Metal nanoparticle—conjugated polymer nanocomposites

Bryan C. Sih and Michael O. Wolf*

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Recent literature describing nanocomposites of metal nanoparticles and conjugated polymers and oligomers are reviewed. Preparation of these nanocomposites by chemical and electrochemical methods are described, and the electronic and optical properties of these materials are discussed. Some initial applications that have been investigated for such nanocomposites are covered.

Introduction

Nanomaterials have emerged as an area of intense current interest motivated by potential applications of these materials in electronics, non-linear optics, and magnetics.[1] Growth in this area has been facilitated by wide accessibility to tools necessary to characterize these materials. Nanocomposites, in which materials are mixed on the nanoscale, are of particular interest as they combine the properties of two or more different materials with the possibility of novel mechanical, electronic or chemical behaviour arising.

Metal nanoparticles (NPs) exhibit properties differing from bulk metal due to quantum size effects, including novel electronic, optical and chemical behaviour.[2,3] The properties may be tuned *via* control of shape, size, inter-particle spacing and dielectric environment, and methods to vary these have been developed.[4–7] Efforts are also being directed towards organizing NPs in two- and three-dimensions—a crucial step if nanoelectronic applications are to be developed using these materials.[8–11] Conjugated materials with π-conjugated backbones represent a particularly intriguing type of environment for metal NPs. Conjugated polymers (CPs) and oligomers have been intensively studied in recent decades due to their remarkable electronic and optical properties which include high conductivities, electrochromism, electroluminescence and chemosensitivity.[12] Nanocomposites of conjugated materials and metal NPs have been recently prepared from a range of different metals, and many different types of conjugated polymers and oligomer linkers. The effect of this on the optical properties of the NPs, electronic behavior of both the NPs and conjugated materials, and some early applications have been investigated. This review summarizes some of these developments.

Methods of preparation

Chemically synthesized nanocomposites

Several chemical approaches have been developed to prepare nanocomposites of metallic NPs and CPs. Generally, these follow one of two routes: a) a "one-pot" approach where the monomer or polymer acts as a reductant for the metal or b) preparation of the NPs followed by either chemical polymerization of the polymer around the particles or dispersion of the NPs into a polymer matrix.

The advantage of the "one-pot" approach is simply the lack of intermediate purification steps which reduce yield. Nanocomposites of polyaniline derivatives and gold NPs have been prepared in this way, using 2-methoxyaniline or *o*-anisidine as reducing agents for gold salts. In the resulting nanocomposite the polymer remains doped.[13,14] A similar approach was used by Chattopadhyay *et al.*, they used hydrogen peroxide to both reduce a gold salt and simultaneously oxidatively polymerize aniline. The nanocomposites prepared in this way are two orders of magnitude more conductive than polyaniline, with nanoparticles ~100 nm in diameter.[15,16]

A one-pot approach has also been utilized by Advincula to prepare sexithiophene linked nanoparticles. Either a tetraalkylammonium functionalized terthiophene[17] or a poly(4-vinylpyridine) (PVP)[18] with pendant terthiophene groups was used in this work as a reductant for solutions of $HAuCl_4$ (Fig. 1). The ammonium salt forms a polyelectrolyte complex with polystyrene sulfonate, and subsequent addition of the $HAuCl_4$ results in formation of gold NPs (>15 nm). In the PVP case, multilayers of the functionalized PVP and poly(acrylic acid) are deposited on substrates, which are then dipped in a solution of $HAuCl_4$ resulting in 6–100 nm gold NPs. In both cases, NP formation is accompanied by the

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*mwolf@chem.ubc.ca

Bryan C. Sih was born in Manila, Philippines. He obtained his B.Sc. from Simon Fraser University in Burnaby, Canada in 2002. Currently, he is a doctoral student under the supervision of Prof. Michael Wolf in the Department of Chemistry at the University of British Columbia and holds a Canada Graduate Scholarship. His research interests are in the area of nanomaterials and their application in electronic and optical devices.

Michael O. Wolf is an Associate Professor of Chemistry at the University of British Columbia. Originally from Halifax, Canada, he obtained a B.Sc. from Dalhousie University in 1989, and a Ph.D. from MIT in 1994. He enjoyed a postdoctoral stint at the University of Texas at Austin, and has been on the faculty at UBC since 1995. Recent awards include a Killam Research Award and the CSC Award in Pure or Applied Inorganic Chemistry. His research interests lie in the area of metal-containing conjugated polymers, chemical sensors and molecular electronics.

simultaneous formation of coupled sexithiophene linkers. Similarly, Li *et al.* prepared composite materials using 3,4-ethylenedioxythiophene (EDOT) as a reductant.[19] The resulting poly(EDOT)/NP composite was found to self-assemble *via* π–π interactions giving aggregates. It is also possible to use a CP as the reductant, the groups of Naka and Chujo have accomplished this, generating nanocomposites of poly(dithiafulvene) and Pd, Au and Pt NPs.[20,21]

Photopolymerization has also been used to obtain nanocomposites of CPs with metal NPs. Sadik prepared films by photopolymerization of pyrrole at 254 nm in the presence of copper, silver or gold salts.[22] The mechanism is believed to involve photoreduction of the metal salt to give the NPs, oxidation of the pyrrole monomer followed by polymerization to give polypyrrole. Similarly, Zhou formed silver–polydiacetylene nanocomposites from a mixture of 10,12-pentacosadiynoic acid and Ag^+, irradiated to cause photoreduction of the silver and simultaneous polymerization of the diacetylene.[23]

The other major chemical route to NP composites is to synthesize the particles first, followed by either dispersion in a polymer matrix or chemical polymerization of monomeric groups on the particle surface. This approach has been used for a number of different types of metal NPs. Athawale prepared Pd nanoparticles ($\sim$20–30 nm) by γ-radiolysis of a heated solution containing $PdCl_2$ and substituted aniline monomers.[24] These NPs were then oxidatively polymerized using ammonium persulfate solutions. They have also prepared copper nanoparticles using a similar approach, however in this case the aniline was added after the NPs were synthesized.[25] This nanocomposite was used as a catalyst for Wacker oxidation of 1-decene. McCullough has prepared gold nanocomposites by reducing $HAuCl_4$ with sodium borohydride in the presence of regioregular poly(3-hexylthiophene).[26] This approach requires addition of excess tetraoctylammonium bromide to prevent oxidation of the poly(3-hexylthiophene). Thin films of these composites were cast and studied by AFM and TEM.

