

Metal nanoparticle enhancement of organic polymer solar cell efficiency: Raman and optical studies

Anne Myers Kelley, University of California, Merced

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