Supporting Information

Colloidal ReO$_3$ Nanocrystals: Extra Re d-electron instigating a plasmonic response

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S1. Brown amorphous product (synthesis with alcohols, amines, or carboxylic acids)

Figure S1. XRD pattern of the brown amorphous product when the NC synthesis was performed in the presence of oleyl alcohol, in reference to database powder XRD line pattern of ReO₃ (AMCSD #0016967). Photograph of the product in the inset. This product is representative of those formed with long chain alcohols, amines or alkylcarboxylic acids.
S2. Photographs of solutions of Re$_2$O$_7$ in tetraglyme and dioctyl ether

a. Re$_2$O$_7$ in tetraglyme

b. Re$_2$O$_7$ in dioctyl ether

Figure S2. Photographs showing the effects of tetraglyme and dioctyl ether on the Re$_2$O$_7$ precursor. The solution of Re$_2$O$_7$ in tetraglyme slowly turns brown, which indicates that this solution should be freshly prepared before injection. Dioctyl ether, on the other hand, turns Re$_2$O$_7$ green almost instantaneously, rendering it an ideal reductant in a hot injection synthesis.
S3. FTIR spectrum of Re$_2$O$_7$-tetraglyme complex

Figure S3. FTIR spectrum of Re$_2$O$_7$ in tetraglyme (red curve), in comparison to the tetraglyme spectrum (green curve). The Re-O-Re stretching mode (shown in inset) is marked at 909 cm$^{-1}$. 
S4. Raman spectrum of as-prepared ReO$_3$ NCs

Figure S4. Raman spectrum of as-prepared ReO$_3$ NCs, showing the characteristics asymmetric stretching ($\nu_{as}$) and bending ($\delta_{as}$) modes of the crystal phase. The spectrum was collected on a dropcast film of ReO$_3$ NCs using Horiba LabRAM Aramis instrument equipped with a confocal aperture, at 632 nm excitation wavelength and acquisition time of 180 s.
S5. High-resolution XPS scans of ReO$_3$ NCs

Figure S5. Re 4f (panel a) and O 1s (panel b) high-resolution XPS scans of the as-synthesized ReO$_3$ NCs in comparison to those of commercially procured Re$_2$O$_7$ powder. The Re 4f signals due to +7 and +6 oxidation states are marked in panel a. The triplet observed in ReO$_3$ NCs is due to convoluted signals from Re(+6) doublets and the surface hydroxyls leading to an ill-defined oxidation state for surface Re atoms (a combination of +7 and +6 oxidation states).
**S6. Proposed reaction intermediate resulting in formation of surface hydroxyls**

![Diagram](image)

**Figure S6.** Sketch of a plausible reaction intermediate that can explain the formation of hydroxyl moieties on the ReO$_3$ NC surfaces and the observation of alkene protons in NMR spectrum (Figure 2, main text).
S7. NMR and FTIR spectra of the synthesis mixture

**Figure S7.** Wider range FTIR (panel a) and NMR (panel b) spectra of the synthesis mixture (blue curves) in comparison to that for TGY (red curve) and DOE (yellow curve).
S8. Optical constants of bulk ReO₃

The real and imaginary parts of the dielectric function ($\varepsilon'$ and $\varepsilon''$, respectively) for ReO₃ were extracted from the data reported by Feinleib et al. obtained from absolute reflectance measurements on a single-crystal of ReO₃. Data extraction was performed using the freely available web-based program, WEBPLOTDIGITIZER (https://automeris.io/WebPlotDigitizer, author: Ankit Rohatgi, Ver: 4.1, Jan, 2018). The real and imaginary parts of the refractive index ($\eta$ and $\kappa$, respectively) for ReO₃ were then calculated using the following equations:

$$\eta = \sqrt{\frac{\varepsilon'\varepsilon'' + \varepsilon'^2 + \varepsilon''^2}{2}}$$ \hspace{1cm} (9.1)

$$\kappa = \sqrt{\frac{\varepsilon'^2 + \varepsilon''^2 - \varepsilon'^2}{2}}$$ \hspace{1cm} (9.2)

The plots for $\varepsilon'$ and $\varepsilon''$ are shown in Figure S8a and S9a, and that for $\eta$ and $\kappa$, in Figures S9b below. The optical absorption coefficient ($\alpha$) was then calculated using the following formula:

$$\alpha = \frac{4\pi\kappa}{\lambda}$$ \hspace{1cm} (9.3)

The absorption coefficient is plotted in Figure S9c.

