCP are acknowledged. **Funding:** This work was supported by the ERC AdG AEROCAT, the National Natural Science Foundation of China (51602226), and the Natural Science Foundation of Zhejiang Province (LY19E020008). J.O.J gratefully acknowledges financial support by the Deutsche Forschungsgemeinschaft (DFG) for M-ERA.NET project ICENAP. **Author contributions:** R.D. conceived and designed the experiments. R.D. and X.F. performed the materials synthesis. Y.H. carried out the SEM, XPS, and TGA analysis. R.H. performed STEM analysis. R.D. performed all other experimental characterizations and measurements. J.-O. J. carried out the computational part. R.D. and Y.H. performed the data analysis and mechanism explanation. R.D., A.E., Y.H., X.F., and K.S. discussed the manuscript organization. R.D. drafted the manuscript and Y.H., A.E., R.H., and J.-O. J. revised it. All authors commented on the manuscript. **Competing interests:** The authors declare that they have no competing interests. **Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data available from authors upon request.
Fig. 1. Analysis of the overall gelation process of gold NPs. (A) Digital photos of the gel preparation process. (B) Schematic demonstration of the gelation process and a corresponding force analysis. (C) The gradient distribution during the gelation characterized by UV-vis absorption spectra. (D) Several pieces of as-prepared hydrogels can assemble to one piece. (E-H) Time-lapse (E) UV-vis absorption spectra, (F) hydrodynamic size, (G) TEM, and (H) optical microscopy characterization during gelation.
**Fig. 2. Analysis of the specific-ion effects on the gelation behavior and ligament size.** (A) Summary of the status of gels induced by different ions. The inverted triangle and the diffused circle indicated the gel and powder, and black and brown indicated the color of the products. (B) Zeta potential upon reaction and (C) maximal hydrodynamic size ($d_h$) versus the color and form of products. The data was obtained by averaging detailed values from the inset diagram. (D) The low-threshold gelation concentration of salts ($c_s$) versus the employed cations. (E) The ligament size (averaged over the anions employed as in the inset diagram) of as-synthesized gold aggregates versus cations. (F) Time-lapse ligament size evolution of gold aggregates induced by three typical salts. (G) Proposed mechanism for gel formation.
Fig. 3. Versatile manipulation of NMAs. (A) Tailor the ligament size of gold gels by introducing NaOH/NaCl hybrid salts. (B) Ligament size of gold aerogels from different references (reference a-d corresponds to ref. 13, 9, 31, 14, respectively). (C) The ligament size variation with Au/Pd ratio. (D) Ligament size modulation of Au-Pd, Au-Pt, Pd, and Ag gels by using different salts. (E) The dependence of density, BET surface area, and pore volume of aerogels versus ligament size. (F) Demonstration of the size-dependent mechanical properties of aerogels by bending with a tweezer. From left to right are Au-Ag-NH$_4$F (5.8±0.7 nm), Au-NH$_4$SCN (8.9±2.5 nm), Au-NH$_4$NO$_3$ (18.2±4.0 nm), Au-NaCl (64.0±13.3 nm), respectively. (G-I) STEM-EDX of three alloy gels with (G) homogeneous and (H-I) core-shell architectures.
Fig. 4. Plasticity and versatile applications of NMAs. (A) A piece of gold aerogel is manually pressed by ca. 98.5 %. The scale bar of the inset SEM image is 30 μm. (B) Original and compressed noble metal foams made of Au, Ag, Pd, and Pt. (C) Hetero-structured welded Au-Ag aerogel by pressing, and the logo “TUD” made by compressing Au, Ag, and Au-Pd-Pt alloy aerogels, and a gold “TUD” logo encased in PDMS. (D-E) Self-propelling behavior of (D) Ag aerogel, and (E) compressed Au-Ag aerogel in H₂O₂ solution. The scale bars are 5 mm. (F-H) Ethanol electro-oxidation performance, (F) CV curves, (G) summarized I_r and I/I_b, and (H) chronoamperometry curves of different catalysts.
Supplementary Materials for

Specific-Ions Effects Directed Noble Metal Aerogels: Structure-Tunable Highly Plastic Materials for Electrocatalysis and Beyond

Ran Du¹, Yue Hu²*, René Hübner³, Jan-Ole Joswig⁴, Xuelin Fan¹, Kristian Schneider¹, and Alexander Eychmüller¹*

This PDF file includes:

