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Nanosecond dynamics in few-layer and heterojunction transition metal dichalcogenides from liquid phase exfoliation

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Summary. — The lifetimes of photogenerated charge carriers must be long enough to guarantee high efficiency of light harvesting devices. Two-dimensional transition metal dichalcogenides (TMDs) are promising materials due to their intense light-matter interaction. Liquid phase exfoliation is a low-cost, versatile, scalable method able to produce polydisperse nanosheets in the form of inks. Here, we use nanosecond transient absorption spectroscopy to investigate the charge carrier dynamics in MoS_2, WS_2, and heterojunctions (HJs) of the two. We observe that the HJ stacking order does not affect the dynamics. We find that in thicker and larger flakes of the single material the carrier lifetime is significantly longer than even in HJs, due to different electronic contributions from nanosheet basal plane and edges. We conclude that there is no need for additional complexity in stacking two TMDs, and transport properties are enhanced in thicker and larger flakes. Our findings can be exploited for device fabrication.

1. – Introduction

Light harvesting devices are based on (sun)light energy conversion into electrical or chemical signal. This is possible when light is absorbed by active material layers, able to convert the photonic energy into electronic excitations of the absorber via the creation of electron-hole pairs. Electrons and holes can move freely as negative or positive charges respectively, or they can form bound states known as excitons. Free charges with long enough lifetimes (> ns) are needed both for optoelectronic applications and catalytic reactions. The design of type-II heterostructures (HSs) [1, 2], that are the stacking of two monolayers, is addressed as a promising solution to reduce the radiative

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losses due to exciton recombination, while promoting the formation of interlayer excitons. These are dark states where an electron and a hole belonging to different layers are bound together. It has been demonstrated that interlayer excitons have longer lifetime with respect to intralayer excitons [3-5]. Moreover, it has been possible to dissect interlayer hole and electron transfer in TMD HSs via two-dimensional electronic spectroscopy [6]. Two-dimensional semiconducting materials such as layered TMDs show a tunable, thickness-dependent, light-matter interaction, and a wide selection of fabrication techniques is available due to their chemical structure. The fabrication routes for TMDs can be divided into bottom-up synthesis methods [7-11] and top-down exfoliation [12]. Among exfoliation approaches, liquid phase exfoliation (LPE) is a low-cost and versatile technique suitable to any layered material [13-17] and it is scalable for mass production of inks that are appealing for the emerging field of printed and wearable electronics. LPE allows preparing dispersions containing polydisperse nanosheets both in lateral sizes and thicknesses [18]. As a result, films made from LPE have been less investigated for potential applications, and the poor electrical contact between individual nanosheets in a network has been overcome only recently [19, 20]. Here, we report the room temperature dynamics of photogenerated charge carriers observed in films of few-layer MoS_2 and WS_2 flakes as well as heterojunctions (HJs) obtained stacking the two materials. We use HJ to distinguish the stacking among thin films from HS, where two or more monolayers are stacked together. The flakes were delaminated via LPE, and the Langmuir-Schaefer method was used for single-flake thick film deposition of tiled nanosheets on fused silica substrates. For the first time, we made a HJ film from LPE. Two HJs, showing opposite stacking order, were obtained via sequential deposition of MoS_2 on top of WS_2 and vice versa. We used pump-probe transient absorption spectroscopy with a broad band probe to follow the charge dynamics in the time domain over a window from 1 ns to 1 μs.

2. – Results and discussion

We dispersed MoS_2 and WS_2 powders purchased from Sigma Aldrich in aqueous solutions containing sodium cholate as a stabiliser to avoid nanosheet reaggregation, and we separated them into three different fractions following liquid cascade centrifugation method [17]. Firstly, the dispersion was centrifuged at a centripetal acceleration of 1 k g (*i.e.*, 1000 times the gravitational acceleration g). The sediment, containing mostly unexfoliated chunks of material, was discarded. The supernatant was collected and was centrifuged at 5 k g. The sediment was labelled as the fraction "1–5 k g". The procedure was reiterated with the supernatant to produce additional fractions "5–10 k g" and "10–30 k g". We prepared films of single-flake thickness from the three fractions of MoS_2 and WS_2, respectively, via Langmuir-Schaefer deposition from a water-hexane interface onto fused silica substrates. Additionally, we fabricated HJs of MoS_2 on WS_2 and vice versa from fraction "10–30 k g" to study synergistic effects on the carrier lifetimes. The absorption spectra of the single-material films and the comparison with the two obtained HJs are depicted in fig. 1.