The loss function is defined as $-\text{Im}(\varepsilon^{-1})$ or in other form as $\varepsilon''/(\varepsilon'^2 + \varepsilon''^2)$, and is plotted in Figures S8c and S9c – peaks in this curve are associated with plasma oscillations.

Figure S8. Optical characteristics of an ReO₃ single-crystal over the entire energy range.2 (a) real (purple) and imaginary (green) parts of the dielectric function, (b) real part of the dielectric function (purple curve) deconvoluted into bound (red curve) and free electron (green curve) contributions, and (c) loss function (red curve).
Figure S9. Optical characteristics of copper (a, b) and silver (c, d). (a, b) real (purple) and imaginary (green) parts of the dielectric function, (c, d) real part of the dielectric function (purple curve) deconvoluted into bound (red curve) and free electron (green curve) contributions.
Figure S10. Optical characteristics of an ReO₃ single-crystal: (a) real and imaginary parts of the dielectric function, (b) real and imaginary parts of the refractive index calculated from the respective dielectric functions, and (c) bulk absorption coefficient (blue curve) calculated from the imaginary part of the refractive index, along with the loss function (red curve).
S9. Simulation of NC extinction spectrum

The COMSOL multiphysics program (https://www.comsol.com) was used to calculate the extinction spectrum for ReO₃ NCs from the bulk values of the real and imaginary parts of the dielectric function measured from the reflectivity of a single crystal of ReO₃.2 The computation uses the electrostatic approximation for the interaction of a conductive sphere, a few nanometers across, with an external electric field.4-5 Since, localized surface plasmon resonance (LSPR) is a non-propagating excitation of the free charge carriers (electrons/holes) in the metallic nanostructures coupled to the electromagnetic (EM) field, the phase of an oscillating field over a sphere of diameter (d) much smaller than wavelength (λ) of light is practically constant. This is called the quasi-static approximation (or limit) and is valid at d << λ, where the spatial variation in the field can be ignored and the problem can be simplified to that of a nanosphere in an “electrostatic” field.

The geometry for this analytical treatment includes a homogeneous isotropic sphere of radius (r) located at the origin in a uniform electric field, with a non-absorbing isotropic surrounding medium (with dielectric constant εₘ) and the field lines being parallel to the z-direction at sufficient distance from the sphere. A lowest order approximation of the full scattering problem can then describe the optical characteristics of nanoparticles of sizes below 100 nm adequately. The Mie solutions to this scattering problem yields an expression for the dipole polarizability (α) of the nanosphere:

$$\alpha = 4\pi r^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}$$  \hspace{1cm} (10.1)

Here, ε is the dielectric function of the NC core material (ReO₃ in the present case). As is apparent from eq 10.1 above, a resonant enhancement occurs in α when the denominator vanishes—this is called the Fröhlich condition and the associated optical mode for a metallic NC like that of ReO₃ is called the LSPR. It is important to note that this resonance red-shifts as εₘ increases – a characteristic feature of an LSPR used for optical sensing.6 The extinction cross-section (σ_{ext}) is then expressed as the sum of absorption (σ_{abs}) and scattering (σ_{sca}) cross-sections i.e. \(σ_{ext} = σ_{abs} + σ_{sca}\). The following (eqs 10.2 and 10.3) are the expressions for \(σ_{abs}\) and \(σ_{sca}\) in terms of α, where κ is the wave-vector of the incident light (EM field):

$$σ_{abs} = \kappa \text{Im}[\alpha] = 4\pi \kappa r^3 \text{Im} \left[ \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \right]$$ \hspace{1cm} (10.2)

$$σ_{sca} = \frac{\kappa^4}{6\pi} |\alpha|^2 = \frac{8\pi}{3} \kappa^4 r^6 \left[ \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \right]^2$$ \hspace{1cm} (10.3)
Building the model in COMSOL:

