Electronic Supplementary Information

Photoexcitation of PbS Nanosheets Leads to Highly Mobile Charge Carriers and Stable Excitons

Jannika Lauth,*[‡abc] Michele Failla, [‡b] Eugen Klein, [d] Christian Klinke, [def] Sachin Kinge [g] and Laurens D. A. Siebbeles *[b]

[a.] *Institute of Physical Chemistry and Electrochemistry, Leibniz Universität Hannover, Callinstr. 3A, D-30167 Hannover, Germany.*
[b.] *Delft University of Technology, Van der Maasweg 9, NL-2629 HZ Delft, The Netherlands.*
[c.] *Cluster of Excellence PhoenixD (Photonics, Optics, and Engineering – Innovation Across Disciplines), Hannover, Germany.*
[d.] *Institute of Physical Chemistry, Universität Hamburg, Grindelallee 117, D-20146, Germany.*
[e.] *Chemistry Department, Swansea University, SA2 8PP, United Kingdom*
[f.] *Institute of Physics, Universität Rostock, Albert-Einstein-Straße 23, D-18059 Rostock, Germany.*
[g.] *Toyota Motor Europe, Materials Research & Development, B-1930 Zaventem, Belgium.*
‡ Equal author contribution.

1. Evaluation of the exciton binding energy for 16 nm PbS-NSs

For 16 nm PbS-NSs, we obtain a value E_B = 21 meV, by taking it as the average value between the value calculated by Yang and Wise for 8 nm thick PbS-NSs (40 meV) and the bulk value.[1] The latter is obtained from the relation:

$$E_B = 13.6\ eV \cdot \frac{m^*}{m_0} \frac{1}{\epsilon_\infty} \quad \text{(S1)}$$

where m^* is the reduced effective mass of the exciton given by $(m_e m_h)/(m_e + m_h)$, ϵ_∞ is the high frequency dielectric constant and m_0 is the free electron mass.[2] From Eq. (S1), the binding energy is E_B = 2.7 meV by considering m_e = 0.12, m_h = 0.11 and ϵ_∞ = 17.[3]

2. Number of absorbed photons per NS

The number of absorbed photons per unit area in a single nanosheet is calculated as:

$$N_a^{NS} = \frac{N_a}{n_{NS}},$$

where N_a is the absorbed photoexcitation density in the NS-film (absorbed photons per unit area) and n_{NS} is the number of NS within the film, which is evaluated by determining the film thickness (see Experimental Section of the main manuscript) and the thickness of a single NS.

3. Fits of the THz response in the frequency domain

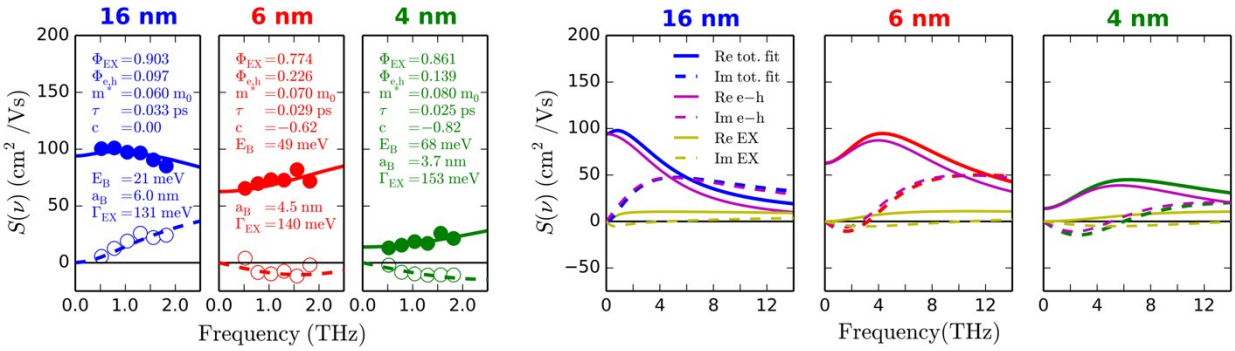

Fig. S1**.** Fits of the THz response at 8 ps for PbS-NSs with different thickness (indicated at the top of panels). In the right panels the total response (same color as the sample), EX response (yellow) and free charge carrier response (magenta) from fits are shown in a wider frequency range. Note that with obtained a_B values the response of more than 70 % of photogenerated charge carriers at t = 8 ps is weak.

