Electronic Supplementary Information for:

Sub-bandgap trap sites for high-density photochemical electron storage in colloidal $SrTiO_3$ nanocrystals

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Synthesis of colloidal $SrTiO_3$ NCs: The synthesis of colloidal $SrTiO_3$ NCs was carried out by a modified hydrothermal method reported earlier by Harrigan *et al*.[1] In a typical synthesis of 1.25 mmol of TALH and 1.25 mmol $Sr(OH)_2{\cdot}8H_2O$ were dissolved in 30 mL of distilled water. The pH of the solution was then adjusted to 12.1 with an aqueous solution of NMe_4OH (10 M) followed by the addition of oleic acid (2.5 mmol) and hydrazine (5 mmol). The resulting solution was transferred to a 45 mL Teflon-lined autoclave (4744 General Purpose Acid Digestion Vessel, Parr Instrument Company) and heated to 200 °C in an oven for 24 hours. The resulting NCs were collected, washed with ethanol several times, suspended in hexanes, and sonicated for about 30 minutes to produce a cloudy suspension. Finally, a transparent hexane layer containing NCs was extracted by centrifuging the cloudy suspension (5 min at 4000 rpm). These NCs can be further purified by precipitation with ethanol.

Photodoping of NCs: The photodoping experiments were performed to introduce excess electrons in as-prepared NCs. Sample preparation was completed in the argon-filled glove box where NCs suspended in hexanes were transferred to a 1 cm air-tight cuvette before removal. Samples were photodoped by prolonged irradiation with unfiltered and unfocused irradiation from 75 W xenon lamp in the presence of EtOH as a sacrificial reductant. The measured power at the cuvette was ca. 150 mW (Molectron EPM 1000 power meter with PM10 detector head). The electronic absorption spectra were taken periodically during the entire photodoping process. The NCs were estimated to be photodoped to their saturation limit when no further spectroscopic changes could be observed following prolonged exposure to UV irradiation.

Carrier estimation: The typical procedure to estimate ⟨n⟩ involves (1) preparation of samples with a known concentration of NCs, (2) photodoping to their steady-state (maximum) level, and (3) titration against a molecular oxidant of a known concentration. Briefly, the concentration of colloidal NCs in the stock solution was determined by the combination of inductively coupled plasma – optical emission spectroscopy (ICP-OES) analysis to provide total Ti concentration and X-ray diffraction pattern to provide average particle size (see Figures S8-10 and Table S2-S6). For the photodoping experiments, sample preparation was completed in an argon-filled glove box where NCs suspended in hexanes were transferred to a 1-cm pathlength air-tight cuvette before removal. Samples were photodoped by prolonged exposure (10 hr) to unfocused irradiation in the presence of EtOH (> 1000 eq/NC) as a sacrificial reductant. It was estimated that the NCs were photodoped to their saturation limit when no further spectroscopic changes could be observed following prolonged exposure. To perform titration experiments, aliquots of a freshly prepared toluene solution of TEMPO were added to photodoped samples under constant stirring using a customized air-tight apparatus shown in Figure S11.

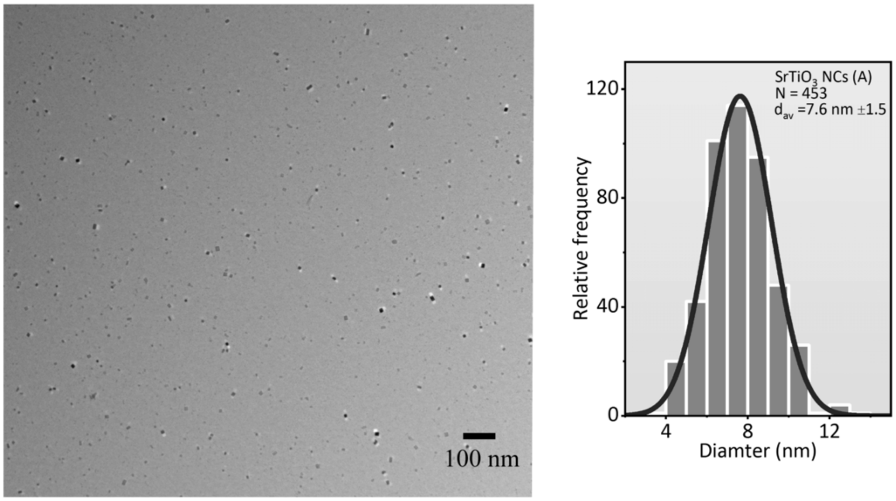

Figure S1. Transmission electron microscopy (TEM) image of SrTiO$_3$ NCs prepared showing a cubic morphology of NCs. The size distribution plot from analyzing over four hundred different particles in raw TEM images using ImageJ software displays an average size of 7.6 ± 1.5 nm.