ReO$_3$ sphere of 2.5 nm in radius was designed using the Wave Optics Module in COMSOL. A surrounding medium was represented by a larger concentric sphere, signifying the solvent chloroform ($\varepsilon_r = 2.08$) provided by built-in Optical Materials Database dielectric constant. The entire system was then immersed in a perfect index matching layer (PML) which prevents unwanted reflections from outside boundary. Further semi-hemispheric symmetry with perpendicular perfect electrical conductor (PEC) and perfect magnetic conductor (PMC) boundary layer was employed at NC core and surrounding medium to optimize computation time. The maximum and minimum mesh sizes were set at 0.5 and 0.05 nm, respectively. This enabled extra-fine physics-controlled meshing and yielded 438,350 degrees of freedom and corresponded to 5.7 GB RAM for the biconjugate gradient stabilized method (BiCGStab) solver. The finite element method solutions to the Maxwell equations were then obtained in the full field mode for the scattered field formulation with the background electric field propagating along the x-axis and polarized along the z-axis. Domain volume integration was set at NC volume to probe absorption loss. Scattering surface domain was set at the medium domain boundary layer with full Euler angle coverage to integrate orientational averaging cross section of scattered field. Time average Poynting vector components of the scattered field were normalized to implemented scattering boundary condition surface.

Figure S11. Model for COMSOL computation. (a) Geometry and meshing of the spherical ReO$_3$ NC, medium, and perfect matching layer (PML) boundary conditions for solving the Maxwell equations. b) COMSOL component model schematic for ReO$_3$ NC (purple core), medium (orange middle layer), and PML boundary (green outer layer). Directional axis is included in inset, with electric field propagation along x-axis and E field polarization along z-axis.
**Figure S12.** Calculated extinction (green curves) with the absorption (orange curves) and scattering (red curves) contributions for (a) ReO$_3$ NCs, (b) ReO$_3$ NCs with a 0.4 nm shell, and (c) ReO$_3$ NCs with a 0.8 nm shell. The dielectric function for the oxy-hydroxide shell comprising of surface Re atoms at ill-defined oxidation states (mixture of +6 and +7) was extracted from Murphy et al.s

**Figure S13.** (a) Comparison of the extinction curves, calculated for no shell, 0.4 nm shell, and 0.8 nm shell for 5 nm ReO$_3$ NCs, showing a broadening and dampening of the LSPR peak with increasing shell thickness. The extinction curves for the core-shell geometries for the (b) 0.4 nm shell, and the (c) 0.8 nm shell were fitted with two Lorentzian curves peaking at about 15000 cm$^{-1}$ (red curve) and 13200 cm$^{-1}$ (green curve). The composite fitted curve is shown as a dotted blue line in each of (b) and (c).
S10. Drude modeling of LSPR response

Since the Drude model is the application of kinetic theory of gases on the gas of “free electrons”, it is appropriate to treat the optical response originating from metallic NCs like those of ReO₃ under its assumptions and results. However, the interband transitions in ReO₃ can best be treated by the Lorentz oscillator model of band-to-band transition. As mentioned in the main text, the dielectric function of ReO₃ has contributions from both free electrons and interband transitions in the system and they have considerable overlap which perturbs the optical response, as shown by Feinleib et al. Ideally, a complete treatment of the optical extinction should be performed with a combined Drude-Lorentz dispersion model. However, in order to predict the LSPR response and extract meaningful quantitative information out of the observed LSPR response of the ReO₃ NCs, we have used the Drude methodology. The dielectric function for a NC of a conductive material like ReO₃, as per the Drude contribution ($\varepsilon_D(\omega)$), is given by the following eq 11.1:

$$\varepsilon_D(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma}$$ (11.1)

Here, $\varepsilon_\infty$ is the high-frequency dielectric (which is fixed at 1, as per Figure S8 above), $\omega_p$ is the bulk plasma frequency given by eq 11.2 and $\Gamma$ is the electronic damping constant.

$$\omega_p^2 = \frac{ne^2}{\varepsilon_0 m^*}$$ (11.2)

Here, $n$ is the free charge carrier (electron) density, $e$ ($1.602 \times 10^{-19}$ C) being the electronic charge, $\varepsilon_0$ ($8.854 \times 10^{-12}$ F/m) the permittivity of vacuum and $m^*$ (= $t.m_e$, $t \leq 1$, $m_e = 9.1 \times 10^{-31}$ kg) the electron effective mass.

