

Semiconductor nanoclusters and fullerenes: A new class of sensitizing dyes for photoconductive polymers

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Abstract: Over the past decade, a large number of nanoclusters including fullerenes have been prepared. The structures of these nanometer-sized inorganic clusters are usually similar to those of the bulk crystals, yet their properties are remarkably different. With the proper surface-capping agents, clusters of varying sizes can be isolated as powders and re-dissolved into various organic solvents just like molecules. The color of these nanoclusters are size-dependent (i.e. the quantum size effect) and they can be regarded as a new class of dye molecules. We will review the synthesis and properties of these materials and then discuss their applications as sensitizers of photoconductive polymers.

Introduction

Over the past decade or so, there has been a great amount of activity and progress in the area of nanocluster research. The basic aim of the research is to study materials in extremely small dimensions, generally in the nanometer size regime, hence the terms nanoclusters, nanoparticles, or quantum dots (1-4). Materials investigated so far include II-VI (e.g. CdS), IV-VI (e.g. PbS), III-V (e.g. InP), and oxides (e.g. TiO₂) as well as single element clusters such as carbon and silicon. The research on carbon clusters lead to the discovery of fullerenes (5) and created an entirely new area of research. These semiconductor nanoclusters and fullerenes can be incorporated into a wide variety of matrices such as polymers, glasses, and zeolites. With the proper surface-capping agents, semiconductor nanoclusters of varying sizes can be isolated as powders and re-dissolved into various organic solvents just like molecules.

One particularly interesting property of these nanoclusters is that their colors are size-dependent. For example, the color of PbS clusters can be varied from black, red, orange, to light yellow with decreasing sizes (6). Likewise, the color of CdS clusters can be varied from orange to white (7). C₆₀ and C₇₀ molecules show the well-known purple and orange-red color in solutions, respectively, compared with the black color of bulk carbon. These nanoclusters therefore can be regarded as a new class of dye molecules, different from the conventional organic or organometallic dyes. The exploration of this new class of dyes for many technological applications has just begun. In this paper, we first review the synthesis and properties of these materials and then discuss their applications as sensitizers of photoconductive polymers.

Semiconductor nanoclusters

For a semiconductor crystal, electronic excitation consists of a loosely bounded electron-hole pair, usually delocalized over a length (the Bohr radius) much longer than the lattice constant. As the size of the semiconductor cluster approaches this intrinsic delocalization length, its electronic properties start to change. This is the so-called quantum size effect (1-4), which can be observed as a blue-shift in the optical band-gap as well as an enhancement in the absorption cross section. This is shown in Fig. 1 for PbS and CdS clusters, two better characterized systems (1,2,6,7).

For CdS, the quantum size effect occurs as the cluster diameter becomes comparable to or smaller than the exciton diameter of ~60 Å (~3000 to 4000 atoms). For PbS, this size effect can be observed for a cluster as large as ~150 Å, which contains over 10⁵ atoms. Similar size effect has been observed for many other semiconductors such as CdSe, ZnS, TiO₂, and some III-V semiconductors (1-4, 9).

Most of the semiconductor clusters prepared so far are not monodisperse. As a result the precise structure, determinable by single crystal x-ray, is usually not known. Powder x-ray data show that for larger clusters their structures are about the same as the bulk phase but as the cluster size becomes

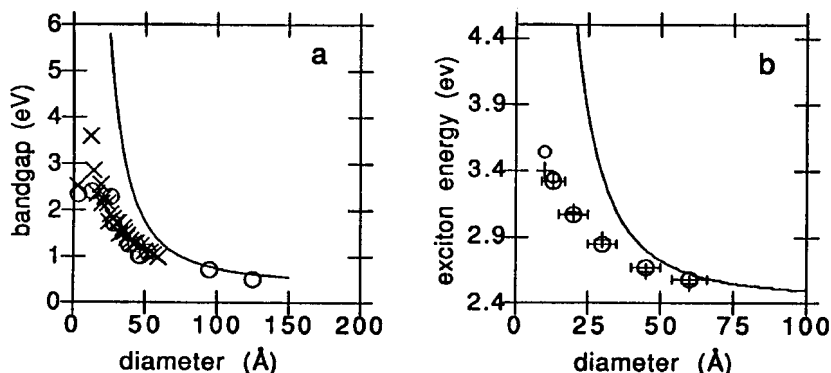
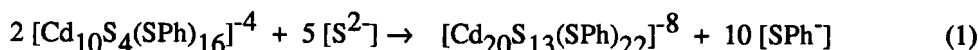