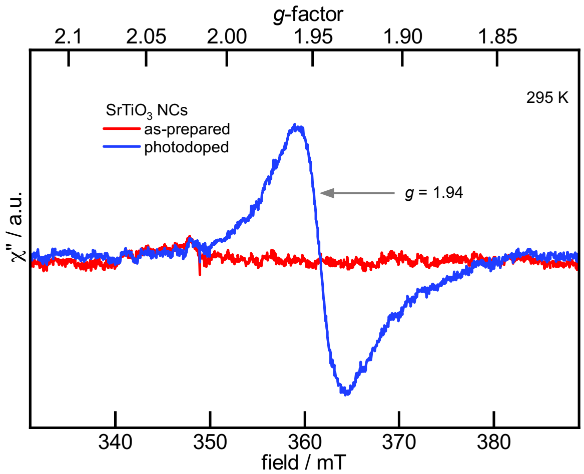

Figure S2. Room temperature EPR spectra of as-prepared (red) and photodoped (blue) colloidal $SrTiO_3$ NCs.

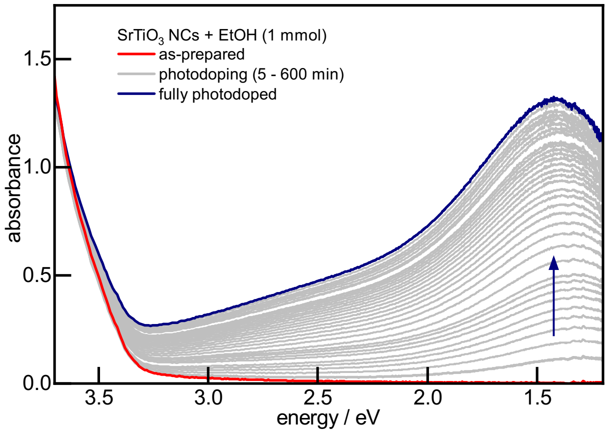

Figure S3. UV-vis spectra of $SrTiO_3$ NCs taken periodically during photodoping in the presence of EtOH (1 mmol).

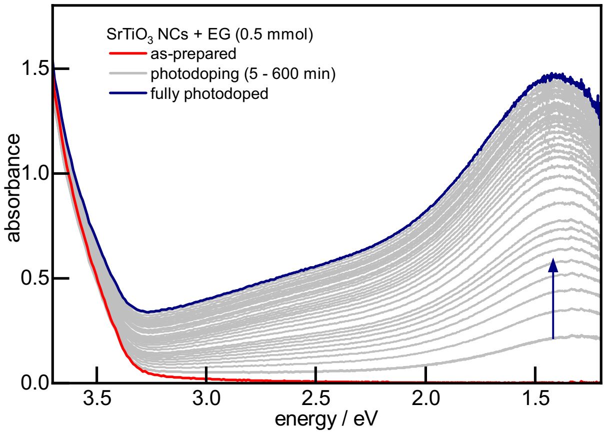

Figure S4. UV-vis spectra of $SrTiO_3$ NCs taken periodically during photodoping in the presence of ethylene glycol (0.5 mmol).