The well-known A and B excitonic resonances are visible both in single materials and in HJs. The dynamics of photogenerated charges were investigated at time scales up to 1 μs, using pump pulses at 355 nm with approximately 1 ns duration, pump fluence on the sample equal to 140 μJcm^{-2}, and broadband probe pulses covering the spectral range 480–750 nm. The white light was generated focusing the output of a femtosecond laser, fundamental wavelength at 1064 nm, on a 1 mm-thick sapphire crystal. The two lasers, featuring femtosecond pulses for white light generation

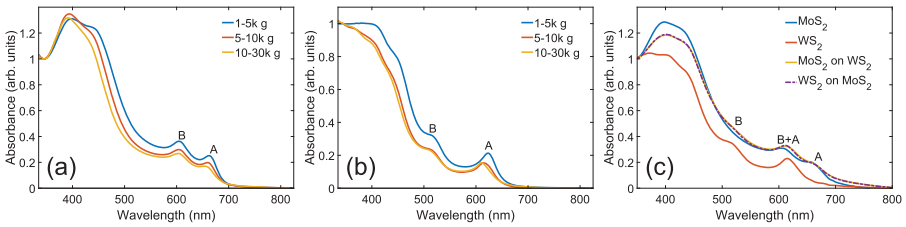

Fig. 1. – (Colour on-line) Absorption spectra for different fractions of MoS_2 in (a), WS_2 in (b), and two HJs compared to single materials in (c). Labels A and B refer to the main excitonic features.

and sub-nanosecond pulses for the pump, were synchronised at 2 kHz and the relative delay was controlled by means of a digital delay generator from Stanford Research Systems with a rms jitter less than 25 ps. Spectra at four selected delays are depicted in fig. 2(a) for the "MoS_2 1–5 k g" sample, and in fig. 2(b) for the "WS_2 1–5 k g" sample, respectively. We remind that the fraction "1–5 k g" refers to the dispersion containing the larger and thicker flakes.

All spectra show the same sequence of positive and negative features. A positive signal is identified as a photobleaching (PB), while a negative one as a photoinduced absorption