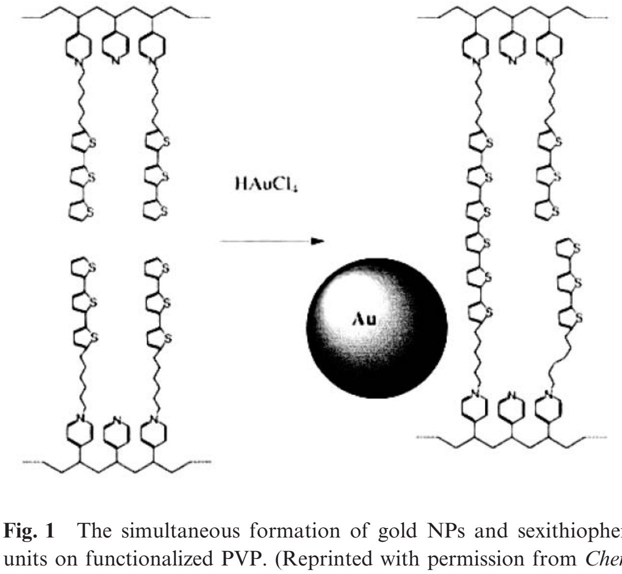


Fig. 1 The simultaneous formation of gold NPs and sexithiophene units on functionalized PVP. (Reprinted with permission from *Chem. Mater.*, 2004, **16**, 5063. Copyright 2004 American Chemical Society.)

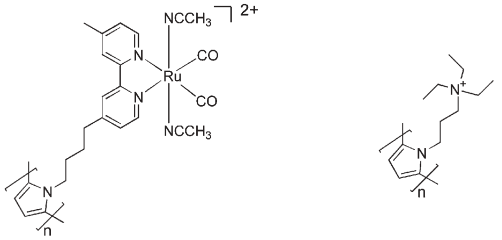
An elegant approach to form nanowires of Au nanocomposites was demonstrated by Feldheim.[27] In this approach gold NPs are drawn into a porous alumina membrane which is then exposed to a solution of iron perchlorate on one side of the membrane, and pyrrole monomer on the other. Chemical polymerization occurs within the membrane which can then be dissolved to reveal the interconnected arrays. Feldheim *et al.* have also used thioacetyl functionalized phenylacetylenes to make gold and silver nanocluster dimers and trimers.[28,29]

Electrochemically synthesized nanocomposites

Electrochemical synthesis is a well-established technique for the preparation of CP films *via* oxidative coupling of monomers.[30] The technique is very versatile and polymers with functional side groups can be synthesized by modifying the monomer prior to electro-oxidation. A wide variety of anions can also be incorporated as counterions, usually from the electrolyte used in the synthesis. In recent years, electrochemical methods have also proved to be effective in incorporating metal NPs in either pre-deposited polymers or in growing polymer films. Depending on the metal, the desired metal NP size and the type of polymer, different techniques have been developed.

Initial attempts to electrochemically impregnate CPs with metal NPs employed a two-step electrochemical process. In the first step, a CP such as polyaniline,[31] polypyrrole[32] or poly(methylthiophene)[33] is deposited onto an electrode by electro-oxidation of the appropriate monomer. Films of the polymers are then dipped in a solution containing metal species such as $PtCl_6^{2-}$, Ag^+ or Cu^{2+} followed by electrochemical reduction yielding Pt, Ag or Cu clusters embedded in the polymer. Longer electrolysis time leads to growth of larger particles as opposed to nucleating new ones, so the metal clusters formed are generally large (>100 nm), have a wide distribution in size, are confined largely to the polymer surface and are unevenly distributed within the polymer matrix.

To improve the size distribution and reduce the particle size, cations can be attached to the polymer backbone such as in poly-**1** and -**2**, (Fig. 2) where the metal complex acts as a template to facilitate metal particle nucleation.[34–36] After polymerization, these films were immersed in an aqueous solution of metal anions (Pd, Ru or Cu) resulting in anion exchange. This was followed by electroreduction to grow the metallic particles. The electrogenerated Pt, Ru and Cu particles generated in this way are much smaller (<6 nm) and the size distribution narrower, than those prepared by electrochemical impregnation. The size and distribution of



poly-**1**

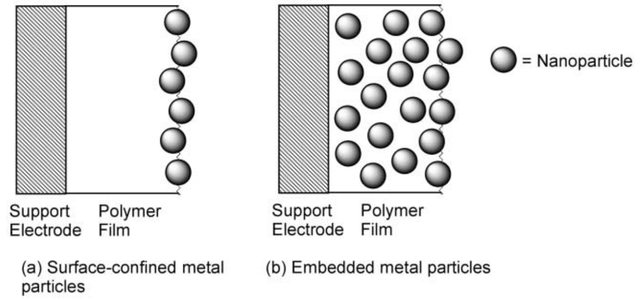
poly-**2**

Fig. 2 Electroactive cationic polymer templates.

particles in the matrix are highly dependent on numerous factors such as the immersion time for anion exchange, the applied voltage or current, and the solution concentration.