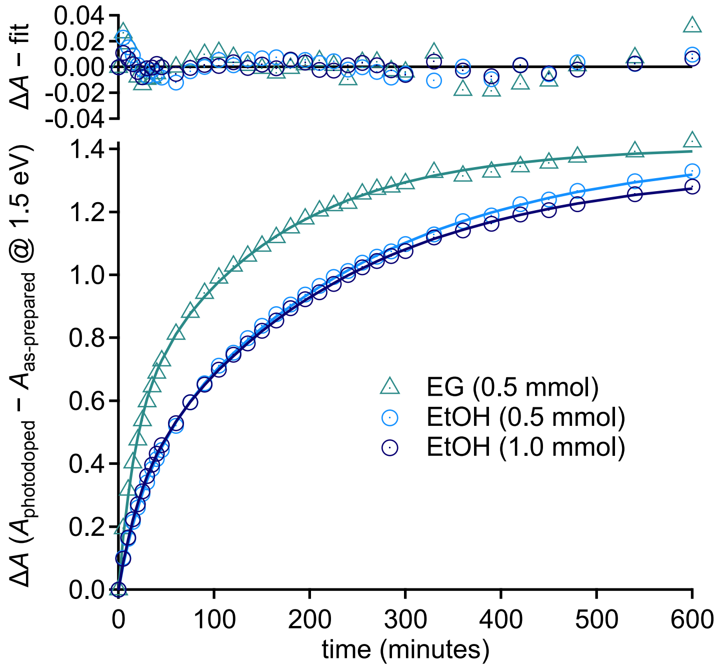

Figure S5. Biexponential fits of kinetics data shown in the main text (Figure 2). The residuals to the fit is shown at the top of the figure.

The biexponential curve-fitting function used to fit the photodoping kinetics data is defined by eq S1.

$$\Delta A = \Delta A_{\infty}\,(1 - c e^{-t/\tau'} - (1-c) e^{-t/\tau''}) \qquad \text{(Eq S1)}$$

where ΔA_{∞} is the saturation or steady-state value as $t \to \infty$, c is a single pre-exponential factor that describes the relative contributions of the two components to the overall photodoping kinetics (c is the factor associated with the slow fast component and $1 - c$ is associated with the slow component), and τ^{i} is the lifetime (1/rate) of the fast (τ') and slow (τ'') components.

Table S1. Fitting results of the photodoping data with eq S1.

Fitting parameter	**EG (0.5 mmol)**	**EtOH (0.5 mmol)**	**EtOH (1.0 mmol)**
ΔA_{∞}	1.41 ± 0.01	1.40 ± 0.01	1.34 ± 0.01
c	0.38 ± 0.01	0.23 ± 0.01	0.22 ± 0.01
τ' (min)	16.6 ± 0.7	26.3 ± 1.9	21.1 ± 1.5
τ'' (min)	146 ± 4	233 ± 9	214 ± 7

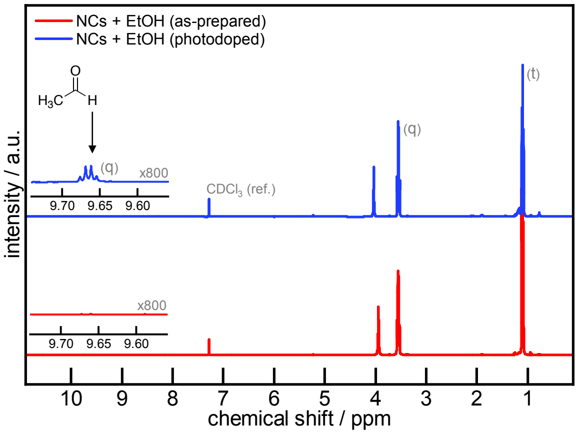

Figure S6. H-NMR spectra of colloidal solution of $SrTiO_3$ NCs suspended in deuterated chloroform before and after the photodoping in the presence of EtOH as hole quencher.

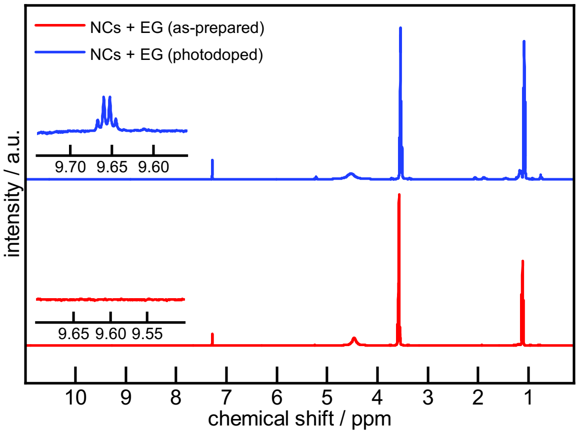

Figure S7. H-NMR spectra of colloidal solution of $SrTiO_3$ NCs suspended in deuterated chloroform before and after the photodoping in the presence of EG as hole quencher.

