Semiconductor nanocrystals in carrier-transporting polymers: Charge generation and charge transport

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Abstract

By incorporating semiconductor nanocrystals in carrier-transporting polymers, an interesting class of photoconductive nanocomposites is created. The presence of semiconductor nanocrystals enhances the photoinduced charge generation efficiency and extends the sensitivity range, while the polymer matrix is responsible for charge transport. A wide variety of semiconductors and polymers have been used. In this paper, we review material synthesis and discuss the effects of semiconductor nanocrystals on the charge transport and charge generation properties.

Keywords: Nanocrystals; Photoconductivity; Semiconductors; Polymers

1. Introduction

Semiconductor nanocrystals (nanoclusters, quantum dots) have been studied extensively for their spectroscopic, photochemical and nonlinear optical properties [1-6]. The research of these materials for technologically important, transport-related applications has received relatively little attention [7-14]. Since semiconductor nanocrystals are electrically confined in all three dimensions, conductive pathways must be established between them in order for carrier (electron or hole) transport to occur.

One approach is to press or sinter the nanocrystals together into contacts [7, 8]. For example, TiO₂ nanocrystals have been sintered into a porous film which shows good photovoltaic efficiency [7]. The other approach is to embed nanocrystals into a polymer matrix capable of transporting carriers [9-14]. The redox potentials of the nanocrystals and the matrix have to allow for efficient electron transfer between them.

There are similarities and differences between such nanocrystal/polymer composites and superlattices as shown in Fig. 1. Compositional superlattices are composed of a periodic sequence of ultrathin crystalline layers of alternating compositions (e.g. GaAs/GaₐAl₁₋ₓAs) with different band gaps (left side of Fig. 1). Such compositional variation produces a 1-D periodic potential, with the period shorter than the electron mean free path, which give rise to unusual transport phenomena [15]. For semiconductor nanocrystals (e.g. CdS) embedded in carrier-transporting polymers, shown schematically on the right side of Fig. 1, there are natural variations in the potentials and distances. These variations are due to the crystal size distributions, amorphous nature of the polymer, and the random packing. Furthermore, being a 3-D system, the mechanism of carrier transport can be concentration-dependent. In low concentrations of
semiconductor nanocrystals, carriers can move in the polymer phase exclusively without being modulated significantly by the presence of nanocrystals.

We have studied the photoconductive properties of a number of semiconductor nanocrystals/polymer nanocomposites [9-13]. Photoconductive polymers are widely used in the imaging industry as either photosensitive receptors or the carrier (electron or hole) transporting material in copy machines and laser printers. This is still the only area in which the photoelectronic properties of polymers are exploited on a large-scale industrial basis. It is also an electronic application where polymers are superior to inorganic semiconductors. Furthermore, such materials have possible uses in other applications such as electroluminescence [14] and photorefractives.

A large number of semiconductor nanocrystals (nanoclusters), such as CdS, InAs, and fullerenes, can be doped into these polymers to form good photoconductive composites [9-13]. Carrier-transporting polymers used include N-polyvinylcarbazole (PVK) [10, 12] (phenylmethyl)polysilane (PMPS) [11], and amine-doped polycarbonate [9, 13]. In this paper, we first review the material aspects of these photoconductive nanocrystal/polymer composites and then discuss their charge transport and charge generation properties.

2. Experimental techniques

The charge generation efficiency of a photoconductor can be conveniently measured by the photoinduced discharge method [16, 17]. The sample consists of a polymer film deposited on an electrically grounded substrate. The film is first corona-charged positively or negatively in the dark and then moved by a translational stage to the underside of an electrostatic voltmeter where the surface potential can be monitored. In the absence of light, the polymer is an insulator so the surface potential stays nearly constant (except some dark decay). Upon irradiation by light, electrons and holes are generated. If the sample is photoconductive, they migrate to the surface, recombine with surface charges, and discharge the surface potential. Quantitative information on the charge generation efficiency can be obtained from the analyses of photoinduced discharge curves. For light of sufficiently low intensity and absorbed within a small fraction of the film thickness, the charge generation efficiency $\phi$ can be obtained from the initial discharge rate of the surface potential $\left(\frac{dV}{dt}\right)_{t=0}$ [16, 17], i.e.

$$\phi = -\frac{\varepsilon}{4\pi e LI} \left(\frac{dV}{dt}\right)_{t=0},$$

where $\varepsilon$ is the dielectric constant, $e$ the electronic charge, $L$ the film thickness, and $I$ the absorbed photon flux. The intensity used has to be low enough to avoid the space-charge effect, typically $10^{12}$–$10^{13}$ photons/cm$^2$ s.

