APPLIED PHYSICS LETTERS VOLUME 78, NUMBER 11 12 MARCH 2001

Enhancing the active lifetime of luminescent semiconducting polymers via doping with metal nanoshells

G. D. Hale and J. B. Jackson
Department of Electrical and Computer Engineering and Department of Chemistry, Rice University, Houston, Texas 77005

O. E. Shmakova and T. R. Lee
Department of Chemistry, University of Houston, Houston, Texas 77005

N. J. Halas[a]
Department of Electrical and Computer Engineering and Department of Chemistry, Rice University, Houston, Texas 77005

(Received 31 August 2000; accepted for publication 22 November 2000)

We report a dramatic, concentration-dependent decrease in the rate of photo-oxidation of semiconducting polymers due to the addition of small amounts of metal nanoshells to the polymer. In each case, the nanoshell resonances are tuned to the triplet exciton-ground state energy of the polymer. The nanoshell dopants slow the oxidation rate yet do not affect the photoluminescent properties of the polymers to which they have been added. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1343854]

The use of semiconducting polymer thin films as the active layers in optoelectronic devices has drawn increasing technological interest over the past decade. Major advances include the development of semiconducting polymer-based devices such as light-emitting diodes,[1,2] photodiodes,[3,4] flat-panel displays, solar cells, lasers, and transistors.[5,6] A critical drawback to the commercialization of these types of devices is due to the rapid rate of photo-oxidation of the semiconducting polymer under ambient conditions,[7,8] which in all cases degrades device performance and ultimately limits device lifetime. Encapsulation techniques are currently used to reduce photo-oxidation in prototypical commercial devices, but are entirely incompatible with devices fabricated on flexible substrates. This letter describes a nanoparticle strategy for frustrating the photo-oxidation in semiconducting polymers in which the polymers are doped with metal nanoshells, silica core-gold shell nanoparticles whose resonances have been tuned to the polymer's triplet exciton. The metal nanoshells appear to quench the triplet exciton lifetime, reducing the rate of production of singlet oxygen, but with no detectable change in the luminescent properties of the polymers.

The dynamics of the photo-oxidation of semiconducting polymers has been studied extensively.[7–12] Singlet oxygen, formed via energy transfer from the polymer triplet exciton, reacts with the polymer to generate exciton traps. These exciton traps are topological defects comprised of carbonyl moieties, which are generated either through side chain modification or backbone scission of the semiconducting polymer. The carbonyl groups provide an additional nonradiative relaxation channel for the polymer singlet excitons, thereby quenching polymer luminescence.[9,13]

By adding a substance to the film that preferentially quenches the polymer triplet exciton, the rate of singlet oxygen formation and consequent rate of photo-oxidation of the polymer can be reduced (see Fig. 1). Triplet energy transfer to dopant molecules in polymer light emitting diodes has been demonstrated. This triplet energy transfer proceeds either by Dexter transfer[14] or electron hole capture at the guest molecule.[14] Electron hole capture is also favored by the long triplet lifetime in the semiconducting polymer[15] and the overlap between the plasmon resonance of the nanoshell and the polymer triplet energy state. It is likely the energy transfer between the polymer triplet state and nanoshell plasmon resonance follows similar schemes. While triplet state quenching is certainly not new in molecular photophysics, this strategy utilizes unique nanoparticles in semiconducting polymers while preserving the active properties of the polymer.

Silica core-gold shell nanoparticles, also known as ‘‘gold nanoshells,’’ exhibit a strong, tunable optical resonance (plasmon resonance) which depends quite sensitively on the ratio of the core and shell dimensions of the

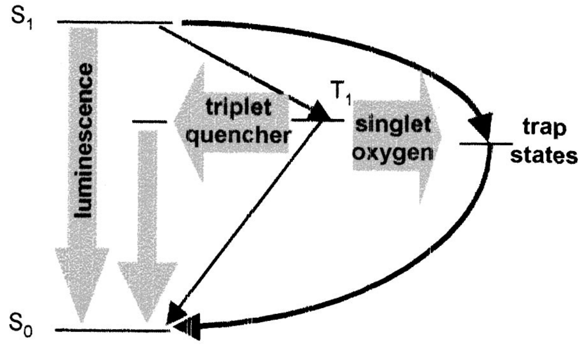

FIG. 1. Diagram of the photo-oxidation process in conjugated polymer/nanoshell composites. Energy from the polymer triplet excitons excites singlet oxygen, which reacts with the polymer chain and forms exciton trap states. By adding a material to quench the triplet excitons, the photo-oxidation process can be impeded.

