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Dynamics of optically excited electrons in the conducting polymer PEDT:PSS

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Abstract Femtosecond time-resolved two-photon photoemission spectroscopy is employed to study the dynamics of the non-equilibrium electron distribution in the conducting polymer poly(3,4-ethylene-dioxythiophene):poly-(styrenesulfonate) (PEDT:PSS) film following optical excitation at 2.1 eV. We found that the electron thermalization occurs on a ultrafast time scale of around 60 fs analogous to the relaxation times of optically excited electrons in Au(111).

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1 Introduction

π -Conjugated polymers are promising as low-cost and easily processable alternatives to inorganic semiconductors or metals in electronic applications. Utilizing intrinsic conducting polymers (ICP) as electrodes and hole injection layers in optoelectronic devices based on organic materials is thereby a key for a successful implementation of organic electronics. One of the prototypical ICP is poly(3,4-ethylene-dioxythiophene):poly(styrene-sulfonate) (PEDT:PSS; see Fig. 1), which has been used for instance for the fabrication of very efficient organic light emitting diodes (OLED) [1], [2] and field-effect transistors [3], [4]. In PEDT, double bonds are alternating with single bonds along the polymer chain. Thereby the unhybridized p_z -orbital of one carbon atom overlaps with the p_z -orbital of the neighboring carbon atom to form a π -bond, in which the electrons are weakly bound and therefore are relatively delocalized. However, due to the different bond length of the single and double bond the Peierls instability splits this band into two sub-bands, the completely filled valence band and an empty conduction band, separated by an energy gap. Hence the material is a semiconductor, but through doping with PSS the polymer become conductive. It has been shown that charge carriers created after absorption of light in π -conjugated polymer are polarons [5]. The strong electron-phonon coupling of these quasi-particles gives rise to new energy states in the band-gap, thus the polymer absorbs in the IR region and is transparent [6]. Moreover varying the ratio of PEDT:PSS induces changes in the micromorphology which

facilitates adjustment of the overall conductivity of thin films [7]. In OLEDs PEDT: PSS is one of the most frequently used anode material due to its high work function and accordingly the low hole injection barrier. It has been shown that the work function possesses values between 5.0 and 5.6 eV which was mainly attributed to the amount of residual water in the thin films [8]. Thus the work function (Φ) can be much higher than the values known for atomically clean gold surfaces (e.g., $\Phi(\text{Au}(111)) = 5.4 \text{ eV}$ [9]).

It is known that the charge transport in this class of polymers is dominated by disorder leading to charge localization that is dominant at all practical temperature, i.e. temperatures where no damage of the material occurs. In this material, polarons are formed in less ordered regions of the doped polymers [10]. Interacting with phonons, charge carriers hop from localized sites to another. Upon transport, the charge carriers can either transfer their energy to the lattice by exciting phonons or radiative recombination gives rise to photoluminescence.

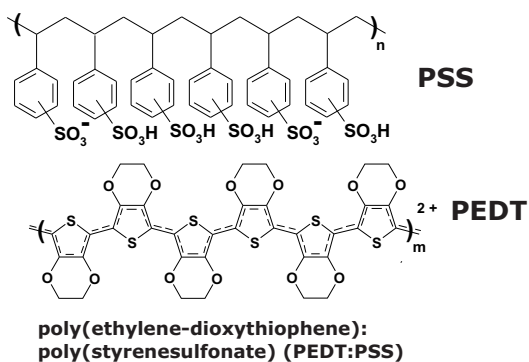


Fig. 1 Chemical structure of the conducting polymer mixture PEDT:PSS.

The dynamics of electronic excitations in organic molecules or polymers with potential application in optoelectronic devices plays an important role. Up to now the dynamics of electrons in PEDT:PSS has only been studied by infrared-induced transient adsorption in the sub-picosecond time-domain [11]. Femtosecond (fs) time-resolved two-photon photoemission (2PPE) spectroscopy has been used to study electron thermalization in various metals, metallic films and semiconductors [12], [13], [14],[15], [16] [17], [18], [19] but interestingly so far this technique has not been utilized to investigate the dynamic behavior of charge carriers in conducting polymer films. In metals, light is adsorbed near the surface within the optical penetration depth of typically 10-20nm. This leads to the creation of free charge carriers, which relax predominantly by electron-electron (e-e)-scattering on a femtosecond timescale. Subsequent energy transfer to the lattice by electron-phonon (e-ph)-scattering occurs on a picosecond timescale. In addition the nascent carrier distribution is also depleted by transport of excited carriers into the bulk. An important difference between metal and polymer films is the penetration depth of light. For the polymer films the cross section for photon absorption is not very high. Moreover, the charge carrier density in PEDT:PSS is in the order of 10^{20} cm^{-3} [20], while in metals it is around 10^{22} cm^{-3} .