The mobility of an electron or hole in a polymer film is measured by the time-of-flight technique shown schematically in Fig. 2.
Fig. 2. Schematics of the time-of-flight method for measuring the hole mobility.

For these measurements, a gold electrode (in an area of 0.3 cm²) was deposited on top of the photoconductive film (Fig. 2). Connecting leads were attached to the gold and ITO electrodes with silver epoxy. An ~10-ns, 308-nm laser pulse from an excimer laser was used to irradiate the sample from the ITO side. The incident laser energy was kept low, ≤ 36 μJ for a 0.3 cm² spot, to insure that only a small fraction of the surface charges were injected. Carriers were generated near the ITO side of the surface and then drifted towards the gold side under the applied field. The current was detected by an external circuit shown in Fig. 2 and digitized by a Tektronix DSA 601A digitizer for data analysis.

Luminescence spectra were measured on a Spex Fluorolog spectrometer. Luminescence lifetimes were measured by the time-correlated single-photon-counting technique using an Edinburg FL900CD instrument.

3. Material synthesis

Films of polyvinylcarbazole (PVK) containing small semiconductor nanocrystals have been prepared by one of two basic techniques. The first involves the preparation of discrete soluble clusters using solution synthesis techniques and then codissolution of PVK and these clusters in a mutual solvent. Casting this solution and drying produces the desired semiconductor cluster doped films. This approach can provide excellent control over cluster size and stoichiometry and is often the method of choice for producing well-characterized films. An alternative, but more general, approach involves casting of a film containing metal ions which are then exposed to heat and a reactive gas whereupon the semiconductor is produced in the film directly as the reactive gas diffuses through the film and reacts with the entrained metal ions. Migration of metal ions and aggregation into clusters is controlled by the inherent viscosity of the polymer matrix. The choice between these two techniques is often dictated by the synthetic chemistry available. Below are listed several examples of both synthetic approaches. More examples can be found in Ref. [13].

3.1. Method–preformed clusters

3.1.1. CdS clusters in PVK

Thiophenol-capped CdS nanoparticles were prepared by taking 0.5 g of (NMe₄)₄Cd₁₀S₄SPh₁₆ and heating to 260°C under 600 Torr nitrogen for 1 h. The resultant pale yellow material has the stoichiometry Cd₁₀S₄SPh₂. 0.06 g of this yellow solid was dissolved into 0.5 ml of a stock solution of 1.5 g PVK polymer dissolved in 7 ccs pyridine. The clear solution was then dip-coated onto an aluminum sheet to give a clear yellow film. The film on the aluminum sheet was then heated to 250°C under 500 Torr pressure of H₂S for 30 min during which time it developed a bright orange coloration.[12]

3.1.2. PbI₂ clusters in PVK

In an inert atmosphere glove box, 0.02 g (NH₃C₆H₅)₃Pb₂[18] was dissolved in 1.0 ml of a stock solution prepared by dissolving 1.5 g PVK in 15 ml pyridine. The solution was dip-coated onto aluminum and, as it dried, the yellow solution became a red film which was used in photoconductivity tests.

3.2. Method II–cluster formation in situ

3.2.1. HgS clusters in PVK

Under an inert N₂ atmosphere, 0.02 g mercuric acetate was dissolved in 1 ml of a stock solution made by dissolving 1–5 g PVK polymer in 15 ml pyridine. The clear solution was then dip-coated
onto an aluminum sheet to give a clear colorless film. The film on the aluminum sheet was then heated to 200°C under 500 Torr pressure of H₂S for 120 min during which time it developed a dark brown coloration. The film was evacuated and recovered for testing.

3.2.2. InAs clusters in PVK
In an inert atmosphere glove box, 0.01 g trimethylindium was dissolved in 0.5 ml of a stock solution prepared by dissolving 1.5 g PVK in 7 ml pyridine. The solution was dip-coated onto aluminum and the dried film on Al was then subjected to 300 Torr AsH₃ gas at 100°C for 30 min. The originally colorless film became dark chocolate brown.