An alternate approach to electrochemically incorporating metal NPs into a polymer matrix was first carried out by Bose *et al.*[37] in which presynthesized NPs are present as a colloidal dispersion during electropolymerization of the monomer. This leads to the NPs being trapped within the growing polymer (Fig. 3b) instead of being confined to the surface (Fig. 3a) as is typically observed when metal particles are deposited onto pre-deposited polymers by reduction of metal ions. Since a large variety of metal NPs can be synthesized and their size controlled,[38] this method has the advantage that significant control of embedded NP size can be exerted. The three-dimensional distribution of metal particles within the matrix also facilitates improved charge shuttling throughout the material. A disadvantage of this approach, however, is that the NPs used are passivated by thiols, amines or citrate which prevent the NPs from being directly chemically bound to the polymer.[38] Leaching of the NPs from the matrix is thus difficult to prevent.

Several different methods to chemically attach pre-synthesized NPs to a polymer film during the electrodeposition process have been developed. Cioffi *et al.*[39,40] have prepared Pd NPs with weakly passivating tetraoctyl ammonium bromide (TOAB) on the surface. As the NPs are trapped during electrodeposition, some TOAB molecules are displaced from the surface and polypyrrole nitrogens partly passivate the Pd NPs as shown by XPS chemical shifts.[40] The Pd NPs carry a slight negative charge due to $Pd(Br)_4^{2-}$ groups surrounding the Pd(0) core, resulting in some ionic interaction between the partially oxidized polypyrrole and the NP. Peng *et al.*[41] used a different approach by covalently tethering Au NPs to the conjugated polymer backbone. Au NPs passivated by 2-mercapto-3-*n*-octylthiophene (**3**) were synthesized and then electrochemically co-polymerized with 3-*n*-octylthiophene (**4**), forming the random copolymer poly-$(\mathbf{3})_n(\mathbf{4})_m$, (Fig. 4). The Au NPs in poly-$(\mathbf{3})_n(\mathbf{4})_m$ are distributed randomly in the polymer but the long alkyl tether between the Au NP and polythiophene backbone prevents efficient shuttling of charge throughout the material.



(a) Surface-confined metal particles

(b) Embedded metal particles

Fig. 3 Schematic diagram of conducting polymer where the metal nanoparticles are (a) surface-confined and (b) distributed throughout the polymer matrix.

A novel method for homogenously distributing Au NPs in a polythiophene matrix was recently described by our group using oligothiophene capped NPs (**5**).[42] The NP surface was functionalized with oligothiophenes *via* a phosphine group, and the individual capped NPs linked electrochemically to form poly-**5** as a film (Fig. 5). This results in the Au NPs being homogenously distributed within a conjugated matrix where the Au NPs are linked to other NPs with π-conjugated linkers.

Electronic properties of nanocomposites

The electronic properties of metal nanoparticles (NPs) have stimulated significant interest due to possible applications in single electron transistors.[43] There is also interest in the enhanced conductivity that may be attained by imbedding NPs in conducting polymer matrices.[15,22] When individual NPs are sandwiched between metal contacts, electrons can only be transferred one-by-one by quantum tunneling where the probability of tunneling is controlled by an applied external voltage. This phenomenon, called single electron tunneling (SET), has been demonstrated for individual NPs at room temperature by Brousseau *et al.*[44] and Houbertz *et al.*[45] using scanning tunneling spectroscopy (STS). However, for these particles to find utility in nanoelectronic devices, organization into functional architectures is needed.

Metallic NPs have been assembled into two- and three-dimensional structures using electrostatic interactions,[9,46] hydrogen bonding[10] and saturated organic linkages.[11,47,48] When non-conjugated linkers connect the particles, electron tunneling is the predominant mechanism for electrical

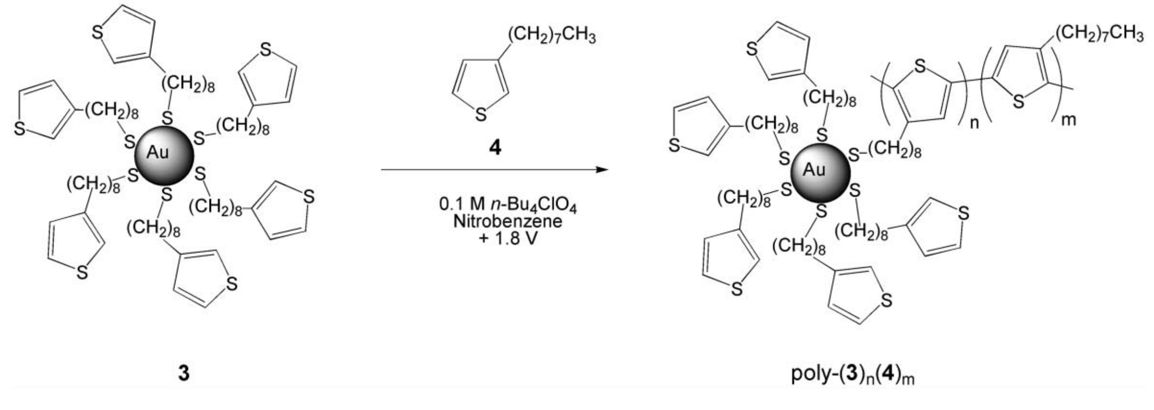


Fig. 4 Thiophene derivatized Au nanoparticles copolymerized electrochemically with 3-*n*-octylthiophene.