In this contribution we investigate the relaxation dynamics of photoexcited electrons in PEDT:PSS and Au(111) in the fs time domain using 2PPE. The comparison of the charge carrier dynamics between this two

classes of material is motivated by the potential use of PEDT:PSS as an electrode material instead of metals in opto-electronic applications . For the polymer we observed electron relaxation times in the order of 60 fs, akin to the time scales determined for Au(111).

2 Experimental

The present experimental setup combines a tunable femtosecond laser system with an ultrahigh vacuum chamber for two-photon photoemission (2PPE) spectroscopy.

For the 2PPE measurements, femtosecond laser pulses are generated by a 300 kHz Ti:Sapphire laser system, which pumps an optical parametric amplifier (OPA). The OPA delivers pulses with a tunable photon energy between 1.7 eV and 2.7 eV output. These pulses can be frequency-doubled in a BBO crystal to generate ultraviolet pulses (3.4–5.4 eV photon energy). After a thorough temporal compression pulses with a duration of about 60 fs are obtained. The laser pulses are incident on the surface with an angle of 45° with respect to the surface normal. While the pump pulse $h\nu_1$ excites an electron from below the Fermi level (E_F) to intermediate unoccupied states at energies $E - E_F = E_{kin} + \Phi - h\nu_2$ (with Φ the work function), the probe pulse $h\nu_2$ photoionizes the sample by lifting the excited electron above the vacuum level (E_{vac}). Photoelectrons are detected in a custom-built time-of-flight spectrometer and are analyzed with respect to their kinetic energy (E_{kin}) (for details see Ref. [21]).

The commercial PEDT:PSS dispersion with a PEDT:PSS ratio of 1:6 (Baytron® P AI4083) was used. Thin films were prepared by spin casting the dispersion on freshly cleaned and UV/ozone-treated (for 30 min) indium tin oxide (ITO; on glass) substrate in ambient. After heating the sample at approximately 200 °C for 5 min there were transferred into the ultrahigh vacuum system for the time-resolved photoemission experiments.

3 Results and Discussion

To gain insight into the dynamics of photoexcited hot electrons after excitation of a PEDT:PSS film with short laser pulses, fs time-resolved 2PPE has been used. In Figure 2, a two-dimensional false color representation of the photoemission intensity of PEDT:PSS recorded with photon energies of $h\nu_1 = 2.1$ eV for the visible and $h\nu_2 = 4.2$ eV for the UV laser pulses represents the electron distribution as a function of both time delay (horizontal axis) and energy (vertical axis). The spectrum is displayed as a function of final state energy above the Fermi level, $E_{Final} - E_F = E_{kin} + \Phi$, thus the energy of the secondary edge corresponds to the work function of PEDT:PSS which is 5.1 eV. Depending on the sequence of laser pulses (or formally the sign of the pump-probe delay), the dynamics are probed either near E_F or at higher intermediate state energies. Negative delays correspond to populating intermediate electronic states with UV light pulses ($h\nu_2$), while the visible pulses ($h\nu_1$) subsequently probe the excited electron distribution. On the other hand, for positive delays the electrons are excited to interme-

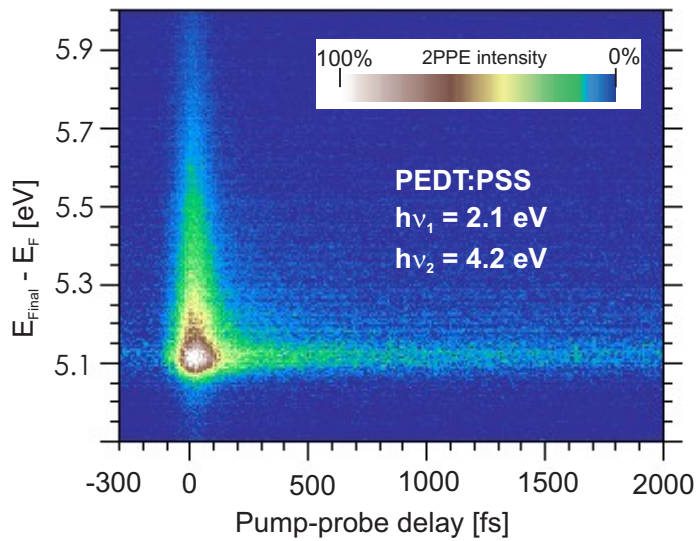


Fig. 2 2PPE intensity (color map) as a function of pump-probe delay (horizontal axis) and final state energy above the Fermi level (E_F) (vertical axis) from PEDT:PSS recorded with photon energies of $h\nu_1 = 2.1$ eV for the visible and $h\nu_1 = 4.2$ eV for the UV laser pulses. The excited electron distribution is probed with $h\nu_1$ at negative delays, while at positive delays it is probed with $h\nu_2$.