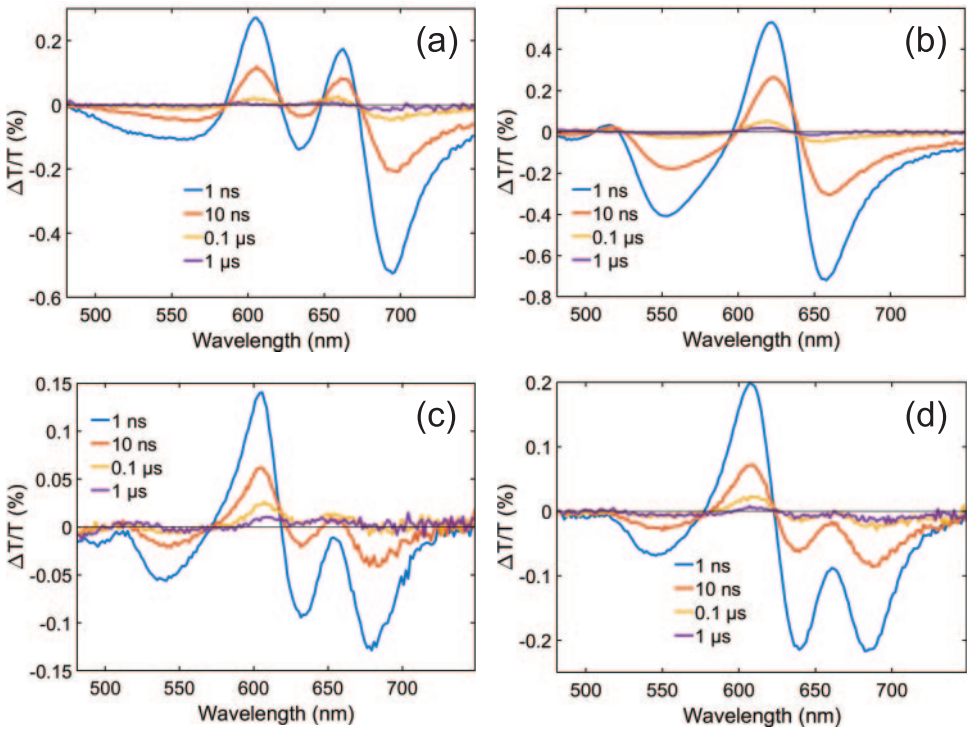

Fig. 2. – (Colour on-line) Spectra at four selected delays for "MoS_2 1–5 k g" in (a), "WS_2 1–5 k g" in (b), "MoS_2 on WS_2" in (c), and "WS_2 on MoS_2" in (d).

(PA) to higher energy excited states. The resulting $\Delta T/T$ value is an interplay of PB and PA features, together with shifts and broadening. All features decay with a characteristic time around 10 ns, with no significant changes in the shape of the spectra during the first 100 ns. This behaviour indicates that the signal is mainly dominated by one population of photogenerated charge carriers. This result holds for all the measured samples. We repeated the same experiments on the two different HJs: MoS_2 on WS_2, and WS_2 on MoS_2. The obtained spectra are depicted in fig. 2(c) for "MoS_2 on WS_2", and in fig. 2(d) for "WS_2 on MoS_2". We observed a variation of signal amplitude at the negative band from 640 nm to 680 nm. We explained this in terms of a dominant contribution from the first excited layer. Nevertheless, we interestingly found that the dynamics are not affected by material stacking order, as reported in fig. 3(c) and (d). Normalised HJ dynamics are evaluated at the PB corresponding to the overlap between the A-exciton WS_2 PB and the B-exciton MoS_2 PB. The HJ dynamics are compared to different fractions from single materials. In particular, we observed a similar trend for both analysed TMDs: the higher the thickness of the material is, the longer the dynamics, as depicted in fig. 3(a) for WS_2, and in fig. 3(b) for MoS_2.

Moreover, contrary to expectations, making HJs did not improve the charge lifetime. Hence, this could suggest that additional complexity in the design of systems where