Predicted LSPR response

Calculation of the bulk plasma frequency ($\omega_p$):

Re⁶⁺ being a $d_1$ system in ReO₃, we assumed an electron concentration of 1 per unit of ReO₃, which translates into 1 mol of electrons per mol of ReO₃. Given the density (6.92 g/cm³) and molar mass (234.205 g/mol) of ReO₃, every cm³ contains $1.78 \times 10^{22}$ ReO₃ units, using Avogadro’s number ($6.022 \times 10^{23}$). This implies that the electron concentration is $1.78 \times 10^{22}$ cm⁻³. Using eq 11.2, a plasma frequency of $7.517 \times 10^{15}$ radians was obtained, which when divided by $2\pi$ yields a value of 1197 THz, equivalent to 4.95 eV. A free electron mass ($t = 1$) was assumed in this calculation.

Calculation of the NC extinction spectrum:

This plasma frequency was then used in eq 11.1 to obtain the Drude contribution to the dielectric function, and then subsequently used in the scheme described in section S9 above to compute the absorption cross-section ($\sigma_{abs}$) as per eq 10.2. An absorption spectrum for NCs dispersed in chloroform ($\varepsilon_m = 1.4459$) was then generated using Lambert-Beer law by the following equation:
\[ A = \left( \frac{V_{frac}}{V_{NC}} \right) \cdot \sigma_{abs} \cdot l \right) \ln 10 \] (11.3)

Here, \( V_{frac} \) is the volume fraction of the solution phase NCs and was taken as \( 9 \times 10^{-9} \), \( V_{NC} \) is the volume of an individual NC \( (V_{NC} = \left( \frac{4}{3} \right) \pi R^3) \) and \( l \) is the path-length of the solution under investigation (typically the cuvette thickness, 1 cm). The absorption spectrum generated as per eq 11.3 comprised of only the LSPR response. The damping constant \( (\Gamma) \) signifies electron scattering by phonons, electrons, impurities and lattice defects, and is the inverse of the bulk relaxation time \( (3.41 \times 10^{14} \text{ s}^{-1}) \).

**Influence of surface scattering**

Since, surface scattering in small metallic NCs contributes to drastic changes in the dielectric functions, significant amount of broadening and damping of the LSPR of these NCs is generally observed.\(^6\) For ReO\(_3\) NCs, the influence of surface scattering on the LSPR response of 5 nm NCs was investigated, given that their diameter is much smaller than the measured bulk electron mean free path (8.9 nm).\(^{10}\) The influence of the additional scattering contributions arising due to the small size of the NCs, such as that due to collisions of conduction electrons with the NC surfaces, is taken into account by using a modified damping parameter expressed as:

\[ \Gamma = \Gamma_{bulk} + \Delta \Gamma(R), \text{ where } \Delta \Gamma(R) = A \left( \frac{v_f}{R} \right) \] (11.4)

Here, \( \Gamma (R) \) is the size dependent phenomenological damping function giving a measure of the surface scattering that is increasingly important at small NC size, \( v_f \) is the Fermi velocity \( (0.77 \times 10^6 \text{ m/s}) \),\(^{10}\) and \( A \) is the scattering parameter of the order of 1. \( \Gamma_{bulk} \) is the bulk ReO\(_3\) damping constant described above and is the inverse of the bulk relaxation time \( (3.41 \times 10^{14} \text{ s}^{-1}) \).\(^2\) The calculated spectra obtained by simple Drude modeling and by including surface scattering are shown in Figure S14. As expected, surface scattering broadens and dampens the LSPR, albeit to a much higher extent than observed experimentally. This result suggests that surface scattering may not have a large influence on the observed LSPR.
Figure S14. Extinction spectrum calculated from Drude model (green curve) and including surface scattering (red curve). The scattering induced broadening of the LSPR is not observed experimentally, which suggests that additional scattering processes do not have much influence.