Fig. S1. Characterizations of nanoparticles (NPs) precursors.
Fig. S2. Self-healing behavior of gold hydrogels.
Fig. S3. Digital photos of gelation behavior of gold NPs induced by different salts.
Fig. S4. Digital photos of gelation behavior of gold NPs induced by four typical salts.
Fig. S5. Zeta potential of gold NP solution after addition of different salts.
Fig. S6. Time-lapse hydrodynamic size evolution during gelation.
Fig. S7. The low-threshold gelation concentration and ligament size versus anions.
Fig. S8. Residual analysis of as-prepared gold aerogels.
Fig. S9. Energies derived by DFT calculations.
Fig. S10. Proposed nanoscale force analysis and gelation mechanism.
Fig. S11. Demonstration of size manipulation of gold aerogels by using specific salts.
Fig. S12. Nitrogen adsorption test of different gold aerogels.
Fig. S13. The relation of ligament size and precursors concentration
Fig. S14. Digital photos of gold gels initiated by other salts.
Fig. S15. Demonstration and characterizations of diverse noble metal aerogels.
Fig. S16. Ligament size manipulation of noble metal gels.
Fig. S17. STEM-EDX analysis of different alloy gels prepared by one-step method.
Fig. S18. HAADF-STEM imaging and EDXS analysis of core-shell structured alloy gels.
Fig. S19. Cross-sectional SEM images of compressed aerogels.
Fig. S20. Electrocatalytic performance of different commercial and gel catalysts.
Table S1. Summary of the gelation behavior of gold induced by different salts.
Table S2. Concentration of different ions in supernatant after gelation.
Table S3. Summary of nitrogen adsorption data and ligament size of as-prepared aerogels.
Table S4. Elemental analysis of different alloy aerogels.
Table S5. Comparison of parameters of noble metal aerogels in literature.
Movie S1. Demonstration of as-prepared black gels, brown gels, and black powders.
Movie S2. Demonstration of pressing original aerogels into shining materials.
Movie S3. Demonstration of self-propelled rotation of compressed Au-Ag aerogel.
Materials and Methods

Experimental Procedures

Reagents and Materials

All reagents, such as hydrogen tetrachloroaurate (III) (HAuCl₄·3H₂O), potassium tetrachloropalladate (II) (K₂PdCl₄), potassium tetrachloroplatinate (II) (K₂PtCl₄), trisodium citrate dihydrate, sodium borohydride (NaBH₄), and others were purchased from Sigma-Aldrich or Alfa-Aesar and used without further purification.

Fabrication of Single-Metal Noble Metal Hydrogels (NMHs)

Hydrogels were synthesized by a two-step method at ambient temperature (~293 K), dividing into nanoparticles (NPs) preparation and hydrogels formation. The fabrication process of a NH₄F-induced gold hydrogel is described as an example as follows:

Preparation of Gold Nanoparticles (NPs) Solution

Aqueous solution of trisodium citrate dehydrate (400 mM, 25 μL) and HAuCl₄·3H₂O (32.5 mM, 30.8 μL) were added successively in 4.93 mL water and stirred for ~15 min. Then freshly prepared NaBH₄ aqueous solution (200 mM, 20 μL) was rapidly injected, followed by stirring for 30~60 min. The molar ratio of metal salt (M), ligand (L), and reductant (R) is 1/10/4. The as-prepared NP solution (c_M=0.2 mM) was aged for ca. 1 day before hydrogel preparation. To prepare high-concentration gold NP solution (c_M≥0.5 mM), β-alanine was used as the ligand to replace the trisodium citrate.

Preparation of Gold Hydrogels

Aqueous solution of NH₄F (1 M, 555 μL) was added in as-prepared gold NP solution (5 mL), stirring for 10~20 s, followed by grounding 4~12 h to get free-standing gold hydrogel. The as-prepared gel is washed by a large amount water for 4~5 times with a total duration of 3 days to remove possible residues. For NP precursor solutions with different c_M, the final concentration of NH₄F (c_salt) was fixed to 100 mM. For hydrogels prepared by using different c_salt the c_M was fixed to 0.2 mM.

For scale-up production, aqueous solution of trisodium citrate dehydrate (400 mM, 4 mL) and HAuCl₄·3H₂O (32.5 mM, 4.92 mL) were added successively in 788 mL water and stirred for ~15 min. Then freshly prepared NaBH₄ aqueous solution (200 mM, 3.2 mL) was rapidly injected in the above mixture, followed by stirring for 30~60 min. Afterwards, aqueous solution of NH₄F (1 M, 88.9 mL) was quickly added, stirring for ~20 s, followed by grounding ~12 h to allow complete reaction.

Fabrication of Alloy NMHs

Alloy hydrogels were synthesized by either one-pot or dynamic shelling approach (DSA). The latter strategy could be used to controlled fabricate core-shell structured gels.

For one-pot method, the procedure is the same to that of single-metal hydrogels, except that single metal precursor salts were replaced by two or more metal precursor salts. The molar ratio of different metal precursor salts is 1:1 for bi-metallic system and 1:1:1 for tri-metallic system, and the total concentration of metal salts in final solution is fixed to 0.2 mM.

For dynamic shelling approach, Au-Pd (molar ratio 1/1) system is taken as an example. Aqueous solution of trisodium citrate dehydrate (400 mM, 25 μL), HAuCl₄·3H₂O (32.5 mM, 15.4 μL), and NaBH₄ aqueous solution (200 mM, 20 μL) were added in 4.93 mL water stepwise under stirring. After ~5 min, aqueous solution of NH₄F (1M, 555 μL) was added and stirring was kept for ~10 s before
switching off. After grounding for ~2 min, aqueous solution of K₂PdCl₄ (32.5 mM, 15.4 μL) was added under stirring for ~10 s. Thereafter, the mixture was grounded for ~12 h to acquire core-shell structured hydrogels.