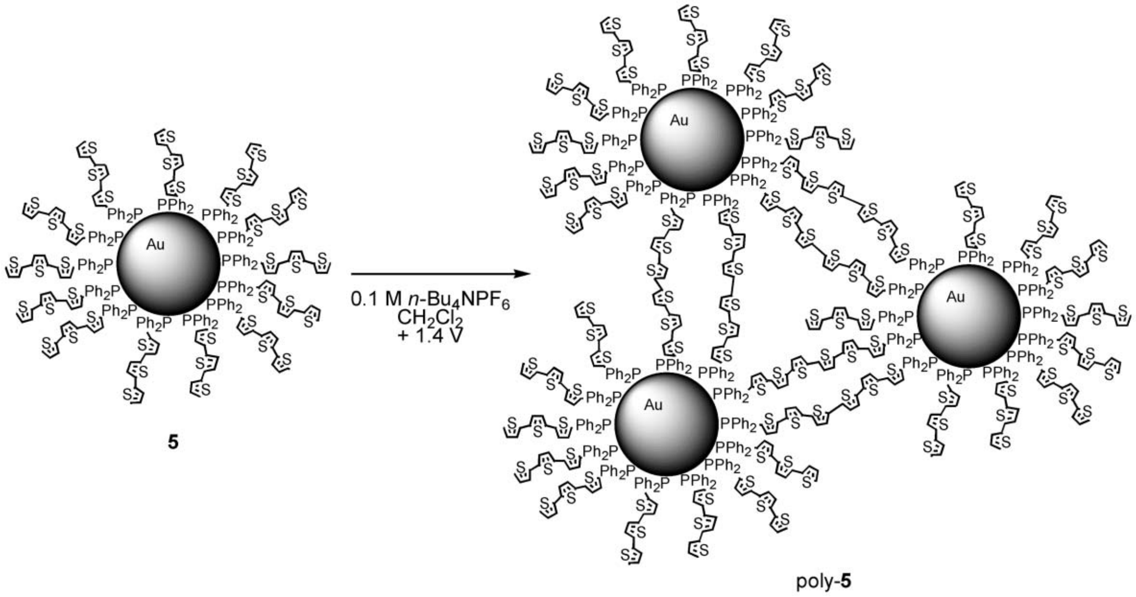


Fig. 5 Preparation of poly-**5**. (Adapted with permission from *Chem. Mater.*, 2004, **16**, 2712. Copyright 2004 American Chemical Society.)

conduction.[49] The electrical conductivity (σ) depends primarily on the charge carrier population (n), the electronic coupling term (β/Å^{-1}) and the activation energy barrier (E_A/kJ mol^{-1}) to electron transfer (eqn. 1 and 2),

$$\sigma = \sigma_0 \exp^{[-\beta\delta]} \exp^{[-E_A/RT]} \tag{1}$$

$$\sigma_0 = ne\mu \tag{2}$$

where δ is the average inter-particle distance (Å), R the universal gas constant, T the temperature (K), e the elementary charge and μ the mobility of the charge carriers. The electrical conductivity of these materials is expected to decrease as the length of the linker is increased due to higher activation energies, this has been observed experimentally.[49] Electron transport between NPs linked with saturated groups is well studied, however systems with improved inter-particle charge transport using either a π-conjugated matrix to embed the NPs or a π-conjugated molecule to link them are of interest. A π-conjugated polymer or molecule between the NPs can serve as a 'molecular wire' and enhance coupling between adjacent particles.[50]

Four-point probe conductivity measurements of Au NPs embedded in polypyrrole,[22] polyaniline[15] and polythiophene[26] demonstrate an increase of approximately two orders of magnitude compared to similar polymers without NPs present. Detailed information on the role of the metal particles in the films is difficult to obtain, due to problems which include: (1) the distribution of NPs is random and challenging to control, (2) the nature of the bonding and the electronic link between the polymer and NP is ill-defined and (3) it is feasible for charge transport to occur without involving the NP by charge percolation through the polymer alone. Model systems where NPs are linked by π-conjugated molecules of well-defined length, are useful as they may be used to probe the effect of the 'molecular wire' on the efficiency of charge transport between NPs.

Initial efforts to construct structures where NPs are linked by π-conjugated molecules used self-assembly to form three-dimensional networks by mixing the two components in solution. Bifunctional molecules (Fig. 6) are used to link the NPs *via* isocyanide[51,52] or thiol functionalities.[50,53] Although initial attempts to ascertain the effect of the conjugated cross-linker compared to unlinked Au particles gave mixed results,[50–52] Andres *et al.* were able to find evidence that Au NPs linked by **6** led to local reordering of the array suggesting a possible electrical link between the NPs. Bourgoin *et al.*[54] carried out the same experiment using **9** as the linking molecule and found three orders of magnitude better conductivity for NPs linked by **9** than for unlinked NPs. The **9**-linked NPs also had a lower E_A indicating a smaller tunneling barrier between NPs suggesting **9** acts as a 'molecular wire'. Snow *et al.*[55] used different cross linkers to compare the effect of a saturated linker (alkanedithiols) to a partially conjugated linker (**8**). Solutions of **8** and Au NP were used to build up a layered structure of crosslinked NPs by successive dipping. The conductivity of the sample after each dipping cycle was determined and even after 10 cycles NPs linked by **8** showed

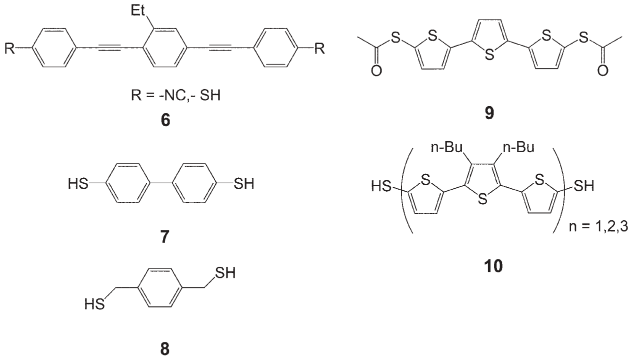


Fig. 6 Bi-functional π-conjugated molecules used to link Au nanoparticles *via* self-assembly.

higher conductivities compared to those linked by alkane dithiols. Au NPs passivated by different molecules (an alkanethiol *vs.* 2-phenylethanethiol)[55–57] were also compared and the Au NPs capped with 2-phenylethanethiol showed an enhanced conductivity by a factor of two. The higher conductivity correlates to the presence of the aromatic group in the shell, which lowers the average barrier between clusters.

