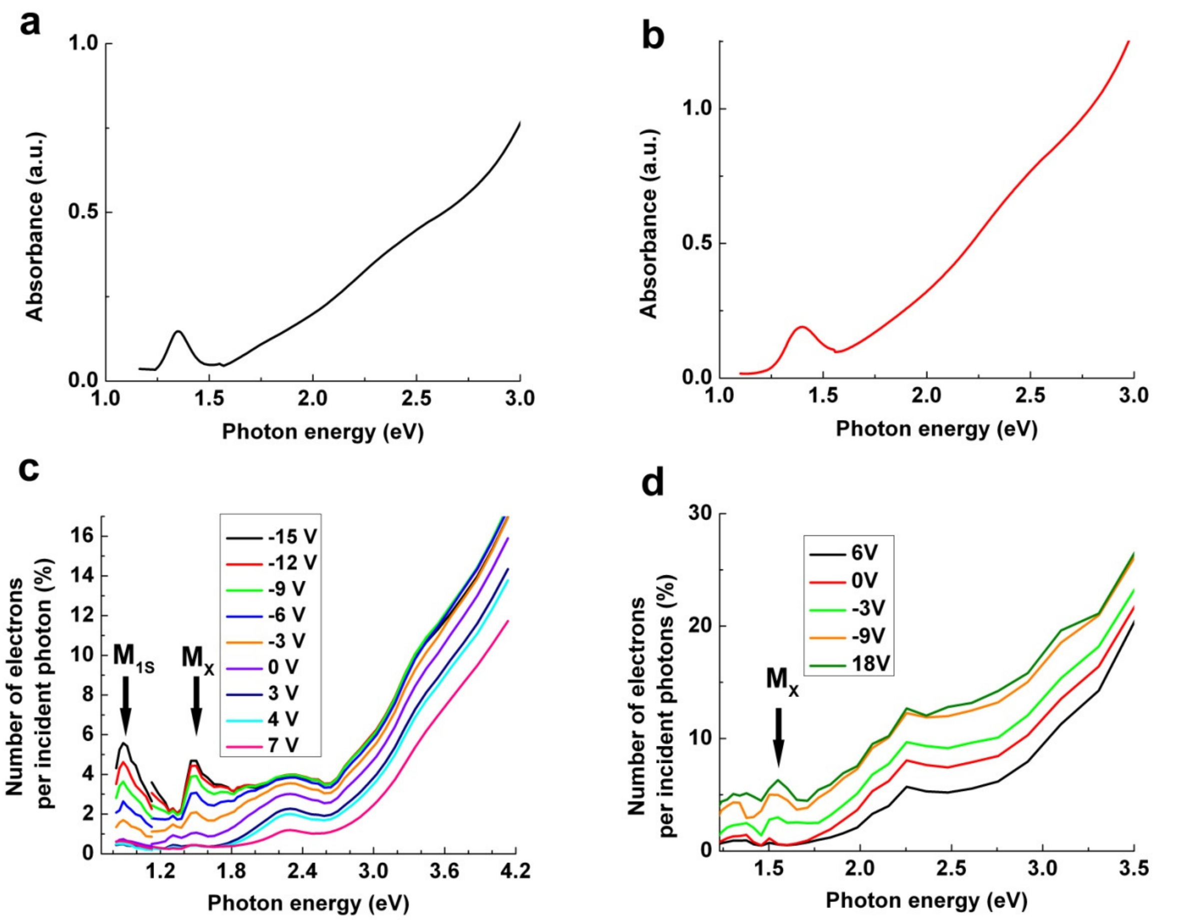
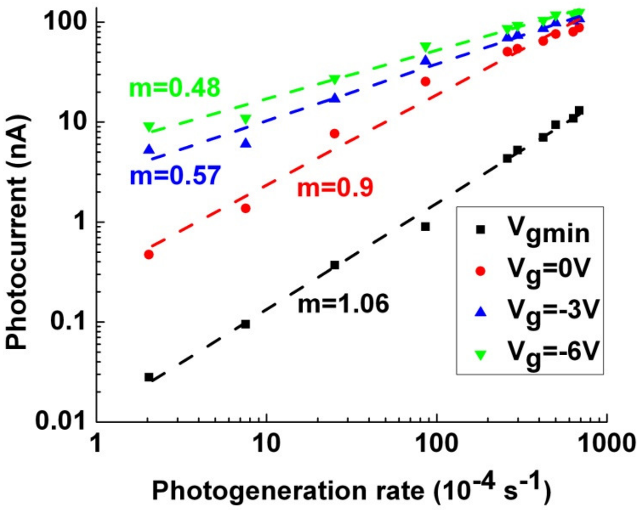
# Supplementary Information