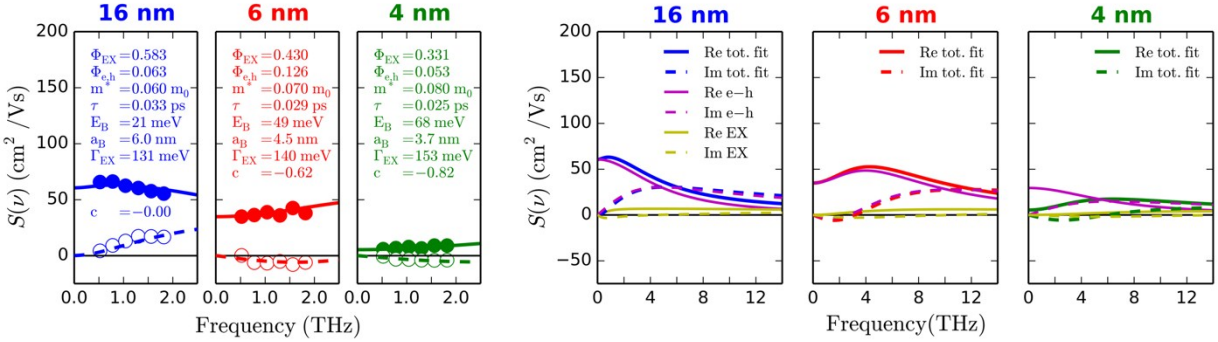

Fig. S2. Fits of the THz response at 200 ps for PbS-NSs with different thickness (indicated at the top of panels). In the right panels the total response (same color as the sample), EX response (yellow) and free charge carrier response (magenta) from fits are shown in a wider frequency range.

4. Normalized THs response at 8 and 200 ps

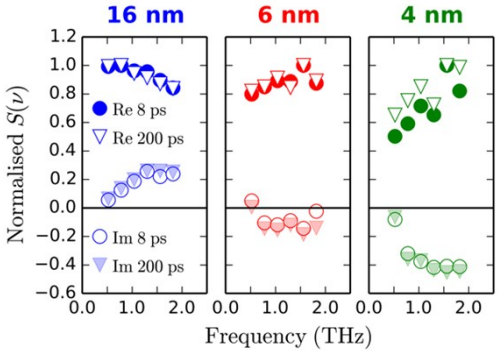

Fig. S3. Comparison of normalized THz spectra at 8 and 200 ps after photoexcitation, showing that the later time response can be described by a scaling factor. In the main manuscript, this is related to the reduction of the fraction of free charge carriers only.

5. Fits of the THz response by considering free charge carriers only

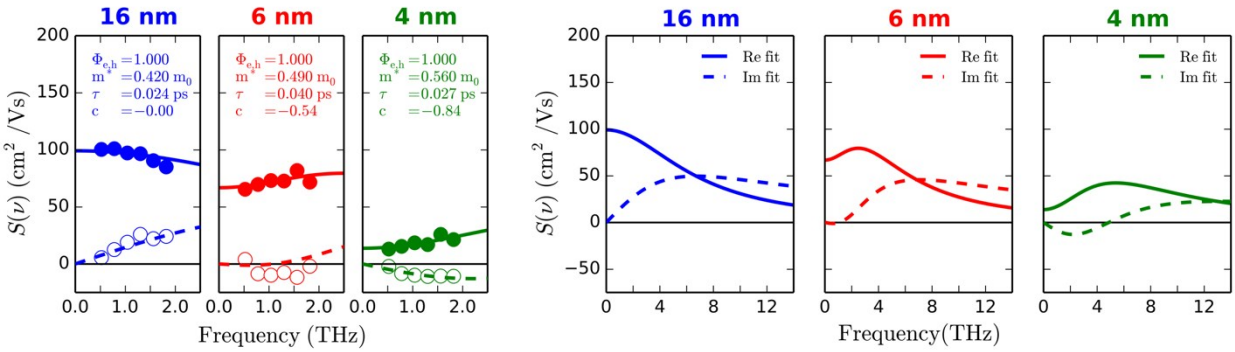

Fig. S4. An attempt for fitting the measured data by considering free charge carriers only and the Drude-Smith model. The response is well reproduced for the 16 and 4 nm samples, while a noticeable disagreement is apparent for the imaginary component of 6 nm thick PbS-NSs. Obtained effective masses deviate substantially from values reported in the main manuscript.

1. J. Yang and F. W. Wise, *J. Phys. Chem. C*, 2015, **119**, 26809-26816.
2. C. Klingshirn, *Semiconductor Optics*, Springer-Verlag Berlin Heidelberg, Germany, **2012**.
3. I. Kang and F. W. Wise, *J. Opt. Soc. Am. B*, 1997, **14**, 1632-1646.