3.2.3. Ga₂S₃ clusters in PVK
In an inert atmosphere glove box, 0.01 g triethylgallium was dissolved in 0.5 ml of a stock solution prepared by dissolving 1.5 g PVK in 7 ml pyridine. The solution was dip-coated onto aluminum and the dried film on Al was then subjected to 500 Torr H₂S gas at 100°C for 30 min. The originally colorless film became pale yellow.

3.2.4. In₂S₃ clusters in PVK
In an inert atmosphere glove box, 0.02 g trimethylindium was dissolved in 1.0 ml of a stock solution prepared by dissolving 1.5 g PVK in 1.5 ml pyridine. The solution was dip-coated onto aluminum and the dried film on Al was then subjected to 500 Torr H₂S gas at 200°C for 120 min. The originally colorless film became yellow.

4. Photoinduced discharge
It is useful to first illustrate the difference between nanocrystals and conventional micron-sized particles. Micron-sized semiconductor particles such as CdS have been mixed with polymer binder to form paste-like films [19], originally intended as an economical alternative for single-crystal thin films. The concentration of CdS particles has to be high enough to establish particle contacts so that conduction can occur. As a result the film quality is poor and these composites usually have low charge generation efficiency and problems of carrier trapping. Examples are shown in Fig. 3. No photoinduced discharge can be observed for 10 wt% micron-sized CdS in polymethylmethacrylate (PMMA), Fig. 3(a), since CdS particles are not in contact and PMMA is an insulator. For 90 wt% micron-sized CdS in PMMA, where CdS particles are now in contact and PMMA acts as a binder, some photoinduced discharge can be observed but the sustainable electric field is low and residual charges are substantial due to the presence of deep traps (Fig. 3(b)).

Materials discussed in this paper are quite different. The size of the semiconductor particles is reduced to the nanometer regime, so good quality transparent films can be made because of the reduced light scattering from nanocrystals. Since a very small nanocrystal is essentially a large molecule, the so-called grain boundaries existing between large particles and polymers, which can act as carrier traps, are now absent. Only a small amount of nanocrystals is needed since the polymer
matrix is capable of transporting carriers. The amount used is typically a few weight percent, well below the percolation threshold of \( \sim 15 \, \text{vol} \% \). The nanocrystals, isolated from each other, are responsible for the photoinduced charge generation, and the polymer is responsible for the subsequent charge transport. Fig. 3(c) shows an example of N-polyvinylcarbazole (PVK) doped with 1 vol% 16 Å CdS nanocrystals. The photoinduced discharge rate is greatly enhanced compared to undoped PVK [12].

Carbon provides another example. While large carbon particles are not known as sensitizers of photoconductive polymers, extremely small carbon clusters such as fullerenes are able to enhance the photoconductivity of polymers such as PVK and PMPS by orders-of-magnitude [9-11]. Fig. 4 shows a representative photoinduced discharge curve of fullerene-doped PMPS in comparison with an undoped PMPS.

Other than CdS and fullerenes in PVK, a wide variety of semiconductors, including II–VI and III–V materials [13], have been doped into various polymers to make photoconductive composites. Representative photoinduced discharge curves are shown in Fig. 5 where fast and complete discharge can be clearly seen.

It should be noted that many of these materials (e.g. InAs/PVK) have small band gaps and are therefore IR-sensitive. Narrow-gap semiconductors such as InAs and PbS in the bulk form usually cannot be made into high-field, room-temperature photoconductors. Other than the typical difficulty of growing large-area single-crystal thin films, the main problem is the dark decay due to thermal excitation of carriers. By doping nanometer-sized InAs into charge-transporting polymers, one retains the charge generation efficiency of InAs, but removes the dark decay problem since charge transport is now performed by the polymer which has large band gap. In addition, thin film preparation with polymers is much easier. The trade-off here is the speed, since carrier mobilities in polymers are significantly lower than those in crystalline semiconductors. These polymeric photoconductors are therefore more suitable for applications involving parallel processing, such as imaging, where speed is less important.
Photoconductivity is the convolution of charge generation (number of carriers generated per absorbed photons) and charge transport (how fast an electron or hole move through the medium under applied field). In the following sections, we will discuss the effects of nanocrystal (nanocluster) dopants on the charge generation and charge transport properties of the polymer.