---

[a] Author to whom correspondence should be addressed; electronic mail: halas@rice.edu

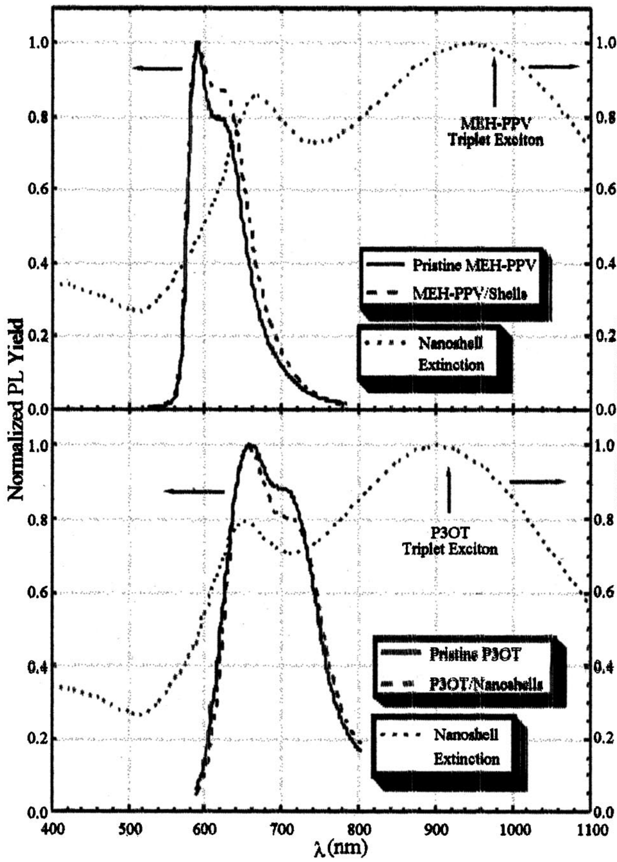

FIG. 2. (a) Normalized PL spectra of MEH–PPV films with and without metal nanoshells added, as well as the calculated normalized extinction of the metal nanoshell component. The MEH–PPV triplet exciton-ground state transition energy is indicated. Differences in the PL feature near 620 nm arise from sample-to-sample variation. (b) Normalized PL spectra of P3OT films with and without metal nanoshells added, as well as the normalized extinction of the metal nanoshells component. The P3OT triplet exciton-ground state transition energy is indicated. Differences in the PL feature near 700 nm arise from sample-to-sample variation.

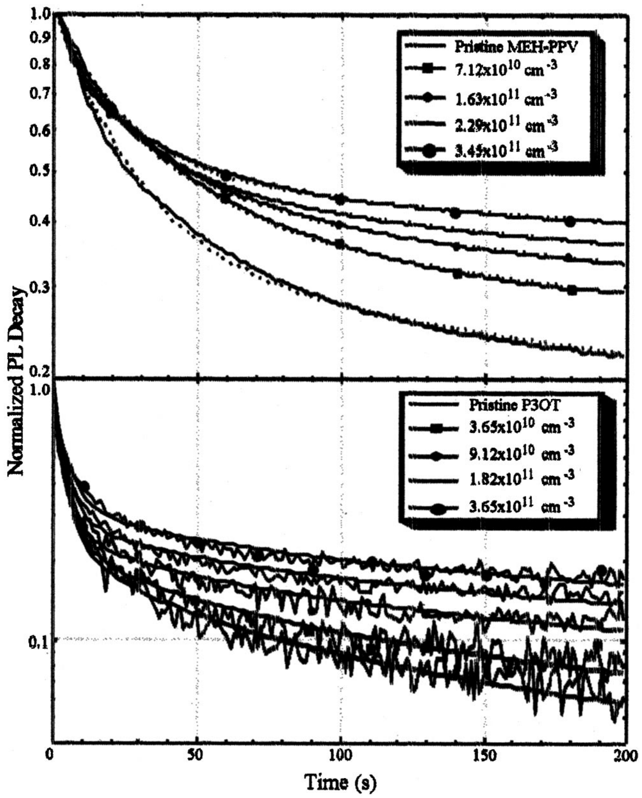

FIG. 3. (a) Normalized photoluminescence decay (PLD) of MEH–PPV films with varying metal nanoshell concentrations. (b) Normalized PLD of P3OT films with varying metal nanoshell concentrations.

nanoparticle.[16] Changing this ratio allows the nanoshell resonance to be positioned at any wavelength of choice across a broad spectral region spanning the visible to the midinfrared.[17] The normalized extinction (absorption plus scattering) spectra for the nanoshells used in these experiments are shown in Fig. 2. The extinction can be measured using UV/visible spectroscopy and calculated using Mie scattering theory.[16] The plasmon resonance of the nanoshells is tuned to overlap the triplet exciton-ground state energy of the semiconducting polymer used. The nanoshell plasmon frequencies are designed to be resonant with the triplet exciton-ground state energy transition in two different semiconducting polymers, poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] (MEH–PPV) and poly(3-octylthiophene) (P3OT).