Spectrum fitting

The 500-850 nm region of the experimentally observed extinction spectrum (LSPR response) was fitted to a Drude response. Our Matlab codes used eqs 11.1 and 11.2 above to perform a least-squares fit to the collected spectra and extract the plasma frequency ($\omega_P$), damping constant ($\Gamma$) and finally the electron density.

<table>
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<tr>
<th>Solvent</th>
<th>$\omega_P$ (cm$^{-1}$)</th>
<th>$\omega_P$ (eV)</th>
<th>$\Gamma$ (cm$^{-1}$)</th>
<th>$\Gamma$ (eV)</th>
<th>n ($\times 10^{22}$ cm$^{-3}$)</th>
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<tr>
<td>Hexane</td>
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<td>4.66</td>
<td>5592.85</td>
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<td>0.64</td>
<td>1.75</td>
</tr>
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</table>
**S11. Optical extinction spectra showing effects of aggregation on LSPR**

**Figure S15.** UV-Vis-NIR extinction spectra of ReO$_3$ NCs: (a) synthesized at less than (blue curve) and more than (red curve) 200 °C, and (b) after multiple washings exhibiting red-shifted curve (green curve) and drop-cast on a glass substrate (purple curve) showing significant red-shift from the original 590 nm LSPR position of the individually suspended NCs. The considerable shift is attributed to increased LSPR coupling upon aggregation and scattering contributions to extinction. (c) Normalized extinction curves for the dilution series used for the calculation of molar attenuation coefficient in Figure 3.
S12. Reversibility of cyclic voltammetry (CV) scans for Li- and TBA-ions

Figure S16. CV scans for Li-ions for different potential ranges with single scans shown on the left panel and multiple scans (depicting reversibility or its lack thereof) on the right panel for each range. (a) 1.8 – 4 V (reversible), and (b) 1 – 4 V (irreversible). Note that the CV scans in the right panel in (b) become irreversible after the first cycle signaling structure breakdown of the ReO₃ lattice.

Figure S17. CV scans for TBA-ions for different potential ranges with single scans shown on the left panel and multiple scans on the right panel for each range. (a) 1.8 – 4 V, (b) 1 – 4 V. Unlike Li-cycling, TBA-cycling is reversible in the full potential range used for cycling.
**Figure S18.** Multiple CV scans for Li-ions for the potential range 1.8 – 4 V – the arrows point to the progressive changes in CV as the number of cycles increase, signifying structural breakdown of the ReO₃ lattice.

**Figure S19.** Multiple CV scans for TBA-ions for different potential ranges. (a) 1.8 – 4 V – relatively stable over 50 cycles, (b) 1 – 4 V – structural disintegration occurs as the number of CV scans increase but the effect is less drastic than for the Li-ion (Figure S14 above).
S13. Perovskite crystal structure of ReO$_3$ showing missing A-site cation

Figure S20. Crystal structure showing the open framework of ReO$_3$ (right) due to the missing large A-site cation from the perovskite ABO$_3$ structure (left). (Oxygen atoms = red; Rhenium atoms = grey; A-site cation = green). The volume of the ReO$_3$ unit cell is 52.75 Å$^3$. All the crystal drawings in this manuscript were produced using the VESTA software. 11
Figure S21. Re 4f narrow region XPS scans for ReO$_3$ NCs charged to 1.2 V (most reduced state, red curve) and those deposited on a cleaned Li-foil (green curve). The blue-green appearance of the NCs immediately converts to black signifying quick reduction by the Li metal. The Li 1s regions are marked.
Figure S21. Raw SEC data for (a) Li-ion, and (b) TBA-ion cycling for the NC films, corresponding to normalized spectra shown in Figure 4c and 4f, respectively.
References

2. Feinleib, J.; Scouler, W. J.; Ferretti, A., Optical Properties of the Metal ReO₃ from 0.1 to 22 eV. Phys. Rev. 1968, 165 (3), 765-774.