**Preparation of Noble Metal Aerogels**

After purification by water, hydrogels were solvent-exchanged with tert-butanol for 2~3 times. Afterwards, wet gels were flash frozen by liquid nitrogen and remained at -196 °C for ~10 min to enable complete freezing. The frozen samples were put into the chamber of freeze drier (TOPTI-12S-80) and dried for 12~24 h at ~1Pa. The temperature of the cold trap was set to -80 °C.

**Compression of Aerogels**

To make a lustrous and solid aerogel pellet, the as-prepared aerogel was pressed manually by using a polished stainless-steel cylinder for a few seconds. To make the hetero-structured compressed Au-Ag aerogel, the original Au and Ag aerogel were placed together with a small overlapping fraction, followed by compressing as described above.
Computational Procedures

Macroscopic Force Analysis during Gelation Process

In solution, the aggregate is imposed by gravity ($G$), buoyancy ($f$), and viscous drag ($F$). (39) When the aggregate falls down, the direction of $F$ is the same with that of $f$, while opposite with that of $G$. To facilitate estimation, given that all aggregates during gelation have the similar shape (quasi sphere) and density, only differ in sizes. $G$, $F$, $f$, and the volume of aggregate ($V$) could be expressed as follow,

$$G = mg = \rho g V$$

$$f = \rho_w g V$$

$$F = 3\pi \eta d v$$

$$V = \pi d^3 / 6$$

Where $\rho$, $\rho_w$, $\eta$, $d$, and $v$ denote the density of aggregate, density of solution, viscosity of solution, equivalent diameter of aggregate, and velocity of the aggregate.

For $F$ that is expressed by Stock’s law, the laminar flow need to be met, where the Reynolds number ($Re$) should be very small, e.g. less than 10 for the system of spheres. In our system, assume the viscosity and density of solution is close to the water ($\sim 10^{-3}$ Pa s and $10^3$ kg m$^{-3}$), the maximum velocity ($v_{max}$) of the aggregate is 10 times of average settling down velocity ($v_s$), and the largest size of aggregate in solution is 100 $\mu$m. Since the precipitate appeared usually after 1 hours upon reaction for a system with a solution height of 5 cm, so the $v_s$ should be less than 5 cm h$^{-1}$, thus a $v_{max}$ of 50 cm h$^{-1}$ was adopted. Then the up-limit of $Re$ is estimated as follows and suggests a pure laminar flow condition:

$$Re = \frac{\rho_d v_{max}}{\mu} = \frac{1000 \times 10^{-4} \times (0.5)}{3600} = 0.0139$$

Then the total force $F_{tot}$ could be expressed as:

$$F_{tot} = mg - \rho_w g V - 3\pi \eta d v = mg(1 - \rho_w / \rho) - 3\pi \eta v m^{1/3} \left(\frac{6}{\pi \rho}\right)^{1/3}$$

Therefore, the acceleration ($a$) at certain velocity, and the maximum velocity ($v_m$) at the force equilibrium state ($F_{tot}=0$) are derived as:

$$a = \frac{F_{tot}}{m} = -m^{-2/3} \rho w (\frac{6}{\pi \rho})^{1/3} + g(1 - \rho_w / \rho)$$

$$v_m = \frac{gd^2 (\rho - \rho_w)}{18\eta}$$

From above equation, it’s clear that acceleration $a$ is determined by the viscous drag term, which is positively related to the mass of aggregate. Hence, at the same velocity, $a$ of big aggregate is always larger than that of the smaller one. So given that the initial velocity is zero, the velocity of larger aggregate should be always larger than that of the smaller one. At the final equilibrium state, the equilibrium speed is also positively related to the size, i.e. the mass of aggregate. Therefore, during whole gelation process, large aggregates would fall down all the way quicker than smaller ones. In this way, during gelation process, the gradually formed large aggregates will continuously fall down and eventually precipitate and gelate at the bottom of the vial.
Density-functional theory (DFT) Calculations

DFT calculations were carried out by using the Amsterdam Density Functional package. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional was employed together with a TZP basis set. The convergence criteria for energy and nuclear gradients were set to $10^{-3}$ Hartree and $10^{-3}$ Hartree/Å, respectively.

The initial structures were generated as follows: a high-temperature trajectory of a single citric-acid molecule was used to scan the conformational space with an approximate DFT method; the optimized lowest-energy structure was taken as the initial structure and a single acidic proton was exchanged for the respective cations (Na⁺, K⁺, NH₄⁺, Mg²⁺, Ca²⁺). All structures generated in this way were optimized with full DFT afterwards. In case of the alkaline earth metals, the molecule was positively charged. Dispersion effects were included by using the three parameter correction developed by Grimme et al.

To mimic the experimental environment, the Conductor-like Screening Model (COSMO) of solvation as implemented in ADF was used. It includes the respective molecule in a molecule-shaped cavity constructed by the atomic radii and surrounded by a dielectric medium (here: water). Taken single-charged cations as example, the binding energies ($E_b$) was calculated based on following equation,

$$RCOO^- + X^+ \rightarrow RCOOX$$

where RCOO⁻ and X⁺ denote deprotonated citrate and cation, respectively. $E_b$ is defined $E_b = E_{RCOOX} - E_{RCOO} - E_{X^+}$ (we will display and discuss absolute values for convenience).
Characterizations

**Microscopy Characterization**

Scanning electron microscopy (SEM) analysis was performed on a Nova 200 NanoSEM scanning electron microscope. Samples were prepared by directly sticking on the conductive tape.

