

# Work Functions at Work: Observing Contact Electrification at Individual Metal–Metal Heterojunctions

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## Article

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**Posted Date:** July 14th, 2026

**DOI:** <https://doi.org/10.21203/rs.3.rs-9930579/v1>

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**Additional Declarations:** There is **NO** Competing Interest.

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# **Work Functions at Work: Observing Contact Electrification at Individual Metal–Metal Heterojunctions**

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## Abstract

Charge redistribution at the contact of two dissimilar metals, referred to as contact electrification, is ubiquitous in nanotechnologies. However, individual nanoscale heterojunctions remain difficult to access experimentally, particularly in terms of real-space charge redistribution and the corresponding electric field. Here we provide local, quantitative access to the hidden phenomena at individual nanoparticle–substrate heterojunctions by combining off-axis electron holography with a predictive computational twin based on orbital-free density functional theory. Electron holography measurements on a grounded metallic architecture isolate phase shifts that originate from work-function difference. In parallel, the computational twin model, calibrated solely by the work functions of the constituent silver and gold, reproduces the measured phase shifts without fitting to the holography data. This quantitative agreement unambiguously identifies work-function difference as the microscopic origin, revealing “work functions at work”. Moreover, charge redistribution is found not merely at the buried contact region but, unexpectedly, at the external surfaces of nanoparticles, causing electric field perturbations in surrounding environment. This spatially-resolved information—inaccessible to ensemble-average techniques—reveals how a single nanoparticle alters its local electrostatic conditions via contact electrification, with direct implications for catalytic properties. Our framework further provides a new capability to probe local contact potentials and to infer individual nanoparticle work function, enabling studies of metal–support interactions to single-particle resolution.

**Keywords:** nanoscale heterojunctions, electron redistribution, metal–support interactions, density functional theory, off-axis electron holography, heterogeneous catalysis

## Main

Nanoscale metal–metal heterojunctions are ubiquitous in modern technologies. They enable internal electron flow in bimetallic nanoparticles (NPs) that couple distinct surface reactions<sup>1,2</sup>, control tip–sample charge exchange in scanning probe microscopy<sup>3</sup>, govern the operation of microelectromechanical systems (MEMS) switches<sup>4</sup>, and exist in Janus particles that exhibit self-propulsive behaviour in nanomotors<sup>5</sup> or plasmonic resonances in optical applications<sup>6</sup>.

Contact electrification, the spontaneous exchange of charge when two surfaces come into contact<sup>7,8</sup>, is among the oldest known electrical phenomena<sup>9,10</sup>. The interpretation of metal–metal contact electrification has been a question of fundamental interest throughout the development of modern physics. From the early observations by Bennet<sup>11</sup> and Volta<sup>12,13</sup> to later debates between Thomson (later Lord Kelvin)<sup>14,15</sup> and Maxwell<sup>16,17</sup>, and their followers (Thomsonians<sup>18</sup> and the Maxwellians<sup>19</sup>), the origin of the contact potential has remained controversial for more than a century<sup>20,21</sup>. Stepping into the twentieth century, Richarson<sup>22</sup> first used the concept of work function to explain the electron redistribution. Harper<sup>23</sup> and Lowell<sup>24</sup> further showed that electron transfer proceeds via tunnelling until the Fermi levels of the two metals match. More recently, time-resolved measurements by Möller and co-workers<sup>25</sup> revealed that charge equilibration occurs within microseconds after the impact of a gold sphere and a copper plate. Together, these studies established the physical picture of contact electrification at the macroscopic scale.

Resolving the local response of contact electrification in nanoscale NP–substrate junctions remains a major challenge. While photoelectron spectroscopy allows estimation of the *average* electron transfer across an ensemble of metal NPs<sup>26</sup>, it cannot resolve the spatial electron redistribution or the local electrostatic characteristics within an *individual* NP–substrate junction. This missing local information has left key questions unanswered: Does charge redistribution remain confined to the buried contact region, or does it extend to external NP surfaces? How does the resulting electrostatic field perturb the surrounding environment experienced by nearby molecules, probes, and nanostructures? To what extent are these phenomena governed by work-function differences, and how can they be deliberately controlled?

Answering these questions requires both theoretical modelling and experimental measurements, yet an integrated framework that combines these capabilities has so far been lacking. On the theoretical side, only a few studies have addressed nanoscale metal–

metal contacts. Peljo, Girault and co-workers calculated the electrostatic fields surrounding bimetallic Janus NPs using classical electrostatics<sup>27</sup>. However, due to the absence of quantum effects in the classical model, a 1 V potential difference had to be prescribed to the two metals to mimic the work function difference<sup>27</sup>. To overcome this limitation, we recently developed a density–potential functional theoretic approach (DPFT)<sup>28</sup>, in which metal electrons are described by orbital-free density functional theory (OF-DFT)<sup>29,30</sup>. The model is parameterized solely by the work functions of the constituent metals, allowing the contact potential to emerge self-consistently through Fermi-level equilibration instead of being prescribed a priori. In this way, DPFT captures the physics of work-function-driven contact electrification. In comparison to Kohn–Sham DFT, the DPFT approach is computationally much more efficient and therefore enables systematic exploration of NP size, morphology and interparticle distance beyond the reach of conventional first-principles calculations.

On the experimental side, off-axis (OA) electron holography provides access to electrostatic potentials at the level of *individual* NPs<sup>31,32</sup>. As a transmission electron microscopy (TEM) technique, OA electron holography records electron phase shifts caused by the local electrostatic potentials<sup>33</sup>, and has been applied to studies of semiconductors<sup>34,35</sup>, electrical-biased nanotips<sup>36,37</sup>, and charge-transfer in oxide-supported metal NPs<sup>38,39</sup>. Quantitative interpretation of holographic measurements, however, has generally relied on simplified electrostatic models in which net charges are represented by effective point charges or surface charge densities whose magnitudes are adjusted to reproduce the measured phase shifts<sup>36,38–40</sup>. Although these simplified models allow estimation of the total transferred charge, they do not provide information on the origin of the observed charging phenomena in experiments. More importantly, the lumped charge models preclude real-space resolution of electron redistribution across the heterojunction, which are critically relevant for various applications, including heterogeneous catalysis and probe-based measurements.