5. Charge transport

The carrier mobility is measured by the time-of-flight method as discussed in the experimental section (Fig. 2). Electrons and holes are created by a short laser pulse near the surface of the polymer film. Depending on the polarity of the electric field applied on the electrodes, either electrons or holes will traverse the bulk of the film. This gives rise to a displacement current which is detected by the external circuit. Fig. 6 shows typical time-of-flight transient curves. In the ideal case (nondispersive transport), the current stays constant and falls off to zero at time $\tau_T$, when the charge carriers arrive at the other side of the film. Usually the fall-off near $\tau_T$ is smeared out due to spreading of the charge carrier packet, as shown in Fig. 6(a) for phenylmethylpolysilane. The carrier mobility $\mu$ is determined from the equation $\mu = l/(\tau_E)$, where $l$ is the film thickness and $E$ is the applied field.

Carrier transport in polymers is characterized by a succession of hops from site to site. The distances between various neighboring sites and the energetics of each site are different. These distributions (dispersions) in energy and distance cause different hopping rates between different sites. This is called dispersive transport, which gives a transient current deviating from the ideal shape [20–23]. In the extreme case, no discernible break at transit time $\tau_T$ can be detected from the time-of-flight curve. This problem was addressed by Sher et al. [20–23]. According to Sher–Montroll model, the dispersive current transient can be analyzed in a double log plot as shown in Fig. 6(b). The transit time is taken to be the break point in such a log–log plot (Fig. 6(b)). This has been the standard way for analyzing dispersive transport for a number of years.

In many instances such double log plots do not yield a clearly defined breakpoint or sometimes give several breakpoints. An alternative method may be used [24]. A unipolar injected photocurrent should be dependent on the light intensity at low intensity and saturates at high intensity when space-charge limitation is reached. The maximum photocurrent $J_C$ is given by Child’s law as

$$J_C = \varepsilon \varepsilon_0 \mu \frac{V^2}{d^3},$$

(2)

Fig. 6. Time-of-flight transient curves for (a) C$_7$O in PMPS at 2.5, 3.1, and $3.7 \times 10^5$ V/cm; and (b) PVK at 4.7, 5.5, $6.3 \times 10^5$ V/cm. The arrows indicate the approximate location of the transit time $\tau_T$. 
where \( \epsilon \) is the dielectric constant, \( \varepsilon_0 \) the permittivity of free space, \( \mu \) the effective mobility, \( V \) the applied voltage, and \( d \) the thickness of the sample. Measuring the photocurrent at saturation with high light intensity, one may then deduce the effective mobility \([24]\).

Time-of-flight photocurrent data for CdS/PVK and PVK is shown in Fig. 7(a). Both show a fast spike followed by a slow decay; the magnitude of the fast spike is much larger for CdS/PVK due to the sensitization effect of CdS. It is known that hole transport in PVK is very dispersive and previously it has been suggested that the fast spike is due to the intrinsic hole transport of PVK while the slow process is due to trap-dominated transport \([24]\). We found it difficult to extract the mobility value by analyzing the data with the conventional log-log plot. Additional intensity dependent experiments have to be performed as shown in Fig. 7(b). At low light intensity, CdS/PVK gives higher current than PVK. However, at higher intensities the saturation currents are essentially the same for both CdS/PVK and PVK for a given applied field (Fig. 7(b)). According to Eq. (2), this result indicates that both materials have the same hole mobility.

We reached the same conclusion with fullerene-doped polysilane and PVK \([25,26]\). It can be summarized that the effect of a small amount of dopant on the hole mobility of the polymer is small. It should be noted that this is only true for the low concentration of dopants discussed here. For very high concentrations of dopants, especially when the concentration is above the percolation threshold, the transport properties of the polymer can be greatly affected. In fact, this represents a promising direction for future research of semiconductor nanocrystal/polymer composites and remains to be explored.

