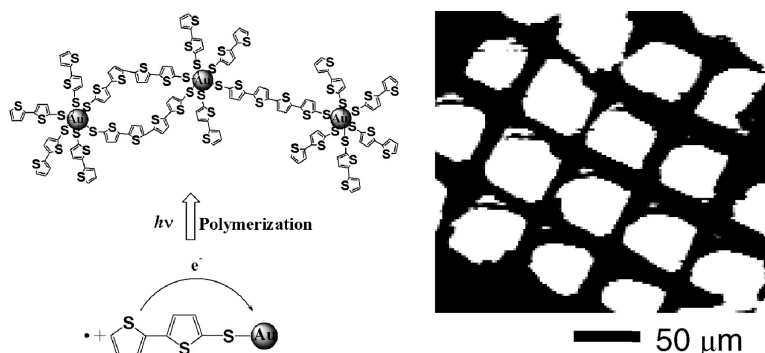


Photopolymerization of Gold Nanoparticles: Size-Related Charge Separation and Emission

Xichen Cai, Kelechi C. Anyaogu, and Douglas C. Neckers

J. Am. Chem. Soc., **2007**, 129 (37), 11324-11325 • DOI: 10.1021/ja073899u • Publication Date (Web): 25 August 2007

Downloaded from <http://pubs.acs.org> on February 14, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 5 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

Photopolymerization of Gold Nanoparticles: Size-Related Charge Separation and Emission

Xichen Cai, Kelechi C. Anyaogu, and Douglas C. Neckers*

Center for Photochemical Sciences, Bowling Green State University, 132 Overman Hall,
Bowling Green, Ohio 43403

Received May 30, 2007; E-mail: neckers@photo.bgsu.edu

Particle size and shape, interparticle distance, and the nature of organic shell have significant effects on the properties of nanoparticles in the diameter range of 1–10 nm.^{1,2} Though much recent work on metal nanoparticles has been reported, little dealt with direct detection of particle size effects on reaction processes. Fox et al. reported properties of *trans*-stilbene- and *o*-nitrobenzyl-ether-functionalized gold nanoparticles (AuNPs),³ while Kamat and Thomas reported intramolecular energy and electron-transfer reactions in fullerene- and pyrene-functionalized AuNPs.^{4,5} These experiments indicate the AuNP to be a good electron acceptor, though there were no further reports on particle-size-related reactions. Further, the preparation of polymeric conducting nanomaterials has not yet been fully explored, and synthesis of nanoparticles in the desired two- or three-dimensional structures remains a challenge.⁶ We report the photopolymerization of 2,2'-bithiophene (BT)-functionalized AuNPs of different diameters (2, 4, and 6 nm). Photoinduced charge separation involving the BT ligand and the AuNP was directly detected using femtosecond transient absorption measurements. Emission was observed with an increase in particle size. Further, the ensuing photopolymerization of the BT-functionalized AuNPs provides a useful method for making two- or three-dimensional designs of conductive polymeric nanomaterials.

One-electron oxidation of thiophene leads to rapid formation of polythiophene.⁷ Given an oxidation potential of oligothiophene less than 1.3 eV vs SCE⁷ and given that AuNPs have a strong electron affinity,^{2,8} intramolecular electron-transfer reactions between thiophene and AuNPs are possible. BT can be attached to a AuNP surface through a thiol–gold bond (S–Au). 5-Mercapto-2,2'-bithiophene (BTSH) was synthesized,^{9,10} and 2, 4, and 6 nm BTSAuNPs were prepared based on literature methods.^{11,12} The UV absorption spectra (Supporting Information) obviously change after irradiation using a 350 nm UV lamp. The absorption band around 400 nm decreased, while the plasmon absorption band of the AuNP (530 nm) broadened and shifted to the longer wavelength region. These changes suggest that aggregation of the functionalized AuNPs may have occurred after irradiation.^{13–15} Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) illustrate the structural changes of BTSAuNPs before and after irradiation (Figure 1 and Supporting Information).