Here we establish an integrated framework that combines OA electron holography with a computational twin model based on OF-DFT. Applied to a well-defined model system of silver NPs supported on gold substrates, the computational twin quantitatively reproduces experimental phase maps using only independently determined work functions, thereby demonstrating “work functions at work”. We show that charge redistribution is not confined to the buried contact region but extends to the external surfaces of the NPs, generating electrostatic perturbations throughout the surrounding environment. These findings provide a quantitative real-space picture of contact electrification at individual metal–metal

heterojunctions and reveal how work-function-driven charge equilibration reshapes the electronic and electrostatic properties.

During OA holography measurement, an object wave passing through the sample interferes with a reference wave that propagates through vacuum by applying a voltage to a biprism filament. Reconstruction of the resulting hologram, formed by interference fringes, yields the projected phase shift,  $\varphi(x, z)$ , of the electron wave within the  $(x, z)$ -plane perpendicular to the beam. In the absence of magnetic contributions, the phase shift is proportional to the line integral of the electrostatic potential through the specimen, given by

$$\varphi(x, z) = C_E \int V(x, y, z) dy, \quad (1)$$

where  $C_E$  is the interaction constant and  $V(x, y, z)$  is the three-dimensional electrostatic potential distribution<sup>33,41</sup>.

The detection limit of electrostatic potential variations using off-axis electron holography is determined by the energy and coherence of incident electron beam, and detector sensitivity. Using an ultra-high energy TEM (1.2 MV), increased phase resolution allows a detection limit below single-electron charging<sup>38</sup>. More generally, using a medium energy TEM (200 to 300 kV), the metal–metal contact electrification can be detected without the risk of significant irradiation damage by the electron beam. In this study, we employ a 300 kV TEM and a high pixel direct electron detector.

To prepare the experimental samples, cubic silver (Ag) NPs (side length ~70 nm) were deposited by simple drop-coating directly onto a gold (Au) TEM grid (UltrAuFoil), which was cut in half, as shown in **Fig. 1a**. The relatively large particle size was chosen to ensure that the resulting phase shift is experimentally resolvable, as discussed below. A unique feature of this model system is that both the NPs and the supporting grid are metallic conductors that were grounded during holography measurements. This configuration reduced charging caused by electron-beam irradiation, since additional free charge introduced into the system was immediately drained to ground. Consequently, the overall system was ensured to be electrically neutral, and any local excess charge must arise solely from the built-in contact potential between Ag and Au.

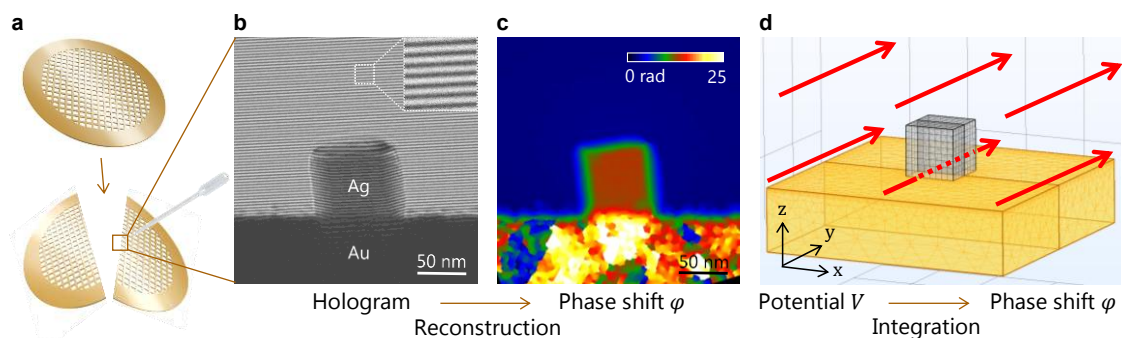


**Fig. 1 | Experimental and computational model systems and procedures for obtaining phase shift maps.** **a**, A solution containing silver NPs was dropped onto a half gold grid. Samples were fully grounded during holography measurements. **b**, Off-axis electron hologram, showing a silver NP supported on the gold grid. The inset shows the interference fringe pitch. **c**, The reconstructed phase shift image. **d**, A computational twin model consisting of a silver NP supported on a gold substrate was built, and the electric potential distribution in the system was determined from the equilibrated electronic density distribution calculated by OF-DFT. The 2D phase image was obtained by integrating the potential along the y direction (red arrows).

The structural configuration of the supported NP system provides an ideal geometry for hologram acquisition and phase analysis. Measuring the electrification effect at direct (buried) contact interfaces between two metals is generally not possible, because in that region the phase shift is dominated by the mean inner potential of the materials, and the contribution from contact-induced charging is orders of magnitude smaller. The supported cubic NP geometry in our samples, in contrast, exposes large and regular external surfaces. We have predicted, in recent articles, that contact electrification gives rise to charge redistribution not only at the buried solid–solid interface but also on the external surfaces of both the NP and the support<sup>28,42</sup>. The vacuum region surrounding the NP therefore provides direct access to the potential distribution, free from the influence of the inner potentials. After acquisition of hologram images (**Fig. 1b**), phase images were reconstructed (**Fig. 1c**), as detailed in the Methods section.

In direct analogy to the experimental system, a computational twin model was constructed. It consists of a cubic silver NP supported on gold substrate, as shown in **Fig. 1d**. Periodic boundary conditions were applied in in-plane (xy) direction, thus defining a regular square lattice array of NPs with inter-particle distance controlled by the size of the simulation box. The equilibrated electron density distribution across the NP–support system in vacuum environment was calculated by the OF-DFT part of the DPFT approach<sup>28,30</sup>. OF-DFT parameters for Au and Ag were calibrated to reproduce literature values for the work functions of extended surfaces of the respective pure metals, as described in

Supplementary Section 2. It is important to stress that no information from holography experiments was used in the calibration procedure. The full formalism of the OF-DFT equations is provided in Appendix and Supplementary Section 1. From the self-consistently calculated electronic charge density, the electrostatic potential  $V(x,y,z)$  was calculated. After integrating along  $y$  (beam) direction and multiplying with the interaction constant  $C_E$ , a phase image in the  $xz$  plane was obtained (see Equation (1)).