6. Charge generation

Photoconductivity is the convolution of carrier generation efficiency and mobility. Since semiconductor nanocrystals have a very small effect on the transport properties of the polymer matrix, their main function is the enhancement of charge generation efficiency. There is a division of functionalities in these semiconductor nanocrystal/polymer composites: semiconductor nanocrystals and their interaction with the polymer are responsible for the charge generation while the polymer matrix is responsible for the charge transport. It is of fundamental importance to understand the molecular mechanism by which the charge generation efficiency of the polymer is enhanced in the presence of semiconductor nanocrystals. Furthermore, a more general question needs to be addressed: how can one quantitatively account for the high charge separation efficiency observed in a low dielectric constant of the polymer?
constant polymeric medium where the coulomb interaction between an electron–hole pair is not screened and the recombination rate is presumably fast? In this section, we will use CdS/PVK as an example to illustrate the mechanism by which semiconductor nanocrystals can enhance the charge generation efficiency.

The wavelength dependence of the charge generation efficiency of CdS-doped PVK for both positive and negative charging is shown in Fig. 8. Efficient photoinduced discharge can be achieved with both positive and negative charging in the longer wavelength region (> 350 nm). However, in the strongly absorbing short wavelength region, where carriers are generated near the surface and have to migrate towards the other side of the film, only positive charging is effective (Fig. 8). These data therefore show that only holes can migrate through the whole thickness of the PVK polymer film [12]. The photoaction spectrum correlates well with the absorption spectrum of CdS, confirming the sensitizing role of CdS nanocrystals.

The electric field dependence of the charge generation efficiency of CdS/PVK is shown in Fig. 9. The film dependence is steep, characteristic of a molecular system instead of a delocalized system. The significance of this data will be discussed later.

The luminescence spectrum of the CdS/PVK film shows a broad peak at 670 nm which is Stokes-shifted from the absorption edge of CdS (Fig. 10(a)). Pure PVK film shows luminescence in the 400–500 nm region which is suppressed in the CdS/PVK film. The broad 670 nm luminescence band is attributed to either a surface state or a charge transfer state of CdS nanocrystals [27,28]. The lifetime of the luminescence is measured by the time-correlated single-photon-counting technique. At room temperature, the luminescence has a fast component with a lifetime of ~70 ps and a slower component of 0.57 ns.

The intensity of the 670 nm band can be quenched by the application of an electric field (Fig. 10(a)). The quenching is reversible, i.e. the intensity recovers upon the removal of the applied field. In these experiments, the film is sandwiched between two transparent ITO and gold electrodes. The light comes in from the side of the ITO electrode which is connected to the ground. The electric field dependence of the luminescence quenching correlates well with the field dependence of the charge generation efficiency (Fig. 10(b)). The precursor for carrier generation is therefore either the state giving rise to the 670 nm luminescence band or the exciton state.
Fig. 10. (a) Luminescence spectra of CdS/PVK in the absence and presence of applied field. (b) The field dependence of luminescence quenching (×) and charge generation (○). $I(E)$ and $I(0)$ represent the luminescence intensity in the presence and absence of the field, respectively.

which is the precursor to the 670 nm band. The time-resolution of our single-photon counting apparatus is not sufficient to distinguish between these two possibilities.

The steep field dependence of the charge generation efficiency (Fig. 9) indicates that the precursor state has to be either neutral or consisting of a closely spaced e–h pair, as elaborated below.

In a semiconductor, photoexcitation creates electrons in the conduction band and holes in the valence band. At room temperature, these electrons and holes are free to move in the lattice because the bonding energy between them is weak. In a semiconductor particle, it is generally believed that these electrons and holes are separately trapped on the surfaces which can lead to further charge transfer reactions with the surrounding media. This is shown schematically in Scheme 1.

On the other hand, in a molecular system photoexcitation generates a tightly bound electron–hole pair (i.e. a Frankel exciton or an excited state). These neutral excited states can react with the surrounding molecules to generate e–h pairs. Or in molecular crystal language, the Frankel excitons can migrate to the surfaces and dissociates into e–h pairs. In the present case of semiconductor nanocrystals, which mechanism is operative?