***Gate-voltage dependent photocurrent spectra***



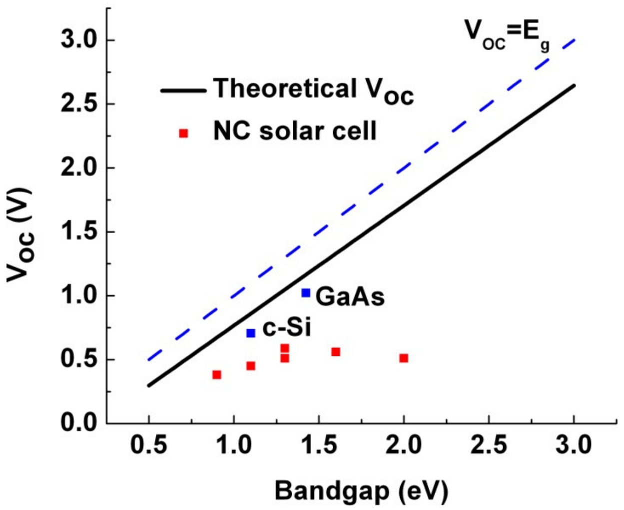

**Supplementary Figure S1. Gate and NC size dependence of photocurrent spectra. a, b** Optical absorption spectra of PbS NCs with the 1S band-edge peaks at 1.3 eV (a) and 1.4 eV (b). **c, d,** Photocurrent spectra (in terms of the number of photoelectrons per 100 incident photons) of the device fabricated from these NCs as a function of gate voltage (shown in the legend in volts). The MGB-related transitions $M_{1S}$ and $M_X$ are marked by arrows. For higher-band-gap NCs, the $M_x$ features shifts to higher energies.

*Generation-rate dependence of the photocurrent*




**Supplementary Figure S2. Generation-rate dependence of photocurrent.** Photocurrent as a function of photogeneration rate for PbS NCs with the 1.18 eV band-gap energy which illustrates a transition from a linear to square-root scaling with light intensity as the gate voltage is tuned from the flat-band potential (MGB is fully occupied) to large negative values (MGB is empty).

*Thermodynamic limits of the open-circuit voltage and photovoltages of NC-based devices*




**Supplementary Figure S3. Relation between semiconductor bandgap and open-circuit voltage.** Theoretical limits of the open circuit voltage (black line) as a function of $E_g$ in comparison with measurements for solar cells made of bulk Si and GaAs (blue squares) as well as NCs (red squares). The dashed blue line corresponds to $V_{oc} = E_g$.

## Supplementary Methods

The maximum value of the open-circuit voltage ($V_{oc}$) of a photovoltaic (PV) device, can be obtained from[37]:

$$V_{oc} = \frac{k_B T}{q} \ln\left(\frac{J_{sc}}{J_0} + 1\right), \qquad \text{(S1)}$$

where $J_{sc}$ is the short-circuit current and $J_0$ is

$J_0 = \frac{q}{k_B} \frac{15\sigma}{\pi^4} T^3 \int_{E_g/k_B T}^{\infty} \frac{x^2}{e^x - 1} dx$. In the last expression, $E_g$ is the semiconductor band-gap energy and σ is the Stefan-Boltzmann constant.[38]

The theoretical value of $V_{oc}$ calculated using Eq. (S1) for different band-gap energies is shown in Supplementary Fig. S3 by the black line. This plot indicates that $V_{oc}$ is always lower than $E_g$ (dashed blue line). In the same figure, we also show open-circuit voltages measured for solar cells made of traditional bulk Si and GaAs (blue squares)[39] as well as PbS[15], PbSe[32], and CdSe[40] NCs (red squares).

The comparison of these data shows that while in bulk semiconductors the measured photovotages are close to the values defined by the thermodynamic limit, in NC solar cells $V_{oc}$ is significantly lower than the ideal values. As discussed in the text, this disparity can be explained by the mixed character of photoconduction, which involves both the intrinsic valence band levels (hole transporters) and the mid-gap states (electron transporters).

## Supplementary References


37 Sinton, R. A. & Cuevas, A. Contactless determination of current-voltage characteristics and minority-carrier lifetimes in semiconductors from quasi-steady-state photoconductance data. *Appl. Phys. Lett.* **69**, 2510-2512 (1996).

38 Baruch, P., Devos, A., Landsberg, P. T. & Parrott, J. E. On some thermodynamic aspects of photovoltaic solar-energy conversion. *Sol. Energy Mater. Sol. Cells* **36**, 201-222 (1995).

39 Green, M. A., Emery, K., King, D. L., Hisikawa, Y. & Warta, W. Solar cell efficiency tables (Version 27). *Prog. Photovoltaics* **14**, 45-51 (2006).

40 Gimenez, S. *et al.* Improving the performance of colloidal quantum-dot-sensitized solar cells. *Nanotechnology* **20** (2009).