Having obtained both experimental and simulated phase shifts, a direct comparison would appear straightforward. However, a fundamental mismatch in length scale remains. The experimentally studied Ag NPs were chosen to have a relatively large size of 70 nm, as smaller particles yield phase shifts that approach the experimental noise level of holography measurements. At typical surface coverages ( $\lesssim 1\%$ ), support dimensions are at least an order of magnitude larger than the NP size. Even with the efficiency of OF-DFT, practical simulations are limited to NPs of  $\sim 10$  nm and support of  $\sim 100$  nm. Bridging this gap between the experimentally accessible and computationally tractable regimes is therefore essential for meaningful comparison. As we show below, this can be achieved through a scaling law that we uncovered between phase shift and NP size.

## Scaling behaviour relating phase shift and NP size

**Fig. 2a-c** shows the calculated phase images of supported NPs with side lengths  $L_{NP}$  of 4, 8 and 16 nm and a fixed NP coverage on the support surface of 1%. The phase images exhibit the same characteristic pattern: a gradual transition from a bright region surrounding the NP, corresponding to positive values of the phase shift, to a darker region of negative values near the support. The calculated phase shifts along the paths perpendicular to the NP's outer facet (indicated by black arrows in **Fig. 2a-c**) are plotted in **Fig. 2e**, including the case of 2 nm NP size. Also shown are the scaled phase shift curves from the 8 nm case to the 2, 4, and 16 nm cases, using the scaling law  $\varphi' = \lambda m \varphi$ . Here,  $\lambda$  accounts for the geometric scaling,  $\mathbf{r} \mapsto \mathbf{r}' = \lambda \mathbf{r}$ , while  $m$  accounts for the variations in the built-in contact potential as NP size changes,  $\Delta V \mapsto \Delta V' = m \Delta V$ . The scaled phase shift curves show excellent agreement with the directly calculated results. This scaling behaviour follows from the scale invariance of the Laplace equation under geometric transformations and the linear dependence of its solution on the boundary conditions (see Supplementary Section 3 for detailed derivations).

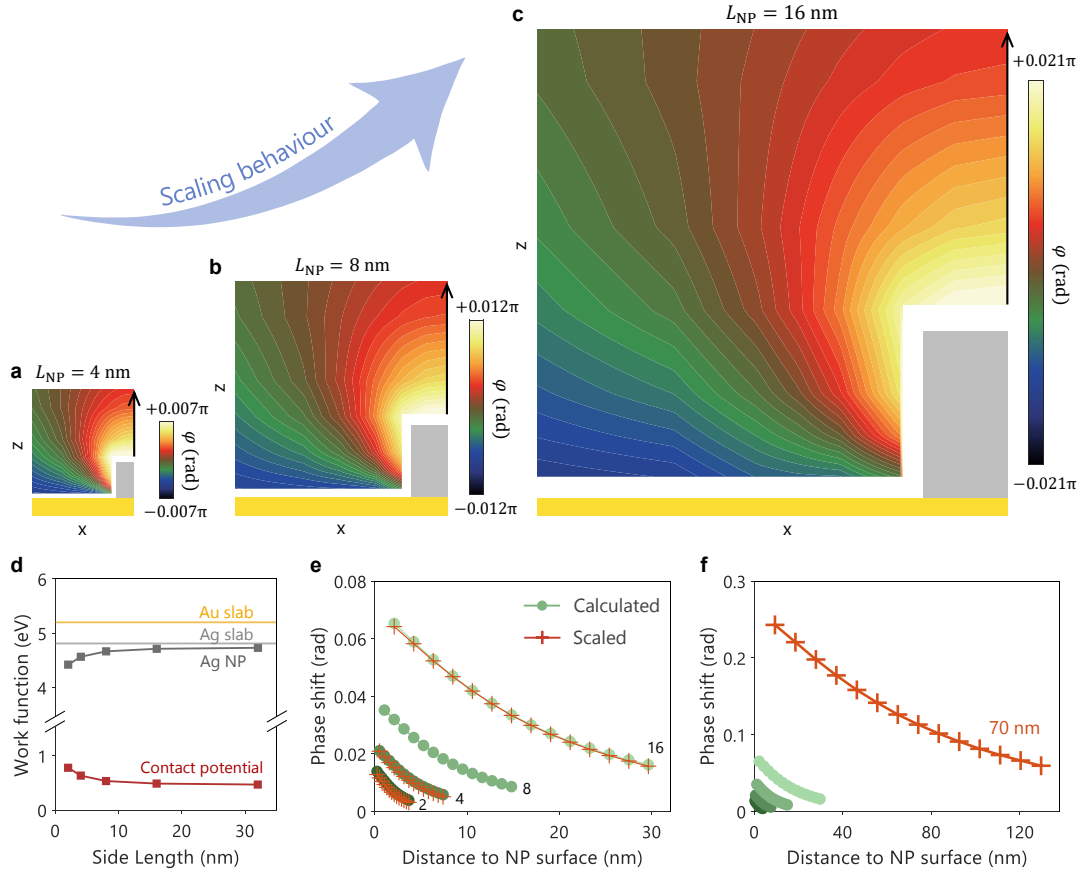


**Fig. 2 | Scaling behaviour of phase shift with NP size.** **a-c**, Simulated two-dimensional phase shift maps of Ag NPs with side lengths of 4 nm (**a**), 8 nm (**b**), and 16 nm (**c**). For clarity, only the left part of each map is shown. **d**, Contact potential between the Ag NPs and Au substrate as a function of NP side length, as calculated by OF-DFT. Also shown are the work function of Au slab, Ag slab and Ag NPs. **e**, Calculated and scaled one-dimensional phase shifts along the paths indicated by black arrows in (**a**)-(c) for NPs with side lengths of 2, 4, 8 and 16 nm. **f**, Predicted phase shift for a 70 nm NP based on the established scaling law. The four green curves in (**e**) are shown in (**f**).

The variation in the built-in contact potential originates from the size dependence of the NP work function. Generally, the work function decreases for smaller NPs owing to the surface-curvature effect<sup>43</sup>. As shown in **Fig. 2d**, the work function  $\Phi$  of Ag NP obtained by OF-DFT decreases from 4.51 eV for a 16 nm particle to 4.17 eV for 2 nm (grey line), which results in an increase in the work function difference  $\Delta\Phi$ , *i.e.*, the built-in contact potential  $\Delta V$ , between the Ag NP and the Au slab (red line).

With the validity of the scaling law established (**Fig. 2e**), the phase shift of a 70 nm NP on a 700 nm support surface was predicted by up-scaling from the calculated phase shift of an 8 nm NP. The extrapolated phase-shift curve is shown in **Fig. 2f**, which can be directly

compared with the results from experimental holography measurements.