One major difference between the two mechanisms is manifested by the field dependence of the charge generation efficiency. In cases corresponding to Scheme 1a, there should be a very weak field dependence since the surface-trapped electrons and holes are separated by large distances and the Coulomb interaction between them is weak. On the other hand, steep field dependence is usually expected for cases corresponding to Scheme 1b since applied field facilitates the separation of closely spaced e–h pairs with strong Coulomb attraction. The field-dependent data of CdS/PVK (Fig. 9) shows that the charge generation efficiency is strongly field-dependent and therefore the initially produced e–h pairs must be closely spaced, which favors the mechanism corresponding to Scheme 1b. According to this picture, photoexcitation of semiconductor nanocrystal creates bound excitons (or excited states) which migrate to the surfaces and then react with the surrounding donors to produce e–h pairs.
To quantitatively account for the field-dependent charge generation efficiency is a challenging task. The Onsager theory [29, 30] has often been used to analyze such field-dependent data but its fundamental inadequacy in addressing this kind of problem is well-known [25, 31, 32]. The model solves the diffusion equation of the relative motion of an electron–hole pair, bounded by their Coulomb interaction, under an electric field. The origin of the electron–hole pair and the pathway by which it is generated are not considered. The model solves for the probability that the pair separates toward infinity with a given initial separation distance \( r_0 \). An important boundary condition (and an assumption) for this model is that if the pair separation distance reaches zero, the pair recombines instantaneously. This is an unrealistic assumption which is the basic reason why unrealistically large e–h separation distances are always needed to fit the experimental data to the Onsager model [25, 31–33]. Furthermore, the creation and recombination rate depend on the field, separation distance, and energetics, which are not considered by the Onsager model.

To remedy the need for a finite recombination rate in the Onsager model, Braun proposed a kinetic model which identifies the geminate e–h pair with the excited charge transfer state [31]. This assumption may hold in a few special cases, but certainly is not generally applicable. Noolandi and Hong [32] give the exact solution of the electron and hole escape probability corresponding to a partly absorbing sphere of finite radius at the origin. The field dependence of the creation rate constant is simply assumed to be an increasing function of the field in such a way that it is isotropic at zero field and becomes more peaked in the direction of the field as the field increases [32]. The arbitrarily chosen form of the rate constant and its field dependence are not justified, a weakness already pointed out by the authors themselves [32].

We have developed a model to analyze charge separation in a low dielectric medium [25, 26]. The creation and recombination rates of the e–h pair are modeled by the Marcus electron transfer theory [34, 35]. Charge diffusion under electrical field is treated with an Onsager-like model. Marcus electron transfer theory in the classical limit is used:

\[
k = \frac{2\pi}{h} \left| V(r) \right|^2 (FC),
\]

\[
FC = (4\pi \lambda k_B T)^{-1/2} \exp \left[ -\frac{(\Delta G(r) + \lambda)}{4\lambda k_B T} \right],
\]

\[
\left| V(r) \right|^2 = \left| V(r_0) \right|^2 \exp \left[ -\frac{z(r - r_0)}{\varepsilon r} \right],
\]

\[
\Delta G(r) = \Delta G(\infty) - \frac{e^2}{\varepsilon r}.
\]

Here \( z \) is taken to be 1.5 Å\(^{-1}\) [32], \( \lambda \) is the reorganizational energy, and \( \Delta G \) is the free energy change of the electron transfer reaction.

Although in principle, the incorporation of Marcus theory can provide a fundamentally sound solution, in practice this is not a trivial problem to solve. The main difficulty is that in low dielectric constant media, the Coulomb interaction between e–h pair is not negligible and is distance-dependent (Eq. (6)). So as the electrons and holes move around, the free energy differences (\( \Delta G \)) and the electron transfer rates are constantly changing. Such distance-dependent electron transfer rates are usually ignored in treating electron transfer reactions in polar fluids [32]. There is no analytical solution for the series of coupled differential equations describing this problem. We therefore solved them numerically on a Cray computer [25, 26]. For a field-dependent charge generation efficiency calculation of 10 points running in double precision, the CPU time used is typically \( \sim 4 \times 10^4 \) s. We have found that this new model can account for the field-dependent charge generation efficiency of fullerene-doped PVK with a realistic e–h separation distance and reasonable reorganization energy [25].