The nanoshells were dispersed in polymer solutions (MEH–PPV/chlorobenzene and P3OT/chloroform) which were then spin cast onto glass substrates. No visible difference between the pristine polymer films and the polymer-nanoshell composite films was observed. The substrates were held under vacuum and photoluminescence was excited using 488 nm light and collected using a monochromator and a photomultiplier tube. At the concentrations used, the absorbance of the nanoshells at the excitation wavelength was negligible. The sample chamber was then opened to ambient air and the decay of the photoluminescence was monitored at the luminescence maximum over several minutes.

A representative photoluminescence spectrum for each respective polymer and polymer-nanoshell composite is shown in Fig. 2. For both polymer systems, the relative quantum yield of the pristine polymer was left unchanged by the addition of nanoshells to the polymer. The relative heights of the two features observed in each photoluminescence (PL) spectrum vary slightly between samples, but show no dependence on nanoshell concentration, suggesting that the small height differences arise from minor variations in the local structure and/or thickness of the polymer and polymer-nanoshell composite films.

The photoluminescence decay for polymer-nanoshell composite films for a range of nanoshell concentrations is shown in Fig. 3. The highest nanoshell concentration shown corresponds to approximately 0.1% volume fraction. For both semiconducting polymers, we observe that the addition of nanoshells gives rise to a dramatic decrease in the decay of the photoluminescence signal upon exposure to ambient conditions. The time-dependent response of the photoluminescence quenching is a combination of a fast, reversible component[8] followed by a slower, nonreversible component with dynamics consistent with exciton trap formation on a one-dimensional (1D) lattice[13,18,19]

$$\Phi_{\mathrm{PL}}=A\exp\left[-\left(\frac{t}{\tau_{\mathrm{fast}}}\right)\right]+B\exp\left[-\left(\frac{t}{\tau_{\mathrm{tran}}}\right)^{1/3}\right], \qquad (1)$$

where $\tau_{\mathrm{trap}}=[2\pi^2(3/2)^3K_{\mathrm{ox}}n_{\mathrm{1D}}{}^2]^{-1}$. The rate constant K_{ox} takes into account several processes, such as the diffusion of

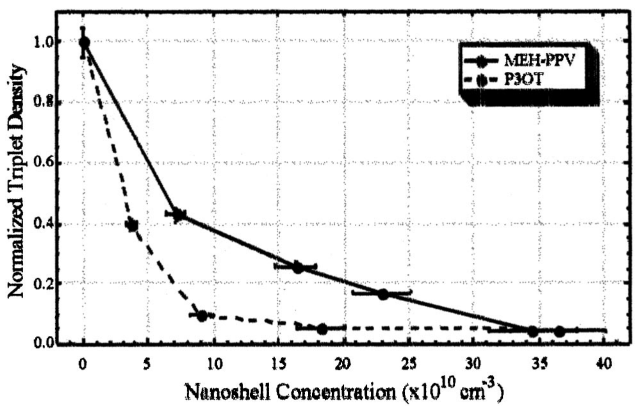

FIG. 4. Density of photo-oxidation induced exciton traps in the conjugated polymer films as a function of metal nanoshell concentration, normalized to the trap density in the pristine films. The density of traps is estimated from the trap formation lifetime by the method of Yan *et al.* (Ref. 13): $n \propto (\tau_{\mathrm{trap}})^{-3/2}$.

oxygen into the film, the interaction of the oxygen with a triplet exciton, and the formation of an exciton trap. It is likely that the latter two processes will be quite fast and that K_{ox} is largely determined by diffusion of oxygen into the film. The density (n_{1D}) is the one-dimensional steady-state density of triplet excitons on a polymer chain.

The fast lifetime (reversible component) obtained from Eq. (1) is significantly shorter in P3OT (3–4 s) than in MEH–PPV (20–30 s), but is insensitive to the nanoshell concentration for both polymers. The shorter lifetime in P3OT might arise from a reversible polymer-oxygen charge transfer complex forming in the P3OT film, which leads to the observed luminescence quenching.[20]

The reduced rates of photoluminescence quenching observed in Fig. 3 can be directly related to a reduced rate of exciton trap formation in the polymer films. Yan *et al.* have shown that the volume density of photo-oxidation induced defects (traps) is related to the trap formation lifetime:[13] $n \propto (\tau_{\mathrm{trap}})^{-3/2}$. Values for n are calculated from the (τ_{trap}) values obtained from Eq. (1). These values, normalized to the defect density for the pristine polymer films, are shown in Fig. 4 as a function of nanoshell concentration. At higher nanoshell concentrations, the defect density is reduced to approximately the same degree in both polymers. However, the P3OT/nanoshell composite films show a markedly higher sensitivity to the presence of metal nanoshells and exhibit saturation behavior as the nanoshell concentration is increased.