The established scaling law is of central importance to this work, as it bridges the gap between experimentally accessible and computationally tractable size regimes. Because work function differences are on the order of 1 eV, contact electrification produces inherently small phase shift variations that are below 0.05 rad for NPs smaller than 10 nm. This magnitude is comparable to the experimental noise level, thus rendering such small particles difficult to detect using general TEM techniques (except for ultrahigh sensitivity and resolution at ultrahigh voltage as used in ref. <sup>38</sup>). Consequently, only larger particles, such as the 70 nm Ag cubes studied here, yield measurable phase shifts. On the modelling side, although the OF-DFT approach offers substantial efficiency gains over Kohn–Sham DFT, the computation time and memory requirement still scale steeply with system size, limiting simulations to NPs of ~10 nm. This is particularly true for supported NPs, where the substrate adds an extra order of magnitude to the overall system dimensions. The scaling law therefore provides the key link between experiment and theory, enabling direct and quantitative comparison to be shown in the next section.

## **Work functions at work: quantitative comparison of experiment and theory**

Experimental phase shifts for five individual Ag NPs obtained from electron holography measurements are displayed in **Fig. 3a**. Projected phase-shift maps are shown on the right, and the phase-shift profiles along the white lines, starting ~20 nm away from the Ag NP surface, are shown on the left. As absolute values of phase shifts are not relevant, the phase-shift curves were vertically offset by a value of 0.2 rad against each other for clarity. A consistent trend is observed across different NPs, with similar slopes in the phase-shift profiles. The measured phase shift reflects electron redistribution to the *external* surfaces of the Ag NP and the Au substrate, generating an electrostatic field and potential distribution in the surrounding vacuum that alters the electron-beam phase. Slight variations among NPs can be attributed to samples non-idealities, including substrate roughness, NP orientation, and minor surface contamination.

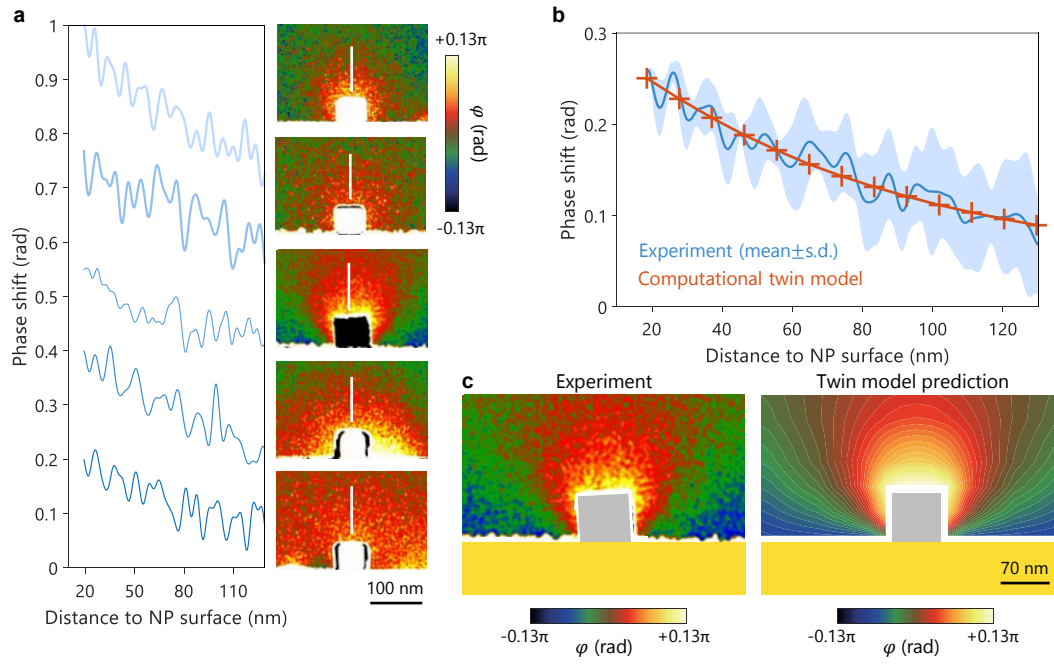


**Fig. 3 | Quantitative comparison between experimental and computational phase shifts.**

**a**, Phase shifts for five different Ag NPs obtained from electron holography measurements. The left panel shows the phase shifts along the direction perpendicular to the NP outer facets, indicated by the white lines in the two-dimensional maps on the right. **b,c**, Comparison between experimental and computational phase shifts, plotted along the surface-normal direction (white lines) (**b**) and over the two-dimensional plane (**c**). The experimental phase shift curve in **b** (blue line) represents the mean value of the five individual phase shifts shown in **a**, with the shaded area indicating one standard deviation. The computational phase shift curve (orange line) was obtained from the computational twin model, *i.e.*, OF-DFT calculations for 8 nm NP, and scaled to the 70 nm case using the established scaling law.

The mean phase-shift, averaged over the five phase shift curves, is plotted in **Fig. 3b** (blue line), with the shaded region indicating the standard deviation. Also shown there is the phase shift predicted by the computational twin model (orange line). Remarkably, the model prediction matches the experimental curve precisely, lying well within the experimental uncertainty. Furthermore, the predicted phase image closely reproduces the experimental phase map, as shown in **Fig. 3c**. This quantitative agreement (without fitting to the measured data) demonstrates that the integrated experimental–theoretical framework provides an accurate and consistent description of contact electrification at individual NP–substrate interfaces. As the theoretical model employs the work functions of extended Ag and Au surfaces as the only input parameters, the experimental observations are clearly demonstrated to be caused by the respective work-function difference.

To the best of our knowledge, such a direct and quantitative demonstration of the origin of

charge redistribution observed at an individual metal–metal junction—combining real-space visualisation with predictive modelling—has not been achieved to date. Previous electron-holography studies focused on metal NPs supported on non-conductive oxide substrates<sup>38,39</sup>, where effects of electronic equilibration, electron-beam-induced charging, and chemical interactions at the NP–oxide interface are superimposed. Our integrated experimental–theoretical framework with a highly conductive metal–metal setup overcomes these complications and thus provides, for the first time, a direct view of *work functions at work*.