Three-dimensional structures similar to the products of electrodeposition¹⁶ were observed after irradiation in all cases (2, 4, and 6 nm BTSAuNPs). Control experiments with 1-dodecanethiol (C₁₂H₂₅SH) as the ligand were carried out under similar conditions, and no changes were observed in the absorption spectra or in TEM images taken before and after irradiation (Supporting Information). This suggests that intramolecular electron transfer and polymerization occurs during 350 nm light irradiation of BTSAuNPs (Supporting Information), but not with 1-dodecanethiol-functionalized AuNPs (C₁₂H₂₅SAuNPs).

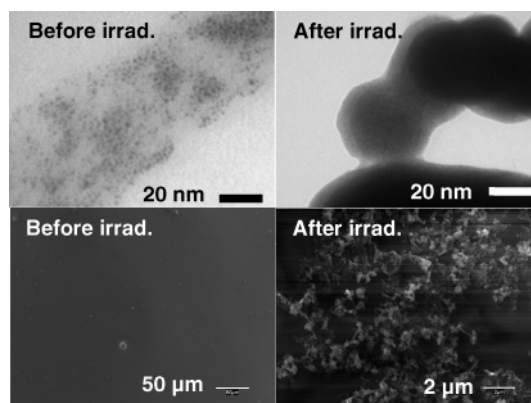


Figure 1. TEM (above) and SEM (below) images of 2 nm BTSAuNPs before and after irradiation with a 350 nm lamp.

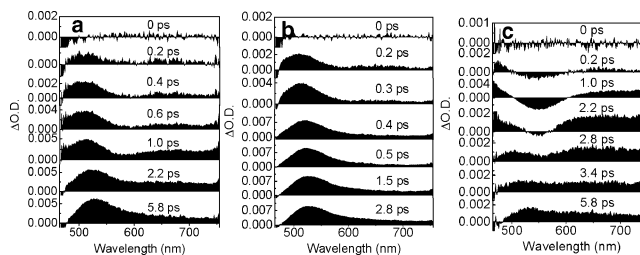


Figure 2. Transient absorption spectra of (a) 2, (b) 4, and (c) 6 nm BTSAuNPs in toluene during the femtosecond laser excitation at 400 nm.

Femtosecond and nanosecond transient absorption measurements¹⁷ show that BTSH in the singlet excited state (BTSH(S₁)), triplet excited state (BTSH(T₁)), and as the radical cation (BTSH^{•+}), have absorption bands at 515, 450, and 440 nm respectively (Supporting Information). BTSH(S₁) ($\tau = 1.3 \pm 0.1$ ps) decays through intersystem crossing (ISC) to give BTSH(T₁). No fluorescence was observed. Transient absorption changes of 2, 4, and 6 nm BTSAuNPs in toluene during a femtosecond laser irradiation at 400 nm are shown in Figure 2.

An absorption band appeared immediately around 500 nm after laser excitation, and shifted to longer wavelength within 3 ps becoming a broad absorption band with a peak at 528 nm. The decay of this 528 nm band is two-part. The short time scale decay is around 25 ps. Using nanosecond laser transient absorption measurements, the long time band was found to decay in 130 ± 5 ns. Oxygen has no effect on the 528 nm absorption, so it was attributed to the absorption of BTSAuNPs in the charge-transfer state, ^{•+}BTSAu(e), formed by intramolecular electron transfer during the 400 nm laser light excitation. With reference to the absorption around 440 nm of BTSH^{•+} and around 420 nm of BT^{•+},¹⁸ the absorption of ^{•+}BTSAu(e) is broad and red shifted, indicating that the BT chromophore has strong electronic interaction with the Au

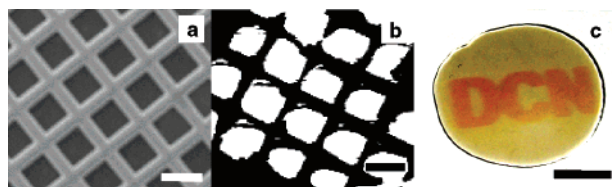


Figure 3. (a) SEM image of Formvar carbon-coated 300-mesh copper grid (scale bar = 50 μm); (b) SEM (BEI) image of poly(butylmethacrylate) matrix embedded with 2 nm BTSAuNPs after irradiation (scale bar = 50 μm). (c) Picture of DCN letter pattern in poly(butylmethacrylate) formed after irradiation using a 395 nm UV lamp (scale bar = 1 cm).