To understand the charge transfer mechanism between Au clusters, Torma *et al.*[58] used a variety of conjugated and non-conjugated molecules to link NPs (Fig. 7). The conductivity was measured between 200 and 300 K to determine E_A, the energy which must be overcome to create mobile charge carriers. For non-conjugated linked NPs, a linear relationship was found (Fig. 7) between E_A and the intercluster distance. Since the distance between NPs governs the hopping energy between them, it is clear that for non-conjugated linkers the specific chemical structure of the linker is unimportant because there are no electronic interactions between NPs *via* the linker. NPs linked by conjugated molecules, on the other hand, show lower E_A's relative to non-conjugated linkers of equivalent length. This suggests that the molecular orbitals of the linking molecules play a role in the charge transfer and provide a different pathway for electrons other than tunneling through the gap. Recent work by our group[42] with Au NPs linked by oligothiophenes supports this conclusion. We have shown that unlinked oligothiophene-capped Au NPs (**5**) have a conductivity several orders of magnitude lower compared to the linked particles (poly-**5**). The greater conductivity of poly-**5** is believed to be due to enhanced charge propagation *via* the conjugated bridge.

Wessels *et al.*[59] have also studied the effect of conjugation on inter-particle electronic coupling using a variety of partially conjugated linkers with a phenyl group in the backbone and non-conjugated linker analogues by substituting a cyclohexyl group for the phenyl group (Fig. 8). All three of the phenyl-containing linkers showed an order of magnitude higher conductivity, and lower activation energies than their cyclohexyl-containing counterparts. Most interesting are the NPs linked by **PBDT** for which a plot of conductivity as a function of T^{-1} has a positive slope indicating metallic behaviour. This has been attributed to the high degree of conjugation in the linker and good Au NP/molecule contact leading to overlap of adjacent NP electronic wavefunctions.

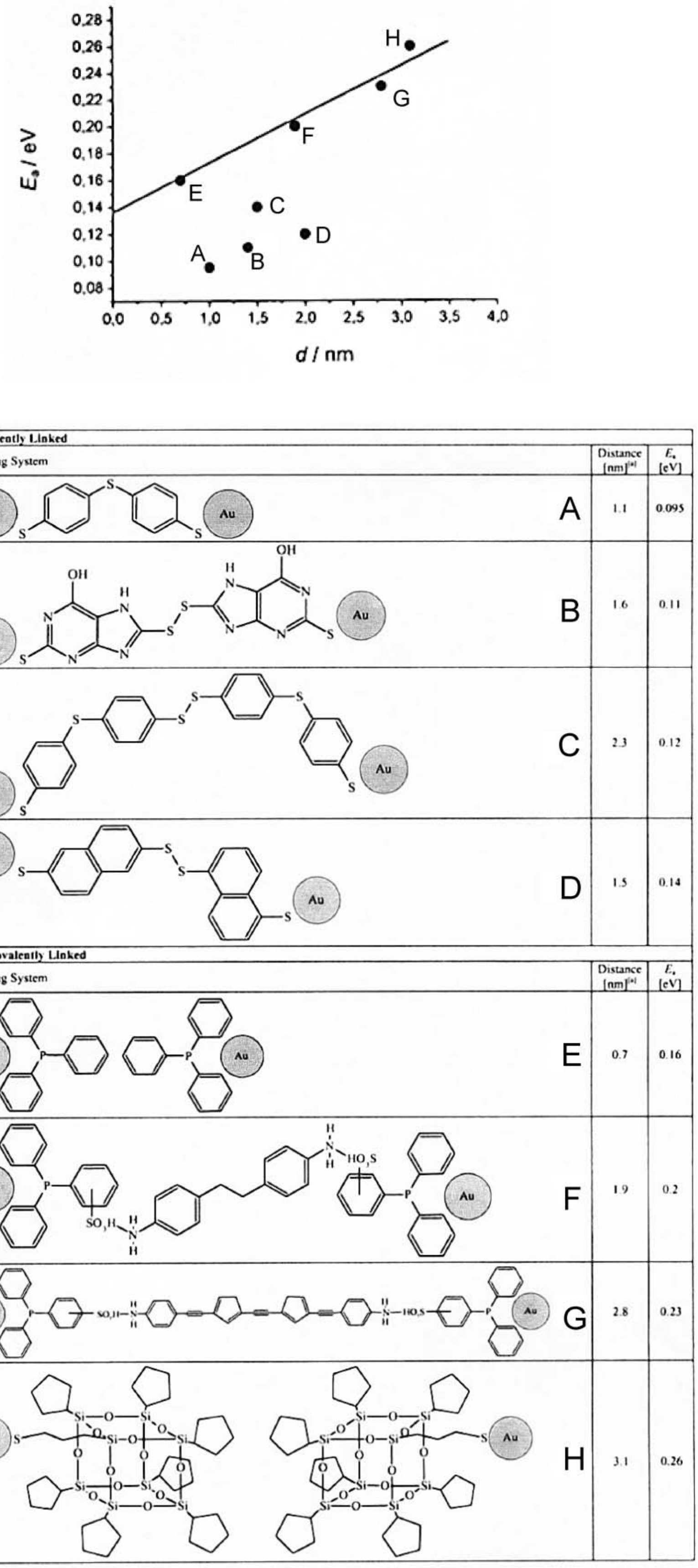
Optical properties of nanocomposites

The optical properties of both CPs[60,61] and metal NPs[62] are well studied and suggest possible applications in light-emitting diodes, solar cells and sensors. In nanocomposites, the effect of metal NPs on the π–π* absorption band of CPs, and the effect of CPs on the coupling between NPs are a subject of debate. Understanding and tuning such effects could lead to hybrid optical devices based on these nanocomposites with improved optical properties.