## Electronic and electrostatic perturbations at individual metal–metal contact

A unique advantage of the computational twin model presented here is that it serves as an independent and complementary analysis tool, rather than a fitting scheme based on an oversimplified model as is routinely used, such as lumped surface-charge<sup>36,40</sup> or point-charge<sup>38,39</sup> descriptions. In contrast to these approaches, the OF-DFT-based twin model provides the entire three-dimensional distribution of electron density, and electrostatic potential and field throughout the supported NP system, which is crucial for more advanced analyses. For instance, changes of catalytic activity of metal NPs induced by the supporting material have been attributed to electron redistributions caused by electronic metal–support interactions<sup>28,42,44–46</sup>. While photoelectron spectroscopy provides access to the average charge transfer per particle across an ensemble of NPs<sup>26</sup>, and electron holography has enabled the counting of net charges<sup>38,39</sup>, how charge equilibration redistributes electrons and reshapes electrostatic fields at individual NP–substrate heterojunctions remains largely unknown. In our developed framework, this limitation is addressed by the computational twin model.

Here, contact-induced electronic perturbation is directly represented by the calculated charge density difference between the combined and separate systems, defined as  $\Delta\rho = \rho_{\text{supNP}} - \rho_{\text{sup}} - \rho_{\text{NP}}$ , where  $\rho_i$  are the charge density distributions of the supported NP system, the bare support, and the isolated NP, respectively, as shown in **Fig. 4a**. Due to the smaller work function of the Ag NP (see **Fig. 2d**), Fermi-level equilibration between the NP and the Au support results in electron depletion, *viz.*, positive net charge (red) on the NP *external* surface and electron accumulation, *viz.*, negative net charge (blue) on the support surface. The corresponding electric field in surrounding vacuum orients from the

positively charged NP surface towards the negatively charged support surface, as depicted in **Fig. 4b**. Strong localization of the electric field is observed at the corners of the NP. The corresponding potential distribution, displayed in **Fig. 4c**, reveals a positive potential region surrounding the NP and a negative potential region in the vicinity of the support.

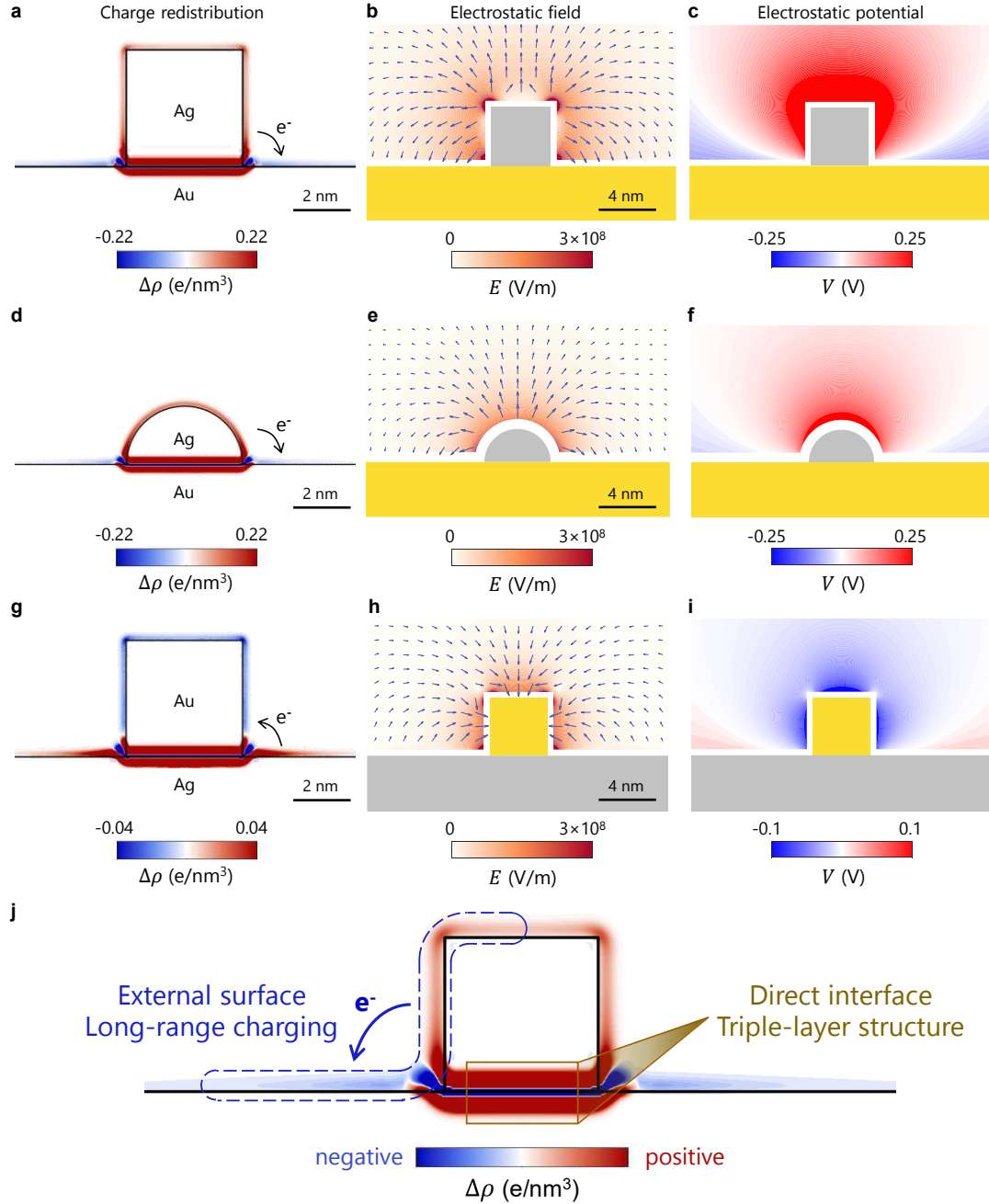


**Fig. 4 | Electronic and electrostatic perturbations at individual metal-metal contact for a 4 nm NP case.** **a**, Charge redistribution at the solid-solid direct interface and the external surfaces. **b,c**, Electrostatic field (**b**) and potential (**c**) surrounding the system. **d**, Charge redistribution for a half-spherical Ag NP supported on Au. **e,f**, Corresponding electrostatic field (**e**) and potential (**f**). **g**, Charge redistribution for the reverse system, viz., a cubic Au NP

supported on Ag. **h,i**, Electrostatic field (**h**) and (**i**) potential, exhibiting opposite behaviours to (**b**) and (**c**). **j**, Illustration of real-space electron redistribution at direct interface and external surfaces of an individual NP–substrate heterojunction. The case of a 2 nm NP is shown here as smaller NPs exhibit clearer effects.