nanocore through the S–Au bond. Two-exponential decay of $^{*+}\text{BTSAu}(e)$ indicates back electron transfer occurs to give BTSAu within 25 ps and radical coupling of $^{*+}\text{BTSAu}(e)$ to give polymeric BTSAuNPs within 130 ns. No significant difference in decay was observed for 2, 4, and 6 nm BTSAuNPs. However, the rate of formation of $^{*+}\text{BTSAu}(e)$ was found to be particle-size-dependent and faster with smaller nanoparticles. Rate constants of $(4.35 \pm 0.17) \times 10^{12} \text{ s}^{-1}$, $(1.27 \pm 0.07) \times 10^{12}$, and $(6.99 \pm 0.16) \times 10^{11} \text{ s}^{-1}$ for the 2, 4, and 6 nm BTSAuNPs were estimated from the growth of the absorption band at 528 nm (Supporting Information). The absence of the absorption of BTSH(T_1) around 450 nm indicated ISC was suppressed or the triplet excited state was totally quenched by electron transfer in BTSAuNPs. On the other hand, a strong emission around 550 nm was detected in the case of 6 nm BTSAuNPs (Figure 2c), but this emission was weak in the 4 nm (Figure 2b) and not observed in the 2 nm BTSAuNPs (Figure 2a). The emission lifetime was almost the same as that of the absorption around 500 nm. This indicates that fluorescence was from BTSAuNPs in the singlet excited state localized at the BT chromophore. In other words, the emission from BTSH(S_1) was enhanced with increased AuNP size.

Since polymerization of BTSAuNPs can be achieved photochemically, construction of two- or three-dimensional designs of conductive polymeric nanomaterials now seems facile.

Molecular exchange at the polar defects (Supporting Information) of functionalized nanoparticles has been utilized by others in making nanoparticle chains by chemical methods.⁶ We carried out ligand exchange reactions by adding 2 mL of BTSH to 5 mL of $\text{C}_{12}\text{H}_{25}\text{SAuNPs}$ in toluene solution. After stirring for 30 min, the reaction was rapidly quenched by the addition of 400 mL of ethanol. The precipitate was separated by filtration and washed with ethanol, the residue redissolved in toluene, and a sample irradiated for 30 min with a 350 nm UV lamp. The linear chain can be easily recognized (Supporting Information). A NP chain was obtained by photopolymerization of $\text{C}_{12}\text{H}_{25}\text{SAuNPs}$ after ligand exchange with BTSH at the polar defects. Furthermore, with extended irradiation time, for example, 90 min, a two-dimensional network was obtained (Supporting Information). This is attributed to the photopolymerization of $\text{C}_{12}\text{H}_{25}\text{SAuNPs}$ with BTSH exchanged not only at the polar positions but also at other places on the surface of $\text{C}_{12}\text{H}_{25}\text{SAuNPs}$. After photopolymerization, the linker between two AuNPs should be α -quaterthiophene formed by dimerization of two BTs. On the basis of the TEM images after photoirradiation, the average distance between AuNPs was estimated to be ~ 3 nm, which is almost the same in length to one α -quaterthiophene (2.7 nm).⁷

A Formvar carbon-coated 300-mesh copper grid, 50 $\mu\text{m} \times 50 \mu\text{m}$ (Figure 3a), was selected as a photomask. A poly(butylmethacrylate) film (~ 0.3 mm) embedded with 2 nm BTSAuNPs was irradiated using a 395 nm UV lamp (UV Process Supplies, Inc., A160-008) for 60 min through the photomask. After

irradiation, a similar mask pattern was reproduced on the film with high accuracy as shown by the backscattered electron image (BEI, Figure 3b) by SEM. The bright square-like regions on the BEI are attributed to areas with high concentrations of AuNPs. This indicates that photopolymerization of the BTSAuNPs occurred only in the exposed areas of the film. In another demonstration, we made a “DCN” letter pattern on a black polycarbonate film used as the photomask such that light passes only through the DCN letters. After irradiation using the 395 nm UV lamp for 60 min, a similar letter pattern made on the mask can be clearly seen in the poly(butylmethacrylate) matrix embedded with 2 nm BTSAuNPs (Figure 3c).