The surface plasmon absorption of individual metal NPs arises from the collective oscillation of free electrons in the conduction band induced by incident electromagnetic radiation. Such resonances can be observed when the incident wavelength is much larger than the NP diameter. For example, Au NPs with diameters of 5–50 nm show an absorption band in the visible region between 520–530 nm.[62] This plasmon absorption is sensitive to the environment surrounding the NPs such that different solvents with varying refractive indices cause the plasmon band to red-shift ∼10 nm.[63] Recently, Templeton *et al.*[64] has shown that as the size of a metal NP decreases the effect of the solvent on the plasmon absorption decreases. This is because for small NPs, the metal and capping group have comparable volumes and the effect on the plasmon absorption is dominated by the latter. The effect of a surrounding CP on the surface plasmon of Au NPs embedded in conjugated poly(3,4-ethylenethiophene)[19] or poly(dithiafulvalene)[65] has been studied. A red-shift in the plasmon absorption band of 30 nm after passivation of the NP with the CP was observed by both groups. This red-shift has been ascribed to the CP lowering the work function of the Au NP, lowering the position of the surface resonance state and thus causing a red-shift in the absorbance. Such shifts in the surface plasmon band suggests overlap between the electronic wavefunctions of the NP surface and CP.

The energy of the π–π* absorption is one method of estimating the conjugation length in CPs; red-shifts in the π–π* absorption indicate an increase in conjugation length. Studies by Zhou *et al.*[23,66] on the effect of metal NPs on the conjugation of poly(diacetylene) showed a red-shift in the π–π* absorption of the polymer as Ag NPs increased in size upon UV irradiation. Masuhara *et al.*[67] reported a similar effect for Ag NPs surrounded by poly(1,6-di(*N*-carbazolyl)-2,4-hexadiyne) where the π–π* absorption red-shifted ∼20 nm than would be expected without the Ag particles. More interesting is the disappearance of the Ag surface plasmon band upon encapsulation in the CP, attributed to strong interaction between the electronic state of the Ag plasmon band and excitons of the CP.

Model systems have been constructed where NPs are linked by π-conjugated molecules to illustrate the effect of the 'molecular wire' on the surface plasmon absorption of inter-linked NPs. Kim *et al.*[68] assembled a network of Au NPs linked together by 1,4-phenylene diisocyanide (1,4-PDI, Fig. 9). UV-vis spectra of Au NPs in solution show a substantial decrease in the surface plasmon band at 522 nm as more linker molecules are introduced. This result is comparable to Masuhara's work described above supporting their claim of electronic interactions between the metal plasmon and the CP. Kim also observed growth of a new band at 720 nm as 1,4-PDI was added to the solution of Au NPs. This new band is a result of coupling of inter-particle surface plasmons[69] upon aggregation of NPs with 1,4-PDI. The type and degree of coupling between surface plasmons of NPs is dependent on two factors:[70] (1) the inter-particle spacing and (2) the conductivity between particles. The former is a dipole resonance effect, where a shorter inter-particle distance produces a larger dipole–dipole coupling energy and causes a red-shift in the surface plasmon band relative to an individual NP (Fig. 10a). The latter gives rise to two absorption bands due to contributions from both dipole and quadrupolar resonances. Initial conductive contact between NPs effectively shorts the dipole interaction and the symmetry and geometry of a 'dumbbell-like' configuration favors quadrupolar resonance



Covalently Linked

Linking System		Distance [nm][a]	E_a [eV]
	A	1.1	0.095
	B	1.6	0.11
	C	2.3	0.12
	D	1.5	0.14

Noncovalently Linked

Linking System		Distance [nm][a]	E_a [eV]
	E	0.7	0.16
	F	1.9	0.2
	G	2.8	0.23
	H	3.1	0.26

Fig. 7 Activation energies for covalently and non-covalently linked Au_{55} clusters of varying inter-particle distances. (Adapted with permission from *Eur. J. Inorg. Chem.*, 2003, 1121. Copyright 2003 Wiley-VCH.)

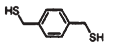
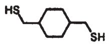
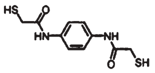
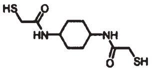
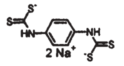
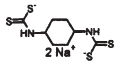
Linker		Length (Å)	$\Delta(E_{HOMO-LUMO})$	
BDMT		7.7[a]	4.0	bis-mercaptomethylenes
cHDMT		8.2[a]	5.0	
DMAAB		14.8[a]	3.5	bis-acetamidothiols
DMAAcH		14.9[a]	4.7	
PBDT		10.7[b]	2.7	bis-dithiocarbamates
cHBDT		9.6[b]	3.2	

Fig. 8 Partially conjugated linkers and their non-conjugated analogues. (Reprinted with permission from *J. Am. Chem. Soc.*, 2004, **126**, 3349. Copyright 2004 American Chemical Society.)