Transmission electron microscopy (TEM) analysis was carried out by using a FEI Tecnai G2 20 microscope operated at 200 kV. Samples were prepared by dispersing in acetone under ultrasonication, followed by dropping onto carbon coated copper grids and drying at ambient temperature.

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging and spectrum imaging based on energy-dispersive X-ray spectroscopy (EDX) were performed at 200 kV with a Talos F200X microscope equipped with an X-FEG electron source and a Super-X EDX detector system (FEI). Prior to STEM analysis, the specimen mounted in a high-visibility low-background holder was placed for 2 s into a Model 1020 Plasma Cleaner (Fischione) to remove contamination.

Optical imaging was acquired by Carl Zeiss Microscopy (Colibri 7), with the magnification of 63×10.

**Diffraction Characterization**

X-ray powder diffraction (XRD) was carried out in reflection mode on a Siemens D5000 X-ray diffractometer operated at a voltage of 30 kV and a current of 10 mA with Cu Kα radiation (λ = 1.5406 Å). The data were collected in the 20°–90° (2θ) range with a step size of Δ2θ = 0.02°. The sample was fixed on the holder by Scotch tape. For single-metal system, the crystal size could be estimated by the Scherrer equation applying crystallite-shape factor K=0.9.(46)

**Spectroscopy Characterization**

FT-IR spectra were recorded by Thermo Scientific Nicolet 8700 FT-IR Spectrometer configured with a Smart iTR diamond accessory.

UV-vis absorption spectroscopy was recorded on Cary 60 UV-Vis Spectrophotometer.

**Thermal Properties Characterization**

Thermogravimetric analysis (TGA) analysis was conducted by Diamond TG-DTA/Spectrum GX with heating rate of 10 K min⁻¹ under nitrogen atmosphere.

**Element Analysis**

X-Ray photoelectron spectroscopy (XPS) was performed by an Axis Ultra spectrometer (Kratos, UK) with a high-performance Al monochromatic source operated at 15 kV. The XPS spectra were taken after all binding energies were referenced to the C 1s neutral carbon peak at 284.8 eV, and the elemental compositions were determined from peak area ratios after correction for the sensitivity factor by CasaXPS.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed by Perkin-Elmer Optima 7000DV optical emission spectrometer.

**Nitrogen Adsorption Measurement**

Nitrogen adsorption experiments were performed with Quantachrome Autosorb 1 at 77 K. The sample was outgassed at 323 K for ~24 h under vacuum before measurement. The filling rod was used to reduce the dead volume and thus improving measurement accuracy. The specific surface area was calculated by using multi-point BET equation (0.1<p/p₀<0.3). The pore size distribution was derived from desorption branch by using DFT method. The total pore volume, which is calculated at p/p₀=0.99, in consistent with the value derived by BJH (Barret–Joyner–Halender) method.
Other Characterizations

Zeta potential and dynamic light scattering (DLS) tests were performed on ZETASIZER NANO (ZEN5600, Malvern Company).

Electrochemical Measurements

All electrochemical tests were performed with a three-electrode system on Autolab/PGSTAT 30 (Eco Chemie B. V. Utrecht, the Netherlands). Glassy carbon electrode (GCE, 3 mm in diameter), Ag/AgCl (saturated KCl aqueous solution) electrode, and platinum foil were used as working electrode, reference electrode, and counter electrode, respectively.

For modification of working electrode, ~1 mg catalyst was dispersed in 1 mL of 2-propanol by sonicating for ~30 min to acquire the catalyst ink. Then specific amount of ink was transferred on GCE electrode and evaporated at ambient temperature, followed by coating with 5 μL Nafion (0.5 wt % in ethanol). The concentration of Pd and Pt in ink was determined by ICP-OES, and the final loading of Pd and Pt \( \mathrm{m}_{\mathrm{Pt}+\mathrm{Pd}} \) was calculated accordingly to be ~20 μg cm\(^{-2}\). For commercial Pd/C (20 wt.% Pd on carbon black, Alfa) and Pt/C (20 wt.% Pt on carbon, Aldrich) catalyst, they were prepared in the same way, except that the initial concentration in 2-propanol was 4 mg mL\(^{-1}\).

Cyclic voltammetry (CV) curves were conducted in nitrogen saturated 1M KOH aqueous solution, with a voltage window between -1.0 and 0.5 V (vs. AgCl/Ag) and a scanning rate of 100 mV s\(^{-1}\).

For electro-oxidation of ethanol, the test was performed under N\(_2\) atmosphere in 1M KOH aqueous solution containing 1M ethanol. CV curves were recorded between -0.9 and 0.3 V (vs. AgCl/Ag) with a scanning rate of 50 mV s\(^{-1}\). The peak current of the forward scanning (from negative to positive potential) and backward scanning are denoted as \( \mathrm{I}_f \) and \( \mathrm{I}_b \), respectively. The stability test was conducted for 10000 s at the potential of forward peak current maximum. For electro-oxidation of methanol, 1M ethanol was replaced by 1M methanol, and all other conditions were remained the same.