In conclusion, our results demonstrate that initial charge separation is related to the size of the NP. The charge separation rate for 2 nm BTSAuNPs is more than 3 times faster than that for the 4 nm and more than 6 times faster than that for the 6 nm BTSAuNPs. The emission observed in the 6 nm BTSAuNPs is strong, but very weak in the 4 nm, and absent in the 2 nm BTSAuNPs. Such unique properties must be very important for fabrication of functional nanodevices. Making conductive polymeric chains or 3D networks by photochemical methods is possible using functionalized nanoparticles, such as BTSAuNPs. This is much more convenient and decidedly simpler than chemical and electrochemical polymerization methods.

Acknowledgment. The present work was supported by Office of Naval Research (N0014-06-1-0948). We thank Dr. Eugene Danilov for his assistance in operation of femtosecond and nanosecond laser systems and helpful discussions. Contribution No. 648 from the Center for Photochemical Sciences.

Supporting Information Available: UV absorption spectra; TEM and SEM images; NP size distribution histograms; transient absorption measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- Templeton, A. C.; Wuelfing, W. P.; Murray, R. W. *Acc. Chem. Res.* **2000**, *33*, 27.
- Daniel, M. C.; Astruc, D. *Chem. Rev.* **2004**, *104*, 293.
- Hu, J.; Zhang, J.; Liu, F.; Kittredge, K.; Whitesell, J. K.; Fox, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 1464.
- Ipe, B. I.; Thomas, K. G.; Barazzouk, S.; Hotchandani, S.; Kamat, P. V. *J. Phys. Chem. B* **2002**, *106*, 18.
- Thomas, K. G.; Ipe, B. I.; Sudeep, P. K. *Pure Appl. Chem.* **2002**, *74*, 1731.
- DeVries, G. A.; Brunnbauer, M.; Hu, Y.; Jackson, A. M.; Long, B.; Neltner, B. T.; Uzun, O.; Wunsch, B. H.; Stellacci, F. *Science* **2007**, *315*, 358.
- Caspar, J. V.; Ramamurthy, V.; Corbin, D. R. *J. Am. Chem. Soc.* **1991**, *113*, 600.
- Quinn, B. M.; Liljeroth, P.; Ruiz, V.; Laaksonen, T.; Kontturi, K. *J. Am. Chem. Soc.* **2003**, *125*, 6644.
- Baauerle, P.; Wuerthner, F.; Goetz, G.; Effenberger, F. *Synthesis* **1993**, 1099.
- Sotgiu, G.; Zambianchi, M.; Barbarella, G.; Botta, C. *Tetrahedron* **2002**, *58*, 2245.
- Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *J. Chem. Soc., Chem. Commun.* **1994**, 801.
- Leff, D. V.; Ohara, P. C.; Heath, J. R.; Gelbart, W. M. *J. Phys. Chem.* **1995**, *99*, 7036.
- Zotti, G.; Vercelli, B.; Battagliarin, M.; Berlin, A.; Hernandez, V.; Lopez Navarrete, J. T. *J. Phys. Chem. C* **2007**, *111*, 5886.
- Wessels, J. M.; Nothofer, H.-G.; Ford, W. E.; von Wrochem, F.; Scholz, F.; Vossmeier, T.; Schroedter, A.; Weller, H.; Yasuda, A. *J. Am. Chem. Soc.* **2004**, *126*, 3349.
- Gilmour, S.; Marder, S. R.; Perry, J. W.; Cheng, L. T. *Adv. Mater.* **1994**, *6*, 494.
- Sih, B. C.; Teichert, A.; Wolf, M. O. *Chem. Mater.* **2004**, *16*, 2712.
- Shah, B. K.; Rodgers, M. A. J.; Neckers, D. C. *J. Phys. Chem. A* **2004**, *108*, 6087.
- Evans, C. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 2694.

JA073899U