We also investigated whether the addition of metal nanoshells inhibit photo-oxidation by directly quenching singlet oxygen. Polymer films with nanoshell dopants whose plasmon resonances were located both at the singlet oxygen (1270 nm) and triplet exciton energy showed quenching rates quite similar to films with triplet exciton-resonant nanoshells only. We thus conclude that nanoshell-resonant triplet exciton quenching, not direct de-excitation of singlet oxygen, is a plausible mechanism for this effect.

In this letter, we have shown that the addition of metal nanoshells to conjugated polymer films dramatically decreases the susceptibility of the polymer to photo-oxidative degradation by providing a triplet exciton decay pathway that competes with singlet oxygen formation. In P3OT, we observe that a concentration of less than 0.1% by volume of nanoshells shows a saturation of this effect, reducing the number of luminescence-quenching exciton traps by a factor of 20. For MEH–PPV, there is no apparent saturation at similar concentrations, but the reduction in the number of traps at high concentration is similar to that in P3OT. This approach to enhancing the active lifetime of semiconducting polymer materials should prove useful in the development of robust, practical polymer devices for a wide range of commercial applications.

This work was supported by the Robert A. Welch Foundation, the National Science Foundation (Grant No. ECS-9801707), and the Office of Naval Research.

[1] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, and A. B. Holmes, Nature (London) **347**, 539 (1990).
[2] G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri, and A. J. Heeger, Nature (London) **357**, 477 (1992).
[3] G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, Science **270**, 1789 (1995).
[4] M. Granstrom *et al.*, Nature (London) **395**, 257 (1998).
[5] F. Garnier, R. Hajlaoui, A. Yassar, and P. Srivastava, Science **265**, 1684 (1994).
[6] L. Torsi, A. Dodabalapur, L. J. Rothberg, A. W. P. Fung, and H. E. Katz, Science **272**, 1462 (1996).
[7] B. H. Cumpston and K. F. Jensen, Synth. Met. **73**, 195 (1995).
[8] Y. Kaminorz, E. Smela, O. Inganas, and L. Brehmer, Adv. Mater. **10**, 765 (1998).
[9] R. D. Scurlock, B. J. Wang, P. R. Ogilby, J. R. Sheats, and R. L. Clough, J. Am. Chem. Soc. **117**, 10194 (1995).
[10] M. S. A. Abdou and S. Holdcroft, Macromolecules **26**, 2954 (1993).
[11] T. Caronna, M. Forte, M. Catellani, and S. V. Meille, Chem. Mater. **9**, 991 (1997).
[12] D. G. J. Sutherland, J. A. Carlisle, P. Elliker, G. Fox, T. W. Hagler, I. Jimenez, H. W. Lee, K, Pakbaz, L. J. Terminello, S. C. Williams, F. J. Himpsel, D. K. Shuh, W. M. Tong, J. J. Jia, T. A. Callcott, and D. L. Ederer, Appl. Phys. Lett. **68**, 2046 (1996).
[13] M. Yan, L. J. Rothberg, F. Papadimitrakopoulos, M. E. Galvin, and T. M. Miller, Phys. Rev. Lett. **73**, 744 (1994).
[14] V. Cleave, G. Yahioglu, P. Le Barny, R. H. Friend, and N. Tessler, Adv. Mater. **11**, 285 (1999).
[15] M. A. Baldo and S. R. Forrest, Phys. Rev. B **62**, 10958 (2000).
[16] S. Oldenburg, R. D. Averitt, S. Westcott, and N. J. Halas, Chem. Phys. Lett. **288**, 243 (1998).
[17] S. J. Oldenburg, J. B. Jackson, S. L. Westcott, and N. J. Halas, Appl. Phys. Lett. **75**, 2897 (1999).
[18] B. Y. Balagurov and V. G. Vaks, Sov. Phys. JETP **38**, 968 (1974).
[19] G. S. Kanner, X. Wei, B. C. Hess, L. R. Chen, and Z. V. Vardeny, Phys. Rev. Lett. **69**, 538 (1992).
[20] M. S. A. Abdou, F. P. Orfino, Y. Son, and S. Holdcroft, J. Am. Chem. Soc. **119**, 4518 (1997).