Self-Propulsion Tests

For the self-propulsion test with original Ag aerogels, the solution is prepared by diluting 30 wt.% H\(_2\)O\(_2\) aqueous solution with deionized water to 1.5 wt.% in a plastic Petri dish. Then a piece of Ag aerogel was carefully transferred in above solution and its behavior was recorded by video.

For the test with hetero-structured compressed Au-Ag aerogel, the sample was transferred in diluted H\(_2\)O\(_2\) aqueous solution (2 wt.%), then the rotation behavior was observed and recorded.

The movement or rotation speed was determined by comparing the position of sample from different frames during certain period. The frame per second (FPS) of recorded video was 25, corresponding to the time resolution of 40 ms.
Figures

**Fig. S1. Characterizations of NPs precursors.** (A-C) The UV-vis absorption spectrum, representative TEM images, and size distribution of gold NPs. (D-F) Representative TEM images of as-prepared silver, palladium, and platinum NPs. (G) HAADF-STEM image (left) and corresponding elemental distributions obtained by EDXS analysis for Au-Pd alloy nanoparticle precursors (3.3±0.4 nm).

**Fig. S2. Self-healing behavior of NH$_4$F-induced gold hydrogels.** (A) Three identical gold hydrogels. (B) The solvent in middle and right vials are exchanged to pure water and acetone, respectively. (C-F) Three gels could readily self-healed to monolithic gels after destroying by either hand-shaking or sonication process.
Fig. S3. Digital photos of gelation behavior of gold NPs induced by different salts. (A-E) After 5 min and (F-J) after 12 h. The employed salts from left to right are, (A,F) (NH₄)₂SO₄, NH₄F, NH₃·H₂O, NH₄Cl, NH₄NO₃, NH₄SCN, (B,G) K₂SO₄, KOH, KCl, KNO₃, KSCN, (C,H) Na₂SO₄, NaOH, NaCl, NaNO₃, NaSCN, (D,I) MgSO₄, MgCl₂, Mg(NO₃)₂, CaCl₂, Ca(NO₃)₂, (E,J) H₂SO₄, HCl, HNO₃. It is of the same order as presented in Fig. S6B.

Fig. S4. Digital photos of gelation behavior of gold NPs induced by four typical salts. The black gel, black precipitation, brown gel, and brown precipitation are induced by NH₄F, KSCN, NaCl, and HCl, respectively, representing four typical status of as-prepared hydrogels.
Fig. S5. Zeta potential of gold NP solution after addition of different salts. (A) Zeta potential of gold NP solution recorded 2 min after salt adding. (B) The corresponding salts in figure (A).

Fig. S6A. Time-lapse hydrodynamic size evolution during gelation, which are classified according to anions. (A-E) represent salts with anions of SO$_4^{2-}$, OH$^-$, Cl$^-$, NO$_3^-$, and SCN$^-$, respectively. In the legend, “NH” represent “NH$_4^+$”, 1, 3, 4, 6, 8 represent SO$_4^{2-}$, OH$^-$, Cl$^-$, NO$_3^-$, and SCN$^-$, respectively.
Fig. S6B. Time-lapse hydrodynamic size evolution during gelation, which are classified according to cations. (A-E) represent salts with cations of NH$_4^+$, K$^+$, Na$^+$, Mg$^{2+}$, Ca$^{2+}$, and H$^+$, respectively.

Fig. S7. The low-threshold gelation concentration and ligament sizes versus different anions. The plotting of (A) low-threshold gelation concentration ($c_{gel}$) and (B) ligament size (averaged by employed cations in the inset diagram) of gel networks ($d_g$) against anions. In general, The $c_{gel}$ increases roughly according to Hofmeister series by SO$_4^{2-}$, Cl$^-$, NO$_3^-$, and SCN$^-$; $d_g$ achieved the maximized value for Cl$^-$, while does not show obvious trend for other anions.
Fig. S8. Residual analysis of as-prepared gold aerogels. (A) TGA, (B) IR spectra, and (C) XPS spectra of gold aerogels directed by different salts. All results suggest few impurities (ligands, salts) exist in aerogels. The “*” in (B) denotes the peak from the noise of IR spectrometer.

Fig. S9. Energies derived by DFT calculations. The plotting of the binding energies (\(E_b\)) versus (A) different cations, (B) the ligament sizes of single-charged ions (\(\text{NH}_4^+\), \(\text{K}^+\), \(\text{Na}^+\), \(\text{H}^+\)), and (C) the ligament sizes of double-charged ions (\(\text{Ca}^{2+}\), \(\text{Mg}^{2+}\)). The ligament sizes in B are obtained by averaging the sizes of products derived from single-charged cations paired with anions of \(\text{SO}_4^{2-}\), \(\text{Cl}^-\), and \(\text{NO}_3^-\).
**Fig. S10. Proposed nanoscale force analysis and gelation mechanism.** (A) As two ligands-stabilized gold NPs approach induced by salts, the ligand on the nanoparticle is attracted by opposite-charged ions in solution (F1), thus leaving the bare surface of gold. Simultaneously, gold NPs attract each other driven by the raised surface energy of the uncapped gold surface, van der Waals attraction, and dipole-dipole interactions induced by the defects from removed ligands (F2, F2'). (B-D) NPs fuse together and grow along both axial- and radial direction depending on specific ions, finally evolving into 3D gel networks.