A subtle yet insightful aspect of these new results is that the phase shift observed in the vacuum region (**Fig. 3**) originates from long-range charging that leads to electron redistribution across the *external* surfaces of NP and support, which directly impacts the catalytic and mechanical properties of surface sites through changes in density of states as well as electric fields<sup>28,42,47</sup>. This long-range charging and the resulting fringing fields have been leveraged, for instance, to design phase plates for electron microscopy<sup>48,49</sup>.

NP size is a readily tunable parameter for catalytic performance, and size-dependent catalytic activity and stability have therefore attracted considerable interest<sup>50,51</sup>. Complementary to the well-documented size dependence of NP band structures<sup>52</sup>, the computational twin model gives access to charge densities at external surfaces of supported NPs over a wide range of sizes. It reveals that electron accumulation becomes increasingly pronounced as the NP size decreases (**Extended Data Fig. 1**). This trend can be understood in terms of capacitive charging between the external surfaces of NP and the support, analogous to the two plates of a capacitor—as the separation between the plates shrinks, the capacitance increases (see **Extended Data Fig. 2c** for a schematic illustration). This capacitive coupling is an inherent feature of supported NP systems, with its strength determined by the dielectric environment. Intuitively, a higher dielectric constant leads to stronger charging. Indeed, external surface charging is substantially enhanced in solution compared with vacuum, as evidenced by **Extended Data Fig. 2**.

The situation at the buried solid–solid interface is rather intricate. Interfacial charge redistribution is typically described within a double-layer picture. Here, however,  $\Delta\rho$  displays a triple-layer structure (**Fig. 4a**), challenging this conventional view. This structure arises from two superimposed effects: (i) net electron transfer from the NP to the support during electronic equilibration, and (ii) pushback of spillover electron tails at both metal surfaces. Unlike simple classical electrostatic models commonly employed in the literature, the OF-DFT approach explicitly accounts for the quantum nature of metal electrons, thereby capturing effects of electron spillover which extends ~0.3 nm beyond the surface into the vacuum. Upon metal–metal contact, these spillover electrons repel and push each other closer to the metal surfaces, producing a net electron excess within the interfacial region (indicated by the blue shades). The resulting triple-layer structure, shown in more

detail in **Extended Data Fig. 3**, has been recently confirmed by KS-DFT calculations<sup>28</sup>. **Fig. 4j** summarises the key findings of this work—real-space electron redistribution at direct interface and external surfaces of an individual NP–substrate heterojunction—which can only be resolved through the integrated holography–computational twin approach.

Beyond the model system investigated experimentally, the computational twin model was leveraged to explore the effects of NP shape and materials composition on contact electrification. As shown in **Fig. 4d–f**, upon replacing the cubic NP with a hemispherical one, the direction of electron transfer is preserved, whereas the strong concentration of the electric field at the cube corners disappears. By contrast, interchanging the elemental compositions of the NP and the support (**Fig. 4g–i**) results in a charge-transfer reversal. Consequently, the electrostatic field points from the Ag support towards the Au NP, giving rise to a positive potential region near the support surface and a negative potential region surrounding the NP. Because the work function difference in this case (0.14 eV between Au NP and Ag support) is smaller than that in the reference configuration (0.62 eV between Ag NP and Au support), the magnitude of electron redistribution is accordingly reduced. The phase shift maps of the three systems are shown in **Extended Data Fig. 4**

## Discussion

Previous studies of contact electrification largely provided ensemble-averaged information, leaving local quantitative information from individual NP–substrate heterojunctions largely unknown. In our study, the combination of electron holography and a computational twin enables direct visualisation and quantitative interpretation of charge equilibration effects at the level of individual particles. Our results reveal that, charge equilibration gives rise to electronic response that extends beyond the immediate interface and reshapes the electrostatic conditions of the entire nanostructure, including its external surfaces (see **Fig. 4j**).

Our integrated framework further provides a route to quantitatively probe contact potentials at individual NPs on a non-uniform surface. This can be achieved by inverting the quantitative relationship between work-function differences and measured phase maps. By adjusting the work-function-related parameters in the OF-DFT model until the calculated and measured phase maps coincide, one can probe the contact potential of an arbitrary metal–metal heterojunction. This capability extends potentiometric measurements to heterogeneous supported NP systems with single-particle resolution, where conventional

approaches remain challenging.

The ability to directly resolve charge redistribution also creates opportunities to investigate how nanoscale structure, surface chemistry and environmental conditions influence charge equilibration. Beyond the Ag–Au model system studied here, a wide range of material combinations can be accessed through substrate replacement or surface coatings. Furthermore, by performing holographic measurements at identical locations before and after controlled chemical modifications or dynamic laser-irradiation<sup>53</sup>, it becomes possible to track how surface reconstruction, oxidation, adsorbate coverage and other interfacial processes modify the electrostatic conditions associated with Fermi-level equilibration<sup>39</sup>.

Charge redistribution is also known to influence mechanical responses of metallic nanostructures through changes in electronic bonding and surface stress, as demonstrated in nanoporous metals<sup>47</sup>. The capability to simultaneously resolve charge redistribution and electrostatic fields provided by our framework therefore opens the door to directly exploring the coupling between electronic and mechanical effects in metallic nanostructures.

## Methods

### Orbital-free Density Functional Theory (OF-DFT)

Our OF-DFT implementation follows earlier work<sup>28,30</sup> and starts with formulating the grand potential,  $\Omega$ , of the system as a functional of the two core variables, namely the electron density,  $n_e$ , and electrostatic potential,  $V$ ,

$$\Omega = \int g d^3r = \int \left( t_{\text{ni}} + u_x + u_c + p_{\text{cc}} - n_e \tilde{\mu}_e - \frac{1}{2} \epsilon_{\text{opt}} (\nabla V)^2 + (n_{\text{cc}} - n_e) e_0 V \right) d^3r, \quad (2)$$

where  $t_{\text{ni}}$  is the kinetic energy of non-interacting (subscript “ni”) electrons,  $u_x$  and  $u_c$  are the exchange and correlation energies,  $p_{\text{cc}}$  is the pseudopotential energy of metal electron–core interactions,  $\tilde{\mu}_e$  is the electrochemical potential of metal electrons,  $\epsilon_{\text{opt}}$  is the optical permittivity,  $n_{\text{cc}}$  is the number density of metal atomic-core charges, and  $e_0$  is the elementary charge.