Fig. 1: (a) The dependence of the optical band gap of PbS on the cluster size (6); (b) The exciton energy of CdS clusters plotted as a function of cluster diameter (8). Open circles: experimental data. Crosses: theoretical calculations. Solid lines: the effective mass approximation.

smaller significant deviation can be observed. Recently a series of monodisperse CdS clusters have been synthesized by the method of controlled cluster fusion (10-13). With this method, a well-defined single size molecular cluster, $(\text{Cd}_{10}\text{S}_4(\text{SPh})_{16})^{4-}$, was used as the starting material. Larger single size CdS clusters are synthesized by fusing together these small starting clusters with the careful addition of properly designed reagents. For example, two single size $[\text{Cd}_{10}\text{S}_4(\text{SPh})_{16}]^{4-}$ clusters are fused together to form a 10-Å $[\text{Cd}_{20}\text{S}_{13}(\text{SPh})_{22}]^{8-}$ clusters (10), according to



Even larger clusters can be made this way. A ~15-Å single-sized CdS cluster with the molecular formula of $\text{Cd}_{32}\text{S}_{14}\text{SPh}_{36}\text{DMF}_4$ (Ph and DMF represent phenyl and dimethylformamide, respectively) has been made recently (13). A single crystal of this cluster was grown and its structure solved by x-ray crystallography. It has a tetrahedron structure and shows sharp absorption bands at 325 and 384 nm (13). All these semiconductor nanoclusters can be dispersed in solutions and recovered as powders. Their surface properties can be modified considerably by using different surface-capping agents.

New photoconductive polymers

By doping semiconductor nanoclusters into carrier-transporting polymers, one can form a new class of photoconductive polymers (14-16). Only small amount of nanoclusters is needed. The amount used is typically a few weight percent, well below the percolation threshold of ~15% by volume. The nanoclusters, isolated from each other, are responsible for the charge generation; and the polymer is responsible for the subsequent charge transport.

Two effective polymers we used are N-polyvinylcarbazole (PVK) and Phenylmethylpolysilane (PMPS). A wide variety of semiconductors, including fullerenes, II-VI and III-V materials, have been doped into these polymers to make them photoconductive (14,15). Many (such as InAs/PVK) are IR-sensitive. It is important to point out that narrow-gap semiconductors such as InAs and PbS cannot be made into high-field, room temperature photoconductors. Other than the typical difficulty of growing large area single crystal thin film, 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.

N-polyvinylcarbazole (PVK) is a known hole conducting material. In the un-doped state, its charge generation efficiency is low as shown by the slow photo-induced discharge rate (14). With the addition of 1 vol.%, ~16-Å CdS clusters, the photo-induced discharge rate is enhanced by orders-of-magnitude (14). The wavelength-dependence of charge generation efficiency of CdS-doped PVK for both positive and negative charging was measured (14). It shows that CdS clusters are responsible for the charge generation and CdS/PVK is a hole conductor. The electric field dependence of the charge generation efficiency is shown in Fig. 2. The field-dependence can be fitted with the Onsager model (17), shown as solid curve in Fig.2b. The best fit parameters are: r_0 (initial e-h separation distance)=26-Å and ϕ_0 (quantum yield for charge generation)=0.16 for CdS/PVK.

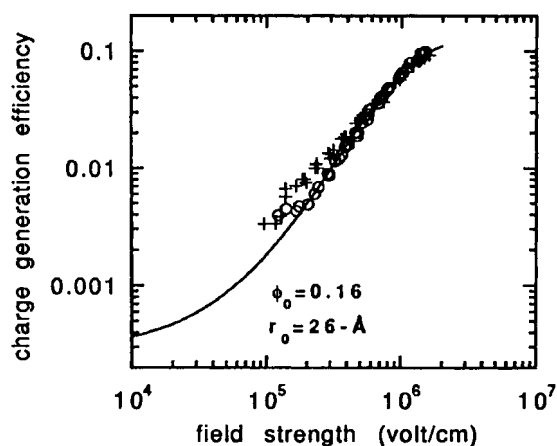


Fig. 2 Charge generation efficiency of CdS/PVK film as a function of applied field (ref. 14)