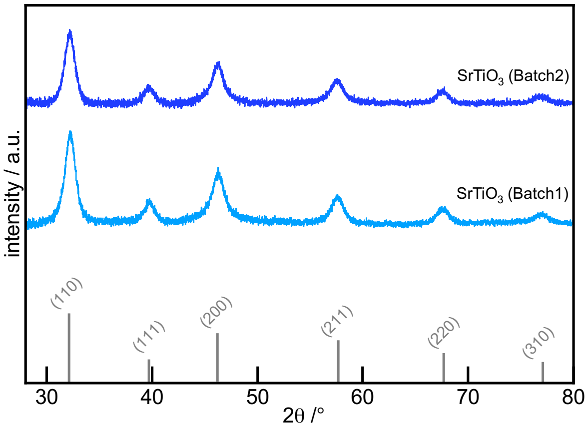

Figure S8. Powder X-ray diffraction patterns of $SrTiO_3$ NCs prepared under identical conditions for average particle size analysis.

Table S2. Determination of average particle size from powder diffraction analysis

$SrTiO_3$ NCs	Crystallite size from various reflections (nm)				Average NCs size
	(110)	(111)	(200)	(211)	
Batch-1	7.172	7.177	6.962	6.889	6.974 ± 0.25 nm
Batch-2	7.165	7.185	6.556	6.690	

Table S3. Determination of the average number of Ti per NC.

Average lattice parameter	3.924 Å
Average volume of unit cell	$(3.924)^3$ = 60.42 $Å^3$
Average size of NCs	69.74 Å
Average volume of NC (cube)	$(69.74)^3$ = 339192.18 $Å^3$
Number of unit cells per NC	339192.18 / 60.42 = 5614
Number of Ti^{4+} per NC (Z = 1)	5614

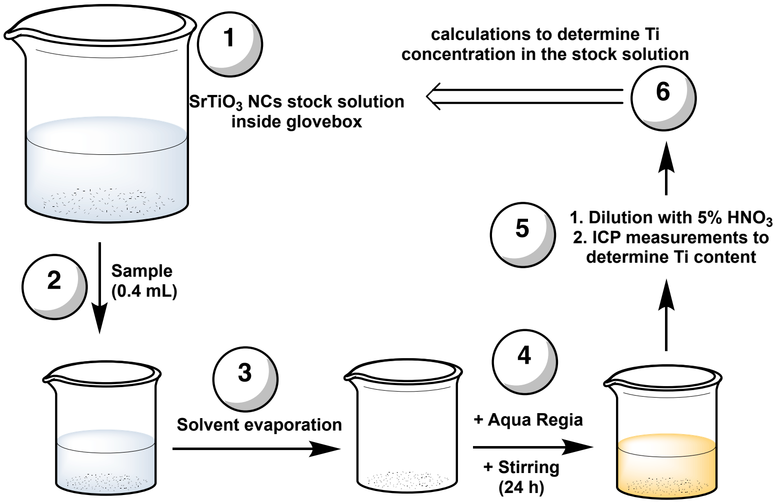

Figure S9. Flow chart describing the steps in the sample preparation for ICP-OES measurements to determine the total titanium content in stock solution.

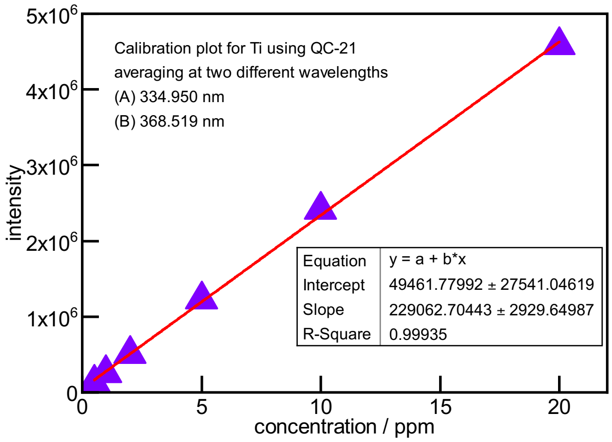

Figure S10. Calibration plot for ICP-OES analysis using standard solutions of different concentrations.

Table S4. Calculations to determine the total Ti content from ICP-OES data.

$SrTiO_3$ NCs	Concentration of Ti (mg/L)			Molarity (mM)	Molarity of stock sol. (dilution factor = 20)
	334.940 nm	368.519 nm	Average		
Sample-1	26.82	27.51	27.26	0.569	11.88 mM
Sample-2	27.11	27.32			
Sample-3	27.23	27.57			

Table S5. Determination of concentration of NCs in stock solution.

Concentration of Ti in stock solution	11.88 mM
Number of Ti making up one NC	5614
Concentration of NCs in stock solution	0.00212 mM = 2.12 µM

Table S6. Preparation of stock solution of TEMPO of known concentration.