In principle this model can also be applied to the case of CdS/PVK. In reality, CdS nanoparticle is not as well-defined as CbO and some parameters necessary for calculation are not precisely known at present. Nevertheless, such calculation based on estimated parameters can still be informative. The results presented here are not quantitative, but intended for illustrative purpose only.
For the $\Delta G$ calculation, the oxidation potential of PVK is taken to be 1.12 V against SCE [36] and the reduction potential of CdS nanocrystals is measured (in pyridine) to be $-1.7$ V against SCE. The energy of the separated e and h with respect to the neutral ground state is therefore $2.82$ eV at infinite separation. The hole diffusion constant in PVK is taken to be $0.0077$ cm$^2$/s [24]. The energy of the precursor state depends on the nature of the precursor, that is $\sim 3$ eV for the exciton state, $\sim 1.85$ eV for the surface state. The reorganization energy $\lambda$ and the minimal e–h separation distance $r_0$ are the fitting parameters.

The results of the calculation are quite interesting. We found that the experimental field dependence data cannot be fitted by assuming the precursor state to be either the exciton state or the surface state. All reasonable combinations of the fitting parameters ($\lambda$ from 0.3 to 1.0 eV, $r_0$ from 5 to 10 Å, lifetime from 1 ns to 1 ps) resulted in a flat field dependence of the charge generation efficiency except at very high fields ($> 5 \times 10^5$ V/cm). A closer examination reveals that this is due to the fact that the energy of the separated e and h, $2.82$ eV, is so large that it always falls in the Marcus inverted region even after correction for the (distance-dependent) coulomb interaction. This leads to a very small recombination rate and weak field dependence (similar to the cases of inorganic semiconductors). The only way the experimental data can be fitted is to introduce an intermediate state for the recombination process. We found that the experimental data in Fig. 9 can be fitted by assuming an intermediate state at 1.65 eV, the exciton state at 3.1 eV, $\lambda = 0.5$ eV and $r_0 = 7$ Å. The suggested existence of an intermediate state remains to be confirmed in the future.

At this point, these results should be regarded as the first step towards the eventual quantitative understanding of the charge generation problem of semiconductor nanocrystal/polymer composites. Many parameters need to be determined more precisely experimentally. Further improvement of the theoretical model includes the use of a quantum mechanical version of the electron transfer theory (which requires additional information such as the electron–phonon coupling parameter, phonon frequencies, etc) and different reorganization energies for forward and backward electron transfer reactions.

The particle size dependence of the charge generation efficiency is another interesting topic to be explored. For small nanocrystals considered here, the field dependence of the charge generation efficiency is steep and a molecular-like mechanism 1(b) is responsible. As the particle size grows, eventually mechanism 1(a) starts to make a contribution. The field dependence of the charge generation efficiency should become weaker and the magnitude of the efficiency higher. However, for larger particles, bulk carrier trapping by defects can diminish the charge generation efficiency. There should be an intermediate size regime where the most efficient semiconductor nanocrystal/polymer photoconductor can be found.

7. Summary

By incorporating semiconductor nanocrystals in carrier-transporting polymers, we have created an interesting class of photoconductive nanocomposites. A wide variety of semiconductors and polymers can be used. The presence of semiconductor nanocrystals enhances the photoinduced charge generation efficiency and extends the sensitivity range, while the polymer matrix carries away the charges under applied field. We found that the presence of low concentrations of semiconductor nanocrystals has a minimal effect on the hole mobility of the polymer matrix. The field dependence of the charge generation efficiency is steep which indicates the initially created e–h pair is closely spaced. An Onsager-like model incorporating Marcus electron transfer theory for carrier creation and recombination has been developed to explain the field-dependent charge generation efficiency in nonpolar media.

In the future, it will be interesting to explore the size-dependent charge generation mechanism, i.e. the transition from a localized (Scheme 1(b)) to a delocalized mechanism (Scheme 1b). Transport properties of these composites with high concentrations of semiconductor nanocrystals represent an unexplored area [38]. Nanocomposites should provide a promising direction for searching for high
mobility electron or hole transporting materials. Exploration of these materials for technological applications such as imaging and electroluminescent display [14, 37] has just begun.

Acknowledgements

We thank Dr. A. Suna for the use of the program originally developed for calculating the charge generation efficiency of fullerene-doped PVK (Refs. [25, 26]). We also thank Dr. J.V. Caspar for measuring the reduction potential of CdS nanocrystals.

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