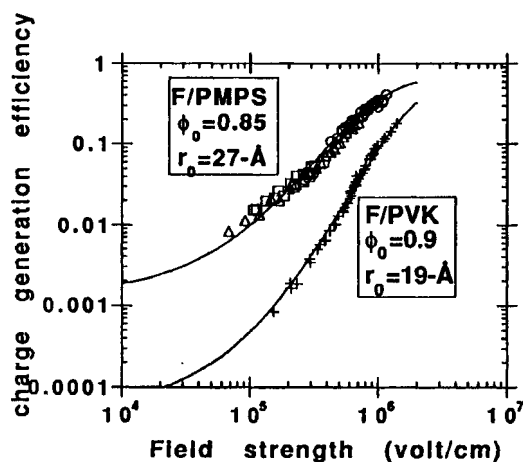
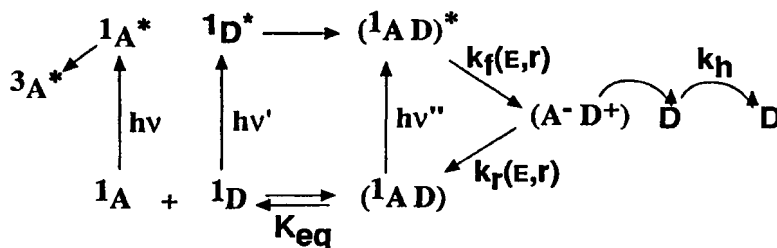


Fig. 3 Charge generation efficiency of fullerene doped PMPS and PVK as a function of applied field (ref. 19).

Fullerenes have also been used effectively as sensitizers for charge generation in photoconductive polymers (18-20). With the addition of ~2 wt% of fullerene, the photo-induced discharge rate of PVK and PMPS shows a dramatic enhancement (18,19). Wavelength dependence of the charge generation efficiency shows that fullerene acts as the sensitizer for the enhanced photoconductivity (18,19). Figure 3 shows the field dependence of the charge generation efficiency, obtained with 340-nm irradiation. The field dependence can be fitted with the Onsager model with the best-fit parameters shown in the figure.

Laser flash photolysis experiment shows that the yield and the lifetime of the triplet state stay the same when applied with a field of 5×10^5 V/cm (21). Applying a magnetic field of ~2600 Gauss has no detectable effect on the charge generation efficiency (21). C_{70} fluorescence in PVK, on the other hand, is quenched with increasing applied electric field. The field effect on fluorescence quenching and charge generation efficiency correlate well with each other. These results clearly establish the singlet state of the CT complex as the precursor for charge carriers. The overall proposed charge generation mechanism is illustrated below.



Here A, D, and $(1AD)$ represents fullerene, donor (i.e. carbazole), and CT complex, respectively. K_s , k_r , and k_h are the forward electron transfer rate constant, the recombination rate constant and the D^+ hopping rate constant, respectively. All these rate constants are field and distance dependent. The direct excitation of a small percentage of uncomplexed fullerene does not lead to charge generation. The excitation of uncomplexed carbazole moieties can lead to excited state complex formation by energy transfer.

Quantitative treatment of field-dependent charge separation in polymers has been discussed extensively in the literature (22-24) and remains to be an un-resolved issue. We have developed a model to analyze charge separation in low dielectric medium. The model incorporates the Marcus electron transfer theory (25,26) to describe the creation and recombination of e-h pairs and an Onsager-like model to treat charge diffusion under electrical field. In spite of the success of the Marcus electron transfer theory in treating electron transfer reactions in polar media, it has not been used successfully to study the photoconductivity of polymers. The main difficulty is that in low dielectric constant media, the Coulomb interaction between e-h pair is not negligible. The free energy change (ΔG) and the electron transfer rate constant are therefore distance-dependent. This distance dependence of ΔG is usually