Molecular weight	186.27
Amount taken	23.9 mg
Volume of solution	20 mL
Molarity of solution	6.4 mM

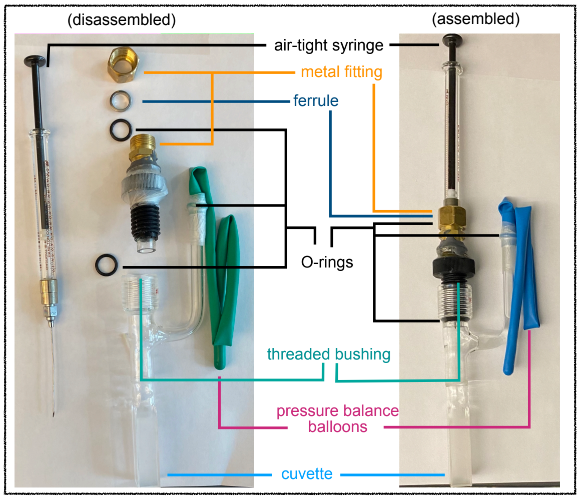

Figure S11. Various components of air-free custom titration setup.

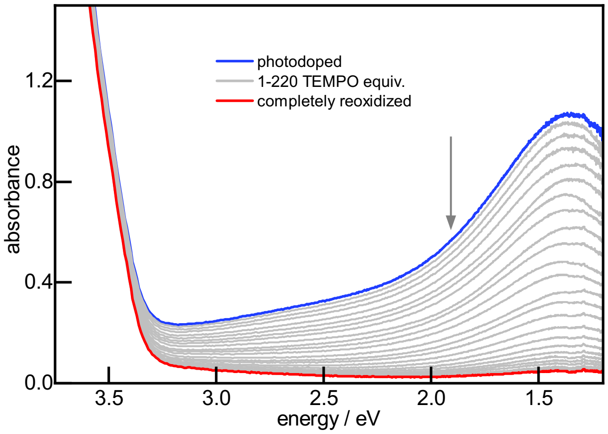

Figure S12. UV-Vis spectra of photodoped NCs collected periodically during titration against TEMPO under air-free conditions (trial 1).

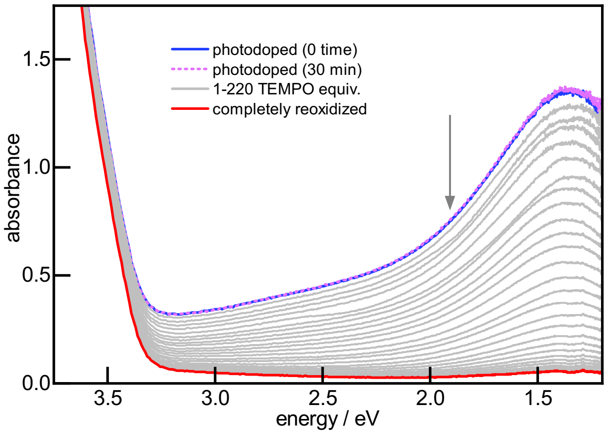

Figure S13. UV-Vis spectra of photodoped NCs collected periodically during titration against TEMPO under air-free conditions (trial 2). The pink spectrum represents the stability of photodoped NCs during the transition between the glovebox and the custom titration setup outside the glovebox to ensure any air does not percolate during experiments

Calculations to determine the number of electrons per NC:

Volume of photodoped NCs = 2 mL
Molarity of photodoped NCs = 0.00212 mM
Number of moles of photodoped NCs = (0.00212 µmol / mL) × 2 mL = 0.00424 µmol = $\boxed{0.00000424 \text{ mmol}}$

Volume of each TEMPO increment = 140 µL = 0.140 mL
Molarity of TEMPO = 6.4 mM
Moles of TEMPO added = 6.4 mM × (0.140/1000) = $\boxed{0.000896 \text{ mmol}}$

Equivalents of TEMPO added against NCs = 0.000896 mmol / 0.00000424 mmol = 211
Equivalents of TEMPO added against NCs per increment = total equivalents / no. of increments = 211 / 28 = $\boxed{\sim 7.5}$

1. W. L. Harrigan, S. E. Michaud, K. A. Lehuta and K. R. Kittilstved, *Chem. Mater.*, 2016, **28**, 430-433.