**Fig. S11. Demonstration of the ligament size manipulation of gold aerogels by using specific salts.** The (A-C) digital photos, (D-F) representative TEM images, and (G-I) representative SEM images of gold aerogels prepared by NH$_4$SCN, NH$_4$NO$_3$, and KCl, respectively. (J-K) XRD patterns of Au (111) and Au (200) Bragg reflections of the corresponding gold aerogels.
Fig. S12. Nitrogen adsorption tests of different gold aerogels. (A) Nitrogen gas adsorption curves of gold aerogels induced by NH$_4$SCN, NH$_4$NO$_3$, and NaCl. (B) Pore size distribution of NH$_4$SCN-induced aerogels derived by the DFT method.

Fig. S13. The relation of ligament size and precursors concentration. The size of gold aerogels change with (A) gold precursor (HAuCl$_4$) concentration and (B) NH$_4$F concentration.

Fig. S14. Digital photos of gold gels initiated by other salts. Gold gels could be prepared by using (A) NaClO$_4$, (B) K$_3$PO$_4$, and (C) trisodium citrate (i.e. the ligand) as initiators.
**Fig. S15A.** Digital photos of diverse noble metal aerogels. (A-C) Silver (Ag), palladium (Pd), and platinum (Pt) aerogels. (D-H) Alloy aerogels composed of Au-Ag, Au-Pd, Au-Pt, Pd-Pt, and Au-Pd-Pt, respectively. All aerogels are prepared by using NH₄F as the gelation initiator.

**Fig. S15B.** Representative bright-field TEM images of diverse noble metal aerogels. (A-C) Silver, palladium, and platinum aerogels. (D-H) Alloy aerogels composed of Au-Ag, Au-Pd, Au-Pt, Pd-Pt, and Au-Pd-Pt, respectively.
Fig. S15C. XPS spectra of diverse noble metal aerogels.

Fig. S15D. XRD characterization of noble metal aerogels. (A) Single noble metal aerogels. (B-E) Alloy noble metal aerogels composed by Au-Ag, Au-Pd, Au-Pt, Pd-Pt, and Au-Pd-Pt.
Fig. S15E. Nitrogen adsorption curves and pore size distribution (PSD) of noble metal aerogels. (A) Pd, (B) Au-Ag, (C) Au-Pd, (D) Au-Pt, (E) Pd-Pt, and (F) Au-Pd-Pt aerogels. PSD data was derived by the DFT method.

Fig. S16. Ligament size manipulation of noble metal aerogels. All sizes were determined from bright-field TEM images unless otherwise specified. Sizes of (A) gold-based alloy gels induced by different salts, (B) gold gels induced by different salts, (C) single noble metal gels induced by NH4F, (D) alloy noble metal gels induced by NH4F. (E) Summary of the size manipulation in gold-based gels by different strategies. (F) The correlation of sizes and densities of different noble metal aerogels.
Fig. S17. STEM-EDX analysis of different alloy gels prepared by one-step method. (A) Au-Ag, (B) Au-Pd, (C) Au-Pt, and (D) Au-Pd-Pt gels were prepared by simultaneously reducing corresponding metal precursors in one pot with NH₄F as the initiator.
Fig. S18. HAADF-STEM imaging and EDXS analysis of core-shell structured alloy gels. (A) Au-Ag (1/1) gels prepared by one-pot method. (B-F) Au-Ag (1/1), Au-Pd (1/1), Au-Pd (9/1), Au-Pt (1/1), and Au-Pd-Pt (1/1/1) gels prepared by the dynamic shelling approach. The green arrows in the HAADF-STEM images indicate the line scanning direction.
Fig. S19. Cross-sectional SEM images of compressed aerogels. (A) gold, (B) silver, (C) palladium, and (D) platinum.

Fig. S20. Electrocatalytic performance of different commercial and gel catalysts. (A) CV curves in nitrogen-gas-saturated 1 M KOH solution, with a scan rate of 100 mV s⁻¹. (B) Current retention of different catalysts in 1M KOH + 1M ethanol solution. (C) CV curves of methanol oxidation catalytic reaction (MOR) conducted in 1M KOH + 1M methanol solution, with a scan rate of 50 mV s⁻¹. (D) Summarized Iᵣ and Iᵣ/I₀ of different catalysts for MOR.
Tables

Table S1. Summary of the gelation behavior of gold induced by different salts. The salting-out ability decrease from $\text{SO}_4^{2-}$ to SCN$^-$, and from $\text{NH}_4^+$ to Ca$^{2+}$ according to Hofmeister series. The symbol of “√” and “×” indicate that the product is the self-supporting gel or unsupported powders. The value in bracket is the relative surface charge density of cations and anions referred to $\text{NH}_4^+$. For calculation, the ionic radii were used according to literature (47).