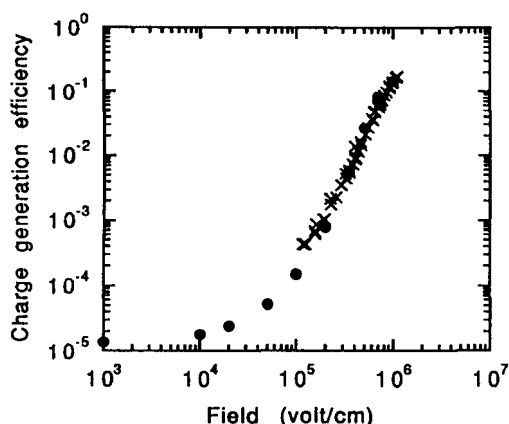


Fig. 4 Comparison of experimental values (x) of the charge generation efficiency of C_{60} /PVK with theoretical calculation (•). The best-fit parameters are given in the text.

ignored in treating electron transfer reactions in polar media (26). There is no analytical solution for this problem. We have solved it numerically on a Cray computer. Fig. 4 shows the comparison of theory to the experimental results of C_{60} -doped PVK. There are two fitting parameters: the reorganization

energy, λ , and the minimal e-h separation distance, r_0 . The data can be fitted quite well using $\lambda=0.64$ eV and $r_0 = 6.65 \text{ \AA}$. The minimal separation distance of 6.65 \AA is a reasonable number for a CT complex. The 0.64 eV reorganizational energy also falls in the commonly observed range for electron transfer reactions. This model can now be used to design rational ways of improving the photoconductivity of fullerene-doped polymers.

Semiconductor nanoclusters and fullerenes are potentially useful as a new class of VIS-IR sensitizers in many applications such as photoconductivity and photorefractivity. If enough clusters can be dissolved into polymers such that the concentration is above the percolation threshold, then it may be possible to create electron-transporting polymers, which are rare and technologically important. These are directions of future research in this area.

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REFERENCES

1. Y. Wang and N. Herron, *J. Phys. Chem.*, **95**, 525(1991).
2. Y. Wang in *Advances in Photochemistry*, Vol. 19, ed., D. C. Neckers, Wiley, New York, 1995.
3. M. L. Steigerwald, L. E. Brus, *Acc. Chem. Res.* **23**, 183 (1990).
4. A. Henglein, *Topics in Current Chemistry*, **143**, 113 (1988).
5. W. Kratschmer, L. D. Lamb, K. Fostiropoulos, D. R. Huffman, *Nature*, **347**, 354(1990).
6. Y. Wang, A. Suna, W. Mahler, R. Kasowski, *J. Chem. Phys.* **87**, 7315 (1987).
7. Y. Wang, N. Herron, *Phys. Rev. B*, **42**, 7253(1990).
8. Y. Wang, M. Harmer, N. Herron, *Isr. J. Chem.*, **33**, 31(1993).
9. Y. Wang, N. Herron, *Res. Chem. Intermedi.*, **15A**, 17 (1991).
10. N. Herron, A. Suna, Y. Wang, *J. Chem. Soc. Dalton Trans.* 2329(1992).
11. Y. Wang, M. Harmer, N. Herron, *Isr. J. Chem.*, **33**, 31(1993).
12. W. E. Farneth, N. Herron, Y. Wang, *Chem. Materials*, **4**, 917(1992).
13. N. Herron, J. C. Calabrese, W. E. Farneth, Y. Wang, *Science*, **259**, 1426(1993).
14. Y. Wang, N. Herron, *Chem. Phys. Lett.*, **200**, 71(1992).
15. N. Herron, Y. Wang, US Patent 5,238,607.
16. Y. Wang, (1996) "Photoconductive Polymers", in *"Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition"*, Wiley, New York.
17. L. Onsager, *Phys. Rev.* **54**, 554(1938).
18. Y. Wang, *Nature*, **356**, 585(1992).
19. Y. Wang, R. West, C. H. Yuan, *J. Am. Chem. Soc.*, **115**, 3844(1993).
20. Y. Wang, US Patent 5,250,378 (Oct. 5, 1993).
21. Y. Wang, N. Herron, J. V. Caspar, *Mat. Sci. Eng.*, **B19**, 61(1993); and unpublished results.
22. L. Onsager, *Phys. Rev.* **54**, 554(1938).
23. C. L. Braun, *J. Chem. Phys.* **80**, 4157(1984).
24. J. Noolandi, K. M. Hong, *J. Chem. Phys.* **70**, 3230(1979).
25. R. A. Marcus, *Annu. Rev. Phys. Chem.*, **15**, 155 (1964).
26. R. A. Marcus, P. Siders, *J. Phys. Chem.*, **86**, 622(1982).