mediate states close to the Fermi level (hot electrons) with the visible pulses ($h\nu_1$) and are subsequently probed by the UV pulses ($h\nu_2$). Analyzing the two-dimensional data set by extraction of the time-dependent 2PPE photoelectron yield integrated over the energy intervals centered on the state of interest, i.e., hot electron distribution, provides the temporal evolution of the electron population, referred to as cross correlation traces as shown in Fig. 3(a). The cross correlation curves are recorded at intermediate state energies $E - E_F$ between 0.9 and 1.8 eV.

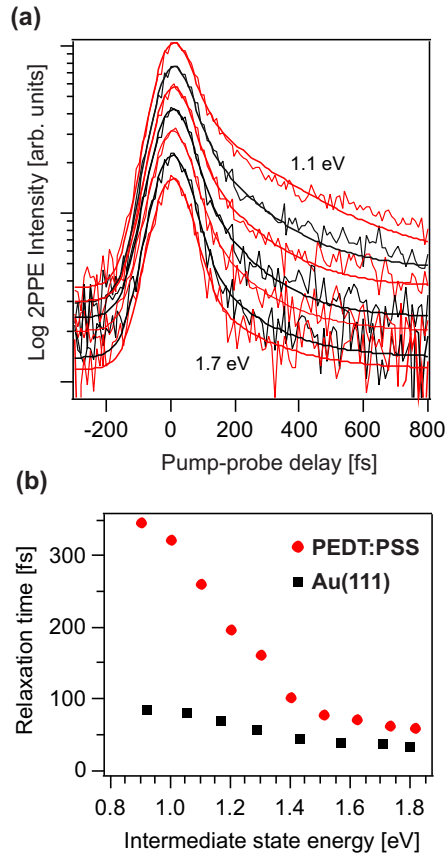


Fig. 3 (a) Cross correlation curves for PEDT:PSS recorded at intermediate state energies $E-E_F$ between 1.1 and 1.7 eV. (b) Relaxation times of the photoexcited electron distribution for PEDT:PSS and Au(111).

In general, several processes contribute to the observed population decay in 2PPE. Relaxation out of a given energy interval above $E-E_F$ is affected by electron-electron (e-e) scattering, electron-phonon (e-ph) or electron-defect scattering and by transport out of the detection volume. The rate of e-e scattering (i.e., the inverse inelastic lifetime) is given by a screened Coulomb interaction and the available phase space depending on the energy above

the Fermi level [22]. However generation of secondary electrons by Auger decay of electrons and holes may also increase the population in particular in energy intervals close to E_F . Therefore the measured relaxation times can not be simply identified with electron lifetimes at least for energies close to E_F .

The relaxation times are determined by fitting the cross correlation curves with a convolution of the pump probe cross correlation with a single exponential decay. For energies above 1.2 eV the fit describes the data well. For lower energies the electron population is more and more dominated by refilling processes with secondary electrons. The relaxation times as a function of intermediate state energy ($E-E_F$) are displayed in Fig. 3(b) together with the corresponding values for Au(111). Two main points we would like to point out: (i) The lifetime, and hence the inelastic mean free path is strongly energy-dependent. The curve shows a clear increase in relaxation time as E_F is approached. This faster relaxation for higher energies above $E-E_F$ is due to availability of more phase space (see above). (ii) The comparison with Au(111) shows that for intermediate state energies above approximately 1.5 eV the relaxation times for PEDT:PSS and Au are very similar. The relaxation time for PEDT:PSS is less than a factor 2 higher. For metals, the e-e interaction is efficiently reduced by screening, which attenuates Coulomb interactions. For PEDT:PSS, despite a lower charge carrier density the screening of carrier-carrier Coulomb interaction seems also efficient. Moreover, due to the polaronic nature of the charge carriers

in the polymer, electron-phonon interaction is much more efficient than in the case of a metal, leading to comparable relaxation times in the two materials. For intermediate state energies below 1.5 eV the relaxation times in both materials differ significantly, in PEDT:PSS the electrons exhibit much longer lifetimes. We attribute this to refilling effects, viz. the creation of secondary electrons by decay of excited electrons into lower energetic states (cascade electrons) and Auger electrons. Furthermore, polaronic hopping to neighboring weakly localized states reduces the probability of radiative recombination by meeting a polaron of the opposite charge at low carrier excitation density. Note that the small slope change in the relaxation time of electrons in Au(111) around 1.5 eV has been associated with photoexcitation of d-electrons as for copper [15].

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