# Ultrafast Carrier Dynamics of CdS Nanowires Wrapped in $C_3N_5$ Nanosheets

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**Abstract—We explore ultrafast photoconductivity dynamics of CdS nanowires wrapped in layers of $C_3N_5$ nanosheets using time-resolved terahertz (THz) spectroscopy. We find that nanowire growth, wrapping, and carrier density impact carrier transport in these nanowires.**

## I. INTRODUCTION

IN 2019 a low bandgap, semiconducting, azo-linked carbon nitride framework ($C_3N_5$) was made for the first time, that shows great promise for photocatalytic and photovoltaic applications [1]. However, as reported by Kumar et al. [1], the optical absorption in this system is weak, a potential limiting factor in its application to photocatalysis that can be overcome by wrapping $C_3N_5$ nanosheets around CdS nanowires [2]. Charge carriers may be photoexcited in the CdS core and injected into the smaller band gap $C_3N_5$, aiding in the formation of new reactive species. Therefore, understanding the nature of charge carrier transport in these $C_3N_5$-wrapped CdS nanowire systems is crucial for their potential application in photocatalysis.

Time-Resolved Terahertz Spectroscopy (TRTS) has become a standard method of characterizing sub-picosecond charge-carrier transport in a variety of nanoscale systems [3,4]. To date, TRTS of $C_3N_5$ nanosheets has not been performed, however, TRTS has been performed on nanoscale systems of CdS [5-8]. Most similar to CdS nanowires wrapped in $C_3N_5$, are bandgap graded $CdS_xSe_{1-x}$ nanowires [5]. Through TRTS it was found that the carrier lifetimes in $CdS_xSe_{1-x}$ nanowires are well described by a biexponential decay, with the longest lifetimes being ~700 ps [5]. Long charge-carrier lifetimes are desirable for photocatalysis applications, as an increased lifetime will allow mobile charge-carriers to diffuse to the nanowire surface and participate in photocatalysis. Ultrafast carrier dynamics in the bandgap-graded nanowires was found to be well described by a Drude-Smith model of conductivity, extracting a mobility of ~400 cm$^2$/Vs [5], which is comparable to measurements of 440 cm$^2$/Vs in bulk CdS [9]. A high carrier mobility is also favorable for photocatalysis applications, to ensure that mobile charge carriers don't become trapped or recombine before reaching the nanowire surface where they can take part in surface chemistry.

In this work, we employ TRTS to investigate the sub-picosecond carrier dynamics of CdS nanowires wrapped in $C_3N_5$ nanosheets for the first time. We explore aspects of carrier transport.

## II. RESULTS

A field emission scanning electron microscope (FESEM) image of the bare CdS nanowires is shown in Fig. 1a. Figure 1b is an FESEM image of the CdS nanowires wrapped in $C_3N_5$ after growth (i.e., post growth, referred to as CdS-MHP). The FESEM images show that nanowires have a diameter of ~50nm and lengths of 1μm scale. Samples grown with $C_3N_5$ in-situ (referred to as CdS-MHPINS) are not shown, but FESEM images reveal similar feature sizes. Samples are prepared by drop-casting nanowires suspended in solution onto c-cut sapphire substrates.

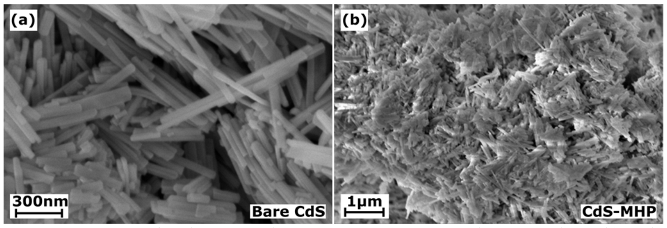

**Fig. 1.** FESEM of CdS nanowire systems. a) Bare CdS nanowires. b) CdS nanowires wrapped in $C_3N_5$ post nanowire growth (CdS-MHP).

Using TRTS, we photoexcite these systems with 410 nm, 100 fs laser pulses, over a range of fluences from 20 - 400 μJ/cm$^2$ to investigate the relationship between carrier density, carrier lifetime, and mobility. Figure 2a shows differential transmission measurements on bare CdS nanowires, CdS-MHP and CdS-MHPINS, with a fluence of 400 μJ/cm$^2$. We see that the peak differential transmission of CdS-MHPINS is significantly lower than the bare nanowires and CdS-MHP. This indicates a strong suppression of mobility the CdS-MHPINS nanowires, and the shorter rise time indicates the presence of ultrafast trapping in this sample, which is solely due to the growth process. It is likely that the $C_3N_5$ nanosheets added in-situ interfere with the growth of the nanowire core, resulting in smaller crystallite sizes [2] and increased number of S vacancies, common in nanoscale CdS [2,5-7]. Wrapping the CdS nanowires after growth seems to have little effect on the charge-carrier mobility and lifetimes, as seen in Fig. 2a.