Minimization of  $\Omega$  with respect to  $n_e$  and  $V$  gives two controlling equations which can be solved for the equilibrium distributions of  $n_e$  and  $V$ . Applying the Euler–Lagrange

equation  $\frac{\partial g}{\partial n_e} - \nabla \cdot \left( \frac{\partial g}{\partial (\nabla n_e)} \right) = 0$ , we obtain

$$\nabla \cdot \left[ \frac{\partial(t_{ni} + u_x + u_c + p_{cc})}{\partial \nabla n_e} \right] = \frac{\partial(t_{ni} + u_x + u_c + p_{cc})}{\partial n_e} - e_0 V - \tilde{\mu}_e. \quad (3)$$

Minimization of  $\Omega$  with respect to the potential  $V$  yields the Poisson equation,

$$-\nabla \cdot (\epsilon_0 \nabla V) = e_0 (n_{cc} - n_e). \quad (4)$$

More detailed explanation and derivations can be found in the Supplementary Section 3 and in Ref. <sup>28</sup>.

While sub- to single-nanometre-sized supported metal clusters are conventionally simulated by Kohn–Sham DFT, the OF-DFT approach enables the simulation of supported NP systems with particle sizes up to 16 nm and supports an order of magnitude larger. It facilitates systematic analyses of the influence of the particle’s chemical nature, size, geometry, and interparticle distance, as well as the effects of the surrounding environment (e.g., vacuum or a polarizable dielectric medium)<sup>28,46</sup>.

### Sample preparation

Ag NPs in cubic shape exposing {100} facets were purchased from NanoSeedz. The particles were originally dispersed in mixed ethanol and water with volume ratio of 1:1. Before preparing TEM samples, they were diluted in distilled water and ultrasonicated for 3 min to ensure dispersion. An UltrAuFoil grid (Quantifoil Micro Tools GmbH), consisting of a R2/2 50-nm-thick Au holey film on a 300-mesh Au support, was cut in half. Then the diluted NPs were deposited by simple drop-coating directly onto the half Au grid. Only particles located along the straight breaking edge of the grid were selected for imaging.

Minor surface contamination during sample preparation is essentially unavoidable, and the vacuum in TEM column is on the order of  $10^{-7}$  Pa. However, such contamination is not expected to dominate the contact potential. Significant contamination would induce electron-beam charging, manifested as a wedge-shaped phase shift across the Ag NP. The absence of such features in our measurements indicates that contamination effects are limited. Nevertheless, the use of ultra-high vacuum TEM and vacuum sample-transfer would further suppress surface contamination.

### Off-axis electron holography measurements

Off-axis electron holography is based on the interference of two electron beams with

different phases<sup>41</sup>. The object wave carries phase information modified by the sample, while the reference wave represents the incident electron wave. A biprism filament, made of quartz and coated with a layer of Au, is placed between the back focal plane and the image plane. Upon applying a bias voltage on the biprism, the object and reference waves generate interference fringes on a detector. The intensity of the resulting hologram,  $I_{\text{hol}}(\mathbf{r})$ , can be expressed as<sup>33</sup>

$$I_{\text{hol}}(\mathbf{r}) = 1 + A^2(\mathbf{r}) + 2\mu A(\mathbf{r}) \cos(2\pi \mathbf{q}_c \mathbf{r} + \varphi(\mathbf{r})), \quad (5)$$

where  $A$  is the electron wave amplitude,  $\mu$  the fringe contrast,  $\mathbf{q}_c$  the reciprocal space vector, and  $\varphi$  the electron wave phase. To obtain the amplitude and phase separately, the off-axis electron hologram is first Fourier transformed, shown in the form

$$\begin{aligned} \text{FT}\{I_{\text{hol}}(\mathbf{r})\} = & \text{FT}\{1 + A^2(\mathbf{r})\} + \mu \text{FT}\{A(\mathbf{r})e^{i\varphi(\mathbf{r})}\} \otimes \delta(q - q_c) \\ & + \mu \text{FT}\{A(\mathbf{r})e^{-i\varphi(\mathbf{r})}\} \otimes \delta(q + q_c). \end{aligned} \quad (6)$$

Through inverse Fourier transformation on one of the sidebands (second or third term), the reconstructed image wave is written as

$$b_{\text{rec}}(\mathbf{r}) = A(\mathbf{r})e^{i\varphi(\mathbf{r})}. \quad (7)$$

Thus, amplitude and phase are extracted. Consistency of the sign of electrostatic potential and phase shift in the experimental and theoretical work is ensured by choosing the sideband in the Fourier transformation which keeps the mean inner potential of the materials positive. Accordingly, the increase in the phase shift is defined from a negatively to a positively charged region.

In the absence of magnetic field, the projected phase shift is proportional to the line integral of the electrostatic potential, in the form

$$\varphi(x, z) = C_E \int V(x, y, z) dy. \quad (8)$$

where  $y$  is the incident electron beam direction, and  $x$  and  $z$  are coordinates in the sample plane. The wavelength-dependent interaction constant  $C_E$  is  $6.53 \times 10^6 \text{ rad}/(\text{Vm})$  at 300 kV<sup>41</sup>.

The off-axis electron holograms were recorded in a FEI Titan G2 TEM operated at accelerating voltage of 300 kV, equipped with a 4K-pixel Gatan K2 direct electron camera.

A Möllenstedt biprism is placed at the position of objective aperture and aligned in parallel with the edge of the half-circle TEM grid. The voltage applied on the biprism is 110 V, generating a field of view (interference area) around 2  $\mu\text{m}$  wide and a fringe spacing of 2.55 nm in Lorentz mode. The electron beam is aligned into elliptical illumination and oriented perpendicular to the biprism filament to increase coherence. The sample was placed in the middle of the field of view to avoid the artefact and noise induced by Fresnel fringes at the edges. Exposure time for data collection was 6 s. The dose rate was approximately 2  $\text{e}/(\text{\AA}^2\text{s})$ . The reference wave is only weakly perturbed due to the weak electrostatic potential.

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## Data availability

All data have been uploaded to the online repository Figshare.