<table>
<thead>
<tr>
<th></th>
<th>NH$_4^+$ (1.00)</th>
<th>K$^+$ (1.15)</th>
<th>Na$^+$ (2.11)</th>
<th>H$^+$ (11.11)</th>
<th>Mg$^{2+}$ (8.45)</th>
<th>Ca$^{2+}$ (4.38)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{SO}_4^{2-}$</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>×</td>
<td>√</td>
<td></td>
</tr>
<tr>
<td>F$^-$</td>
<td>√</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH$^-$</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>×</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>SCN$^-$</td>
<td>√</td>
<td>×</td>
<td>×</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table S2. Concentration of different ions in supernatant after gelation.

<table>
<thead>
<tr>
<th></th>
<th>K (mg L$^{-1}$)</th>
<th>Na (mg L$^{-1}$)</th>
<th>Mg (mg L$^{-1}$)</th>
<th>Ca (mg L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KNO$_3$</td>
<td>3861 (3909)$^a$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NaNO$_3$</td>
<td>-</td>
<td>2180 (2364)$^b$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mg(NO$_3$)$_2$</td>
<td>-</td>
<td>-</td>
<td>322 (810)</td>
<td>-</td>
</tr>
<tr>
<td>Ca(NO$_3$)$_2$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>892 (1336)</td>
</tr>
</tbody>
</table>

$^a$ The value in the bracket denotes the theoretical original concentration of corresponding element after mixing salts and gold nanoparticles solution.

$^b$ Theoretical concentration of Na include a combination of different sources from NaNO$_3$ (100 mM), NaBH$_4$ (0.8 mM), and sodium citrate (2 mM).
Table S3. Summary of nitrogen adsorption data and ligament sizes of as-prepared aerogels. Specific surface area $S_{BET}$ ($m^2 g^{-1}$) was calculated in the partial pressure ($p/p_0$) range of 0.1-0.3. Total pore volume $V_{tot}$ is derived at the volume at $p/p_0=0.99$. Average ligament size $d_{ave}$ is derived from the statistic analysis of TEM measurements.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Metals</th>
<th>Salts</th>
<th>$S_{BET}$ ($m^2 g^{-1}$)</th>
<th>$S_{BET}$ ($m^2 mol^{-1}$)</th>
<th>$V_{tot}$ ($cm^3 g^{-1}$)</th>
<th>$d_{ave}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Au</td>
<td>NH$_4$SCN</td>
<td>29.7</td>
<td>5843</td>
<td>0.218</td>
<td>8.9</td>
</tr>
<tr>
<td>2</td>
<td>Au</td>
<td>NH$_4$NO$_3$</td>
<td>4.7</td>
<td>933</td>
<td>0.023</td>
<td>18.2</td>
</tr>
<tr>
<td>3</td>
<td>Au</td>
<td>KCl</td>
<td>2.5</td>
<td>492</td>
<td>0.010</td>
<td>80.3</td>
</tr>
<tr>
<td>4</td>
<td>Au</td>
<td>MgCl$_2$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>113.7</td>
</tr>
<tr>
<td>5</td>
<td>Au</td>
<td>CaCl$_2$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>57.2</td>
</tr>
<tr>
<td>6</td>
<td>Au</td>
<td>HCl</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>199.6</td>
</tr>
<tr>
<td>7</td>
<td>Au</td>
<td>NH$_4$F</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.9~17.2$^a$</td>
</tr>
<tr>
<td>8</td>
<td>Ag</td>
<td>NH$_4$F</td>
<td>5.2</td>
<td>563</td>
<td>0.030</td>
<td>21.9</td>
</tr>
<tr>
<td>9</td>
<td>Pd</td>
<td>NH$_4$F</td>
<td>122.7</td>
<td>13605</td>
<td>0.021</td>
<td>3.7</td>
</tr>
<tr>
<td>10</td>
<td>Pt</td>
<td>NH$_4$F</td>
<td>3.4</td>
<td>665</td>
<td>0.021</td>
<td>42.0</td>
</tr>
<tr>
<td>11</td>
<td>Au-Ag$^b$</td>
<td>NH$_4$F</td>
<td>34.8</td>
<td>6080</td>
<td>0.319</td>
<td>5.8</td>
</tr>
<tr>
<td>12</td>
<td>Au-Pd$^b$</td>
<td>NH$_4$F</td>
<td>63.9</td>
<td>9694</td>
<td>0.640</td>
<td>4.5</td>
</tr>
<tr>
<td>11</td>
<td>Au-Pt$^b$</td>
<td>NH$_4$F</td>
<td>68.8</td>
<td>13488</td>
<td>0.405</td>
<td>3.1</td>
</tr>
<tr>
<td>12</td>
<td>Pd-Pt$^b$</td>
<td>NH$_4$F</td>
<td>58.0</td>
<td>8744</td>
<td>0.283</td>
<td>4.0</td>
</tr>
<tr>
<td>13</td>
<td>Au-Pd-Pt$^c$</td>
<td>NH$_4$F</td>
<td>95.8</td>
<td>15919</td>
<td>0.549</td>
<td>3.8</td>
</tr>
</tbody>
</table>

$^a$ The value represented the all available range of sizes by altering concentrations of HAuCl$_4$ and NH$_4$F (0.01~2 mM and 7.5~1000 mM, respectively).