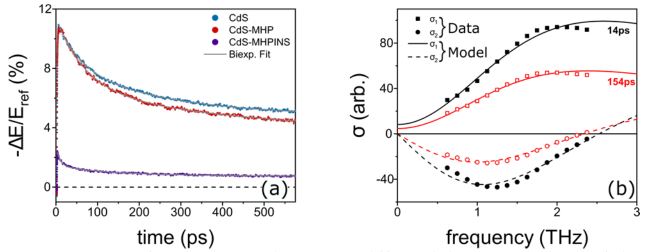

**Fig. 2.** TRTS of CdS nanowires. a) Differential transmission of bare nanowires, nanowires grown with $C_3N_5$ in-situ, and nanowires grown with $C_3N_5$ added after growth (MHP-wrapped). All samples were photoexcited with 410nm, 100fs pulses with a fluence of 400 μJ/cm$^2$, fit to biexponential decays (grey lines). b) The photoconductivity spectrum taken from bare nanowires at 14 ps and 154 ps time delays and fit to a Drude-Smith model.

We find that the photoconductive lifetimes are fit well by a biexponential decay (grey lines in Fig. 2a), where short lifetimes are on the order of ~10 ps, and long lifetimes are ~100 ps. In all samples and all fluences, we find that there is a persistent photoconductivity that lasts for more than 500 ps. Furthermore, in the bare nanowires we find that the carrier lifetime decreases as the density increases, similar to what is seen in density-dependent recombination pathways such as Auger recombination. Lifetimes in the wrapped nanowires vary little as the fluence is increased.

In Fig. 2b, we present the conductivity spectrum of bare CdS nanowires, taken at pump-probe delay times of 14 ps and 154 ps. We find that our data agrees well with the Drude-Smith model of conductivity. The Drude-Smith model is used to describe carrier dynamics in nanoscale systems where carrier localization is prominent [2, 3, 5-7, 10-12]. The Drude-Smith conductivity spectrum is given by,

$$\tilde{\sigma}(\omega) = \frac{\mathrm{ne}\mu_{\mathrm{DS}}}{1 - \mathrm{i}\omega\tau}\left[1 + \frac{\mathrm{c}}{1 - \mathrm{i}\omega\tau}\right], \tag{2}$$

where $\tau$ is the carrier scattering rate, n is the photoexcited carrier density, $\mu_{\mathrm{DS}}$ is the carrier mobility within a nanowire crystallite, and c is a phenomenological fit parameter that varies between -1 and 0, encompassing the suppression of low frequency conductivity resulting from carrier backscattering and drift diffusion that occurs in localized geometries [12]. We note that the plasmon model is commonly used to describe carrier dynamics in nanowire systems, however, fitting our data to the plasmon model across all fluences fails to reproduce the expected scaling of the plasma frequency [4].

We find that the mobility within the confined geometry changes little with fluence, as shown in Fig. 3. The mobility of the bare nanowires is similar to CdS-MHP, which is likely due to the high crystallinity in the CdS cores of these samples [2]. In CdS-MHPINS we find the mobility within the crystallite is much lower, which is likely due to interactions with defects such as S vacancies, as noted in other CdS based nanostructures [5-8]. This agrees with the shorter carrier lifetimes and decreased mobility observed in the differential transmission measurements and supports the notion that the presence of $C_3N_5$ nanosheets during growth can negatively impact carrier transport in the CdS nanowire core. The mobilities of the bare nanowires agree well with the mobility along the c-axis in Wurtzite CdS (440cm$^2$/Vs [9]) and bandgap graded $CdS_xSe_{1-x}$ nanowires [5], as shown by grey dashed line in Fig. 3.

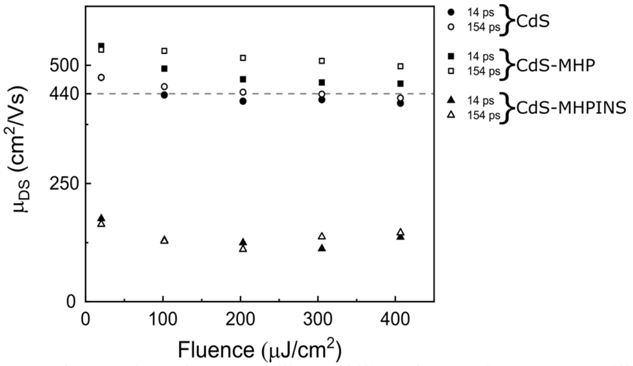

**Fig. 3.** Fluence dependent crystallite mobility of nanowire systems. Filled (hollow) squares indicate measurements taken at pump-probe delay time of 14ps (154ps). Circles, squares, and triangles denote bare CdS nanwires, CdS-MHP and CdS-MHPINS, respectively. Literature value (440 cm$^2$/Vs) is indicated by the grey dashed line [9].

## III. SUMMARY

In this work we study how growth, wrapping, and charge-carrier density impact the ultrafast carrier dynamics of novel CdS nanowires wrapped in $C_3N_5$ nanosheets. We find that growing CdS nanowires in the presence of $C_3N_5$ nanosheets results in increased ultrafast trapping and lower mobility. Wrapping the nanowires post-growth results in little change to the carrier lifetimes and mobility, as compared to bare CdS nanowires. Increasing carrier density in these samples seems to have little effect on recombination lifetimes in the $C_3N_5$ wrapped systems, however the fluence-dependent lifetimes of the bare nanowires indicates the presence of density-dependent recombination pathways such as Auger recombination.

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