## Code availability

All calculations were performed using established commercial or publicly available software. All source codes are available from the authors upon reasonable request.

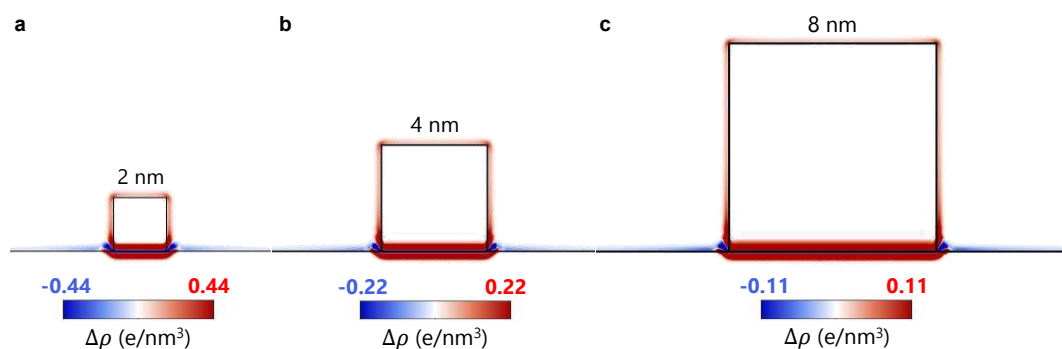
## Acknowledgements

The authors acknowledge funding from the Helmholtz-Gemeinschaft Deutscher Forschungszentren e.V. (HGF), Program-oriented Funding (PoF IV), under the Research Program: Materials and Technologies for the Energy Transition (MTET). Y.Z. thanks Prof. Dr. Jun Huang from Forschungszentrum Jülich and Prof. Dr. Weiqiang Tang from

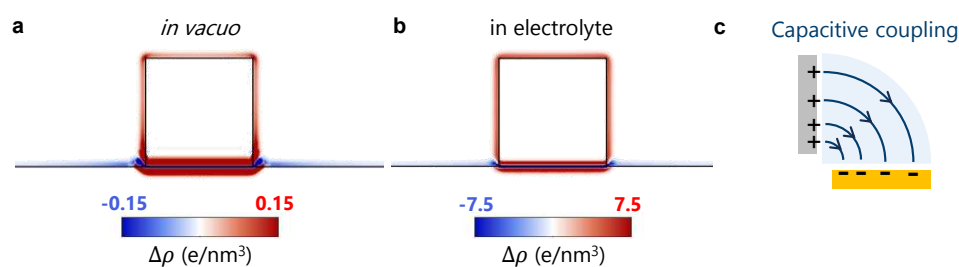
Zhengzhou University for helpful discussions. Dr. Marc Heggen from Forschungszentrum Jülich is acknowledged for valuable inputs.

## **Author contributions**

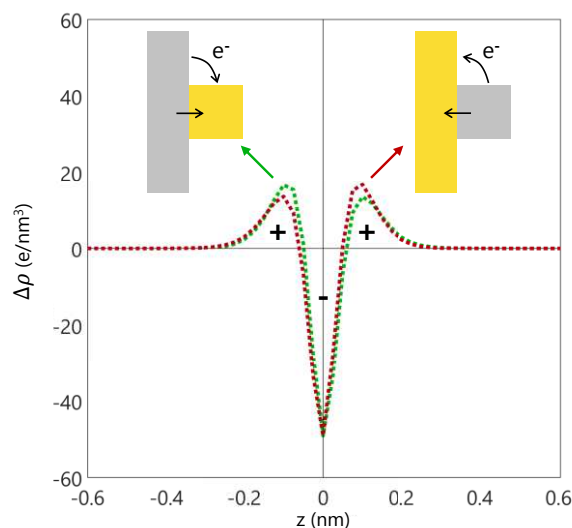
Y.Z. and T.B. conceived the project. Y.Z. performed the modelling and wrote the paper. Y.L. performed the experiments, data analysis and wrote the paper. R.D.B and M.E. revised the paper. T.B. assisted in the theoretical analyses and supervised the project.



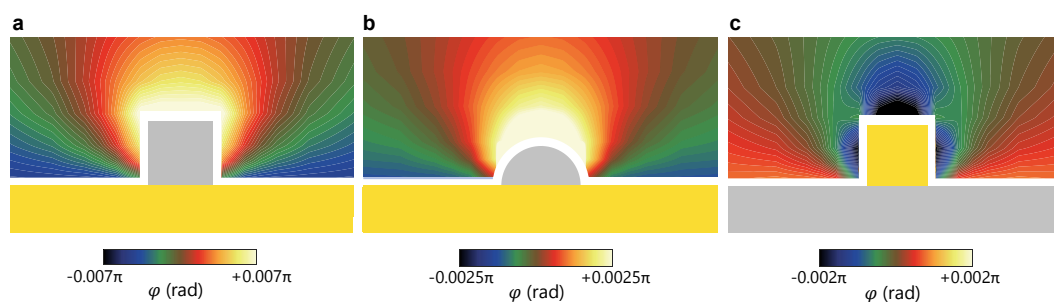
**Extended Data Fig. 1 | Electron redistribution for increasing NP sizes. a, 2nm. b, 4nm. c, 8nm.** Ag NPs are supported on Au substrates with coverage fixed at 1%. Colorbars are rescaled to maintain consistent visual contrast of the color shades.



**Extended Data Fig. 2 | Comparison of the magnitude of electron redistribution between vacuum and electrolyte environment. a, In vacuum. b, In solution.** The Ag NP has 4 nm side length. **c, Schematic illustration of the capacitive coupling between the external surfaces of Ag NP and Au support.**



**Extended Data Fig. 3 | Triple-layer structure of electron redistribution at the buried metal–metal interfaces revealed by the computational twin model.** Both Ag supported Au NP and Au supported Ag NP exhibit a triple-layer redistribution structure. At the Ag supported Au NP system, the Ag side shows a higher positive charge due to Ag-to-Au electron transfer (green line). In contrast, the reverse distribution is observed for the Au supported Ag NP system (red line).



**Extended Data Fig. 4 | Calculated phase shift maps. a,** Cubic Ag NP on Au support. **b,** Hemispherical Ag NP on Au support. **c,** Cubic Au NP on Ag support. In all three systems, the side length (or diameter) of NP is 4 nm, and the coverage of NP on support is fixed at 1%.

## Supplementary Files

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