$^b$ The molar ratio of the metals in original metal solution is 1/1.

$^c$ The molar ratio of the metals in original metal solution is 1/1/1.

Table S4. Elemental analysis of different alloy aerogels.

<table>
<thead>
<tr>
<th></th>
<th>Au-Ag</th>
<th>Au-Pd</th>
<th>Au-Pt</th>
<th>Pd-Pt</th>
<th>Au-Pd-Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>XPS</td>
<td>1.00/1.14</td>
<td>1.00/1.01</td>
<td>1.00/1.04</td>
<td>1.00/1.06</td>
<td>1.00/0.98/0.94</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>1.00/0.25</td>
<td>1.00/0.99</td>
<td>1.09/1</td>
<td>1.00/0.96</td>
<td>1.00/0.89/0.97</td>
</tr>
</tbody>
</table>
Table S5. Comparison of parameters of noble metal aerogels in literature.

<table>
<thead>
<tr>
<th>Metals</th>
<th>Methods</th>
<th>Gelation Time</th>
<th>Size (nm)</th>
<th>Surface area (m² g⁻¹)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>Conc*a &amp; H₂O₂</td>
<td>~1 week</td>
<td>100~500</td>
<td>Very small</td>
<td>14</td>
</tr>
<tr>
<td>Au</td>
<td>Dopamine</td>
<td>6~72 h</td>
<td>5~6</td>
<td>50.1</td>
<td>31</td>
</tr>
<tr>
<td>Au</td>
<td>Dealloy</td>
<td>/</td>
<td>20~40</td>
<td>3.7</td>
<td>9</td>
</tr>
<tr>
<td>Au</td>
<td>Conc<em>a &amp; FD</em>b</td>
<td>/</td>
<td>200~500</td>
<td>Very small</td>
<td>13</td>
</tr>
<tr>
<td>Au</td>
<td>Salts</td>
<td>4~48 h</td>
<td>6.9~199.6</td>
<td>2.5~29.7</td>
<td>This work</td>
</tr>
<tr>
<td>Ag, Pt, Pd, Au-Ag,</td>
<td>Salts</td>
<td>4~12 h</td>
<td>3.1~142.0</td>
<td>5.2~122.7</td>
<td>This work</td>
</tr>
<tr>
<td>Au-Pd, Au-Pt, Pd-Pt,</td>
<td>Au-Pd, Ag-Pt</td>
<td>Conc*a</td>
<td>8~15 d</td>
<td>3~10</td>
<td>46~48</td>
</tr>
<tr>
<td>Au-Pd, Pd-Pt, Ag-Pd,</td>
<td>Conc*a &amp; 348 K</td>
<td>Several hours</td>
<td>3~6</td>
<td>57~79</td>
<td>48</td>
</tr>
<tr>
<td>Au-Ag-Pd</td>
<td>(C(NO₂)₄ &amp; dealloying</td>
<td>16~24 h</td>
<td>3~5</td>
<td>76~269</td>
<td>38</td>
</tr>
<tr>
<td>Au-Ag, Pd-Ag, Pt-Ag</td>
<td>NaCl</td>
<td>1~2 d</td>
<td>/</td>
<td>32~42</td>
<td>25</td>
</tr>
<tr>
<td>Au-Pt</td>
<td>343 K</td>
<td>2~4 h</td>
<td>2~5</td>
<td>/</td>
<td>49</td>
</tr>
<tr>
<td>Ag</td>
<td>Dextran templating</td>
<td>/</td>
<td>~4000</td>
<td>0.1~0.5</td>
<td>10</td>
</tr>
<tr>
<td>Ag</td>
<td>(C(NO₂)₄</td>
<td>4~12 h</td>
<td>3~8</td>
<td>45~160</td>
<td>17</td>
</tr>
<tr>
<td>Pd</td>
<td>Conc*a &amp; Ca²⁺</td>
<td>5 min ~ 2 month</td>
<td>3~10</td>
<td>40~108</td>
<td>15</td>
</tr>
<tr>
<td>Pd</td>
<td>β-CD</td>
<td>3~10 d</td>
<td>3~4</td>
<td>92</td>
<td>20</td>
</tr>
<tr>
<td>Pt</td>
<td>N₂H₄ in organic phase</td>
<td>1~5 h</td>
<td>3~8</td>
<td>30~40</td>
<td>50</td>
</tr>
<tr>
<td>Pd-Pt</td>
<td>NaBH₄</td>
<td>3~17 d</td>
<td>4~5</td>
<td>73~168</td>
<td>19</td>
</tr>
<tr>
<td>PdxAu-Pt</td>
<td>NaBH₄ &amp; UPD<em>c &amp; GRR</em>d</td>
<td>very long</td>
<td>4~5</td>
<td>83~105</td>
<td>21</td>
</tr>
</tbody>
</table>

*a Concentration of nanoparticles solution by centrifuge filters.

*b Freeze drying.

*c Underpotential deposition.

*d Galvanic replacement reaction.