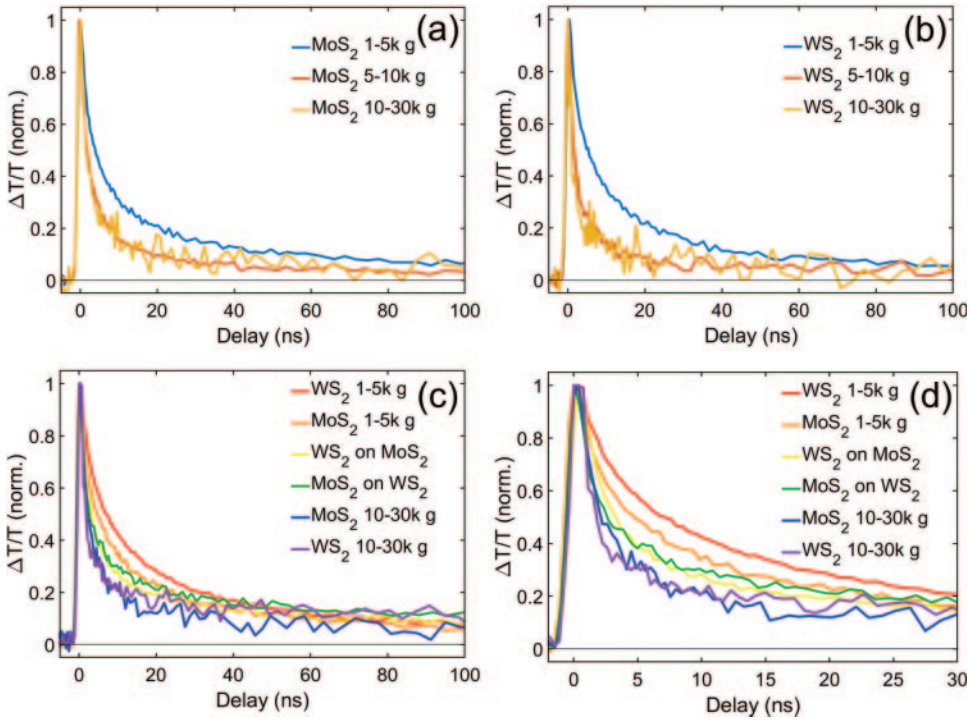

Fig. 3. – (Colour on-line) (a) Normalised dynamics up to 100 ns around the negative peak at 690 nm for the three different fractions of MoS_2. (b) Normalised dynamics up to 100 ns around the negative peak at 660 nm for the three different fractions of WS_2. Normalised dynamics evaluated at the PB for the two HJs are compared to the single material dynamics in (c) up to 100 ns, and a zoom up to 30 ns is reported in (d).

two TMDs are stacked together is not necessary for light harvesting applications. The crucial parameter affecting the dynamics is the density of defects, *i.e.*, sulfur vacancies and edges. The longest dynamics are observed in the "WS_2 1–5 k g" sample because the electronic contribution from basal plane is more dominant than the one from edges due to nanosheet size. The edges act as recombination centres causing faster dynamics. This is also visible when analysing the HJs where each layer belongs to the fraction 10–30k g containing thinner but also smaller flakes with higher surface density of edges. In the future it would be interesting to investigate how the HJ performance changes when the defects are passivated by metal nanoparticles or organic molecules.

3. – Conclusions

We investigated the dynamics of charge carriers in few-layer TMD flakes using nanosecond transient absorption spectroscopy. We found that charge carriers live longer in thicker and larger flakes compared to thinner and smaller ones, due to electronic contribution from edges. We demonstrated that it is possible to make HJ from LPE. The stacking order during deposition of MoS_2 and WS_2 films affects the spectra, which are more sensitive to the first excited layer, but does not affect the dynamics. The two systems show the same decay, which is slightly slower than the one observed in the single material from the same fraction 10–30k g. Nevertheless, the most relevant improvement in making the recombination slower is obtained when photogenerating free charges in thicker and larger flakes, where the electronic contribution from basal plane is dominant over the one from edges. Our studies of LPE few-layer TMDs give useful insights into transport properties in these prospective light harvesting materials. As a further step, defect passivation must be intensively investigated to improve the transport properties crucial for better device performance.

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REFERENCES

[1] Mikhailova M. P. and Titkov A. N., *Semicond. Sci. Technol.*, **9** (1994) 1279.
[2] Zhang C. *et al.*, *2D Mater.*, **4** (2017) 015026.
[3] Rivera P. *et al.*, *Nat. Commun.*, **6** (2015) 6242.
[4] Nagler P. *et al.*, *2D Mater.*, **4** (2017) 025112.
[5] Miller B. *et al.*, *Nano Lett.*, **17** (2017) 5229.
[6] Policht V. R. *et al.*, *Nano Lett.*, **21** (2021) 4738.
[7] Lee Y.-H. *et al.*, *Nano Lett.*, **13** (2013) 1852.

[8] Zhan Y. *et al.*, *Small*, **8** (2012) 1852.
[9] Wu S. *et al.*, *ACS Nano*, **7** (2013) 2768.
[10] Zhang Y. *et al.*, *Nat. Nanotechnol.*, **9** (2014) 111.
[11] Fleischauer P. D., *Thin Solid Films*, **154** (1987) 309.
[12] Novoselov K. S. *et al.*, *Proc. Natl. Acad. Sci. U.S.A.*, **102** (2005) 10451.
[13] Coleman J. N. *et al.*, *Science*, **331** (2011) 568
[14] Nicolosi V. *et al.*, *Science*, **340** (2013) 1226419.
[15] Paton K. R. *et al.*, *Nat. Mater.*, **13** (2014) 624.
[16] Hughes J. M. *et al.*, *J. Appl. Polym. Sci.*, **127** (2013) 4483.
[17] Backes C. *et al.*, *ACS Nano*, **10** (2016) 1589.
[18] Backes C. *et al.*, *Nat. Commun.*, **5** (2014) 4576.
[19] Ippolito S. *et al.*, *Nat. Nanotechol.*, **16** (2021) 592.
[20] Piatti E. *et al.*, *Nat. Electron.*, **4** (2021) 893.