MATERIALS SCIENCE

Highly mobile hot holes in $Cs_2AgBiBr_6$ double perovskite

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Highly mobile hot charge carriers are a prerequisite for efficient hot carrier optoelectronics requiring long-range hot carrier transport. However, hot carriers are typically much less mobile than cold ones because of carrier-phonon scattering. Here, we report enhanced hot carrier mobility in $Cs_2AgBiBr_6$ double perovskite. Following photoexcitation, hot carriers generated with excess energy exhibit boosted mobility, reaching an up to fourfold enhancement compared to cold carriers and a long-range hot carrier transport length beyond 200 nm. By optical pump–infrared push-terahertz probe spectroscopy and frequency-resolved photoconductivity measurements, we provide evidence that the conductivity enhancement originates primarily from hot holes with reduced momentum scattering. We rationalize our observation by considering (quasi-)ballistic transport of thermalized hot holes with energies above an energetic threshold in $Cs_2AgBiBr_6$. Our findings render $Cs_2AgBiBr_6$ as a fascinating platform for studying the fundamentals of hot carrier transport and its exploitation toward hot carrier–based optoelectronic devices.

INTRODUCTION

Optical excitation of semiconductors by photons with energy ($h\nu$) exceeding their bandgap (E_g) creates energetic, "hot" carriers with an excess energy $E_{ex} = h\nu - E_g$. These initially nonthermalized hot carriers can reach thermalization with a defined electronic temperature following the Fermi-Dirac distribution via carrier-carrier interactions in tens to hundreds of femtoseconds (fs) (*1*–*3*). The thermalized hot carriers can subsequently dissipate their excess energy to the lattice, becoming "cold" carriers at the band edge within a few picoseconds (ps) in most conventional semiconductors (*4*, *5*). The ultrafast energy loss during hot carrier cooling represents one of the major loss channels for solar cells, limiting the energy conversion efficiency to ~33.7% (so-called Shockley-Queisser limit) (*6*, *7*). Harvesting hot carriers before their relaxation is a much sought-after goal for achieving efficient optoelectronics, specifically photovoltaics (*8*, *9*). One of the main challenges is the relatively short transport length of hot carriers before dissipating their excess energy to the environment. This is due to the typically short hot carrier lifetimes combined with substantially reduced mobilities of hot charge carriers resulting from the enhanced momentum scattering rates, as reported in conventional semiconductors (e.g., Si and GaAs) (*4*, *10*, *11*).

Recent reports on remarkably long-lived hot carriers (with lifetimes over 100 ps) in lead halide perovskites have attracted enormous interest in exploiting hot carriers for fundamental research and developing efficient hot carrier–based optoelectronic devices (*5*, *12*). In addition to the lifetime, some recent ultrafast spectroscopic studies on perovskites have reported fascinating hot carrier transport properties on (sub-)picosecond time scales following light absorption and charge generation. For instance, Sung *et al.* (*13*) have reported that hot carriers can propagate more than 150 nm within 20 fs upon photon absorption in a methylammonium lead iodide system applying transient absorption (TA) microscopy, providing experimental evidence for ballistic transport (i.e., charge transport without scattering) of hot carriers on a sub–20 fs time scale. For the transport of relatively long-lived hot carriers from subpicoseconds to tens of picoseconds, different and even contradictory spectroscopic results have been reported. For instance, using the same techniques as by Sung *et al.* (*13*) with, however, a lower time resolution (more than 300 fs), Guo and colleagues (*14*) observed a quasi-ballistic transport in $MAPbI_3$ over 200 nm in the first 300 fs, followed by a diffusive transport regime of nonequilibrium hot carriers persisting for tens of picoseconds over a distance of 600 nm. This ultrafast, long-range transport seems to imply higher mobility for hot carriers than for cold ones. On the other hand, combining TA and terahertz spectroscopy, Monti *et al.* (*15*) reported that, while hot carriers show a long lifetime over 100 ps in a mixed Pb-Sn halide perovskite as observed by TA, time-resolved terahertz spectroscopy shows no difference in photoconductivity between hot and cold carriers. This led to the conclusion that hot carriers display mobilities similar to cold carriers. Clearly, hot carrier transport properties in metal halide perovskites, especially the transient hot carrier mobility, have so far remained elusive and merit further investigation.

Among the metal halide perovskites, $Cs_2AgBiBr_6$ double perovskite has emerged as a promising alternative to toxic, unstable lead halide perovskites for various optoelectronic applications owing to its outstanding chemical stability, nontoxicity, and outstanding optoelectronic properties, e.g., long carrier lifetimes (*16*, *17*) and large carrier diffusion lengths (*18*, *19*). In particular, $Cs_2AgBiBr_6$ double perovskite has shown exceptional performance for high-energy photon detection applications: For instance, it exhibits excellent x-ray detection with a low detection limit (*17*, *20*, *21*). Therefore, a study of hot carrier transport in $Cs_2AgBiBr_6$ double perovskites following high-energy photoexcitations is of great fundamental interest and could provide insights into their further optoelectronic applications. Here, using optical pump–terahertz probe (OPTP)

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