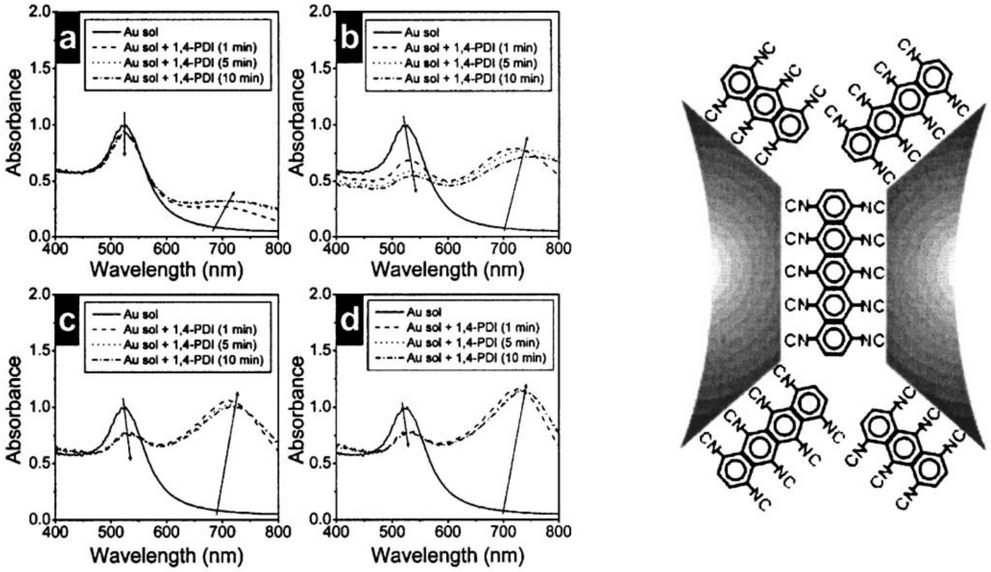


Fig. 9 Left: UV/vis spectra of Au sol after the addition of 1,4-phenylene diisocyanide (1,4-PDI) with a final concentration of (a) 4.0×10^{-6}, (b) 1.6×10^{-5}, (c) 3.2×10^{-5}, and (d) 3.2×10^{-4} M. Right: Schematic of Au NPs linked by 1,4-PDI. (Reprinted with permission from *Langmuir*, 2003, **19**, 6701. Copyright 2003 American Chemical Society.)

(Fig. 10b). As the conductive link and physical overlap of the NPs increases, the charge distribution rearranges again to the dipolar mode (Fig. 10c) as observed for ellipsoidal NPs.[71] The intensity ratio of these two resonances is dependent on the degree of conductive overlap between the particles.

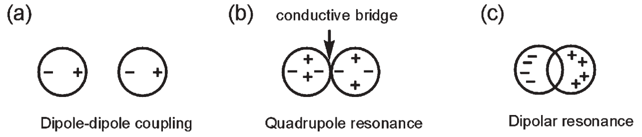
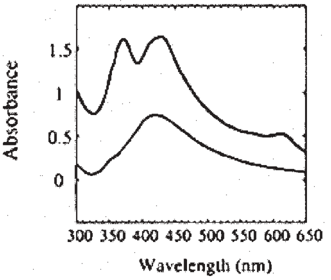
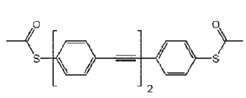


Fig. 10 Charge distribution for (a) dipole–dipole plasmon coupling, (b) quadrupolar mode due to shorting of dipole interactions and (c) strong conductive overlap causing 'dumbbell' shaped dipolar resonance.

Whether a CP or a π-conjugated molecule linking adjacent NPs can provide a conductive link between NPs and short the dipole moments, and result in perturbation of the coupled surface plasmons is still under debate. Marinakos *et al.*[27] reported little effect on the Au NP surface plasmon absorption with or without a polypyrrole coating. Studies on model systems by Osifchin *et al.*,[53] Chen *et al.*[72] and Musick *et al.*[73] using phenylacetylene and phenyl oligomers to bridge Au NPs showed red-shifts (~30 nm) in the plasmon band upon linking compared to unlinked NPs. This red-shift appears to be mostly due to dipole–dipole plasmon coupling. However, studies on phenylacetylene oligomers bridging Ag and Au NPs by Novak *et al.*[28] give contrary evidence. UV-vis absorption of Ag NPs in solution before and after introduction of the π-conjugated bridging molecule **11** is shown in Fig. 11. After **11** is





11

Fig. 11 UV-visible spectra for dimers linked by structure **11** (upper trace) and silver particle 'monomers' (lower trace). The monomer spectrum was acquired under solvent conditions identical to those of the dimers but in the absence of a linker. (Reprinted in part with permission from *J. Am. Chem. Soc.*, 2000, **122**, 3979. Copyright 2000 American Chemical Society.)

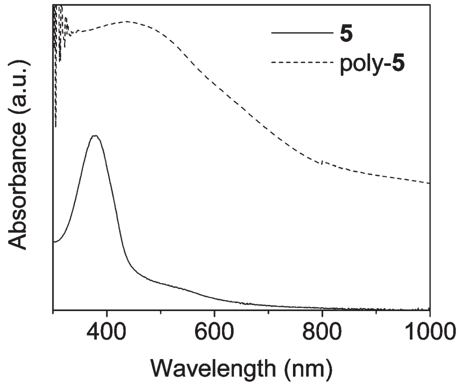


Fig. 12 UV-vis absorption of oligothiophene-capped NPs (**5**) before and after crosslinking (poly-**5**). (Adapted with permission from *Chem. Mater.*, 2004, **16**, 2712. Copyright 2004 American Chemical Society.)

introduced, there are two new peaks that appear in the spectrum at 370 and 600 nm corresponding to quadrupolar and dipole resonances of the linked NPs.[28, 74] This is what would be expected from conductively linking NPs and shorting the dipole moments.[70] Since the quadrupolar resonance peak at 370 nm is much larger than the dipolar resonance at 600 nm, this ratio is indicative of a weak conductive link between the NPs.

Wessels *et al.*[59] and our group[42] observed an even larger effect in the UV-vis absorption when Au NPs were linked by either **PBDT** or oligothiophenes, respectively. In the case of the **PBDT** linker, the surface plasmon band due to the individual NPs nearly disappears and the linked NPs exhibit a strong absorbance in the near-IR comparable to that observed for gold films. Metallic absorption has been previously observed for Au NPs linked by 1,3-propanedithiol[75] and 2-mercaptoethylamine.[73,76] However, the inter-particle distances for these saturated linkers are quite short (about half the length of **PBDT**) and metallic absorption has been attributed to close proximity of the NPs that allows overlap of the metal NP wavefunctions. For **PBDT**-linked NPs where the inter-particle spacing is ~1 nm, the metallic absorption is due to overlap of the molecular orbitals of the linker and metal wavefunctions causing the formation of a resonant state affecting the absorption of the material. In the oligothiophene-linked case, there is a π–π^* transition at 380 nm for the terthiophene moiety of **5** that red-shifts to 435 nm upon cross-linking due to increased conjugation upon formation of sexithiophene (Fig. 12). A broad absorption appears in the near-IR after electrodeposition suggesting metallic absorption. However according to Musick,[73] "when the cross-linker dimensions are of the same order of magnitude as the particles…there is no interaction between particles, and the multilayers remain essentially transparent in the near-IR region". Since the inter-particle spacing after linking is larger (~2.5 nm) than the average particle diameter ($d_{\mathrm{mean}} = 1.7 \pm 0.4$ nm), the absorption cannot be due to wavefunction overlap of adjacent NPs or dipole–dipole interactions. The absorbance in the near-IR suggests overlap between the molecular orbitals of the linker and metal wavefunctions and results in the perturbation of the absorbance. Both results are remarkable noting the large inter-particle distance between particles and suggests that π-conjugated molecules can provide a conductive link between NPs, short the dipole moments and perturb the plasmon resonances. This conclusion is supported by conductivity measurements on these same materials (*vide supra*).

Applications

The unique properties of CP/NP nanocomposites has led to several possible applications. To date, the most extensively explored of these is electrocatalysis where catalytic behavior of the nanocomposite can be turned on or off depending on the externally applied voltage. A comprehensive review of this application has recently been published[77] and thus is not explored in detail here.

Another possible application is in polymer light emitting diodes (PLEDs). A challenge to commercialization of PLEDs is rapid photo-oxidation of the CP under ambient conditions, which severely limits device lifetimes. The photo-oxidation process is well understood[78] and results when singlet oxygen, formed *via* energy transfer from the triplet state of the CP, reacts with the polymer to generate exciton traps. These traps are believed to be carbonyl groups introduced by oxidation of the CP and provide a non-radiative pathway for relaxation of singlet excitions and quench CP luminescence (Fig. 13a). Hale *et al.*[78] showed that the rate of photo-oxidation decreases when a small amount of metal nanoshells are added to the CP. The metal nanoshells are able to preferentially quench the triplet exciton of the CP, effectively decreasing the rate of singlet oxygen formation and consequently increasing the lifetime of the devices (Fig. 13b). Park *et al.*[79] found a similar effect in poly(9,9′-dioctylfluorene)/Au NP composites. The blue PLEDs had improved luminescence stability after addition of the Au NPs due to quenching of the triplet state by the CP. Furthermore, the nanocomposite also exhibited improved quantum efficiencies compared to pristine polymer as a result of improved charge injection.

CP/NP composites may also find utility as cathode materials. Embedding Ag[80] or Pd[81] NPs in a 2,5-dimercapto-1,3,4-thiadiazole (DMcT)-polyaniline (PANI) composite resulted in an increase in redox activity compared to pristine material. This increase in redox activity has been attributed to electroactivity of the NPs and improved conductivity of the

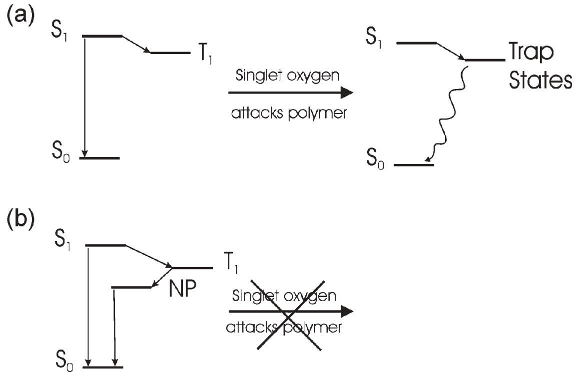


Fig. 13 Diagram of the photo-oxidation process in conjugated polymer nanoshell composites. (a) energy from the polymer triplet excitons excites singlet oxygen, which reacts with the polymer chain and forms exciton trap states. (b) adding a material (NP) to quench the triplet excitons impedes photooxidation process.

nanocomposite. The enhanced redox activity leads to better charge–discharge performance potentially making these useful as cathode materials in improved lithium rechargeable batteries.

Concluding remarks

The last few years have seen advances in the preparation, by chemical and electrochemical means, and characterization of NP/CP nanocomposite materials. Optical and electronic studies of these nanocomposites have revealed interesting properties. Conductivity measurements reveal that the charge transfer barrier between NPs is lowered when a CP or oligomer is the intervening medium, and in one case metallic behavior was observed for the nanocomposite. Preliminary exploitation of this in PLEDs has already occurred, and one can envision future exploration in the area of chemically sensitive materials where the organic component of the nanocomposite is tuned to show sensitivity to an analyte allowing ON–OFF switching of metallic behaviour. It is also apparent that studies involving a larger range of metals and NP sizes with conjugated linkers of varying lengths would be useful to further understanding of the effect of a conjugated matrix on the electronic properties of the composites. Optical measurements on nanocomposites show shifts in both the NP plasmon resonance and CP π–π^* transition, supporting observations from conductivity measurements of strong interactions between the components. These observations bode well for future applications, and it is likely that in addition to some of the ongoing studies on applications of these materials in PLEDs and as electrocatalysts, molecular electronics applications will also be explored to take advantage of the electronic and optical properties of the nanocomposites. Such applications, however, will require improved two- and three-dimensional manipulation of structures formed from these materials.

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Bryan C. Sih and Michael O. Wolf*
Department of Chemistry, University of British Columbia, Vancouver, BC V6T 1Z1, Canada. E-mail: mwolf@chem.ubc.ca;
Fax: +1 604 822 2847; Tel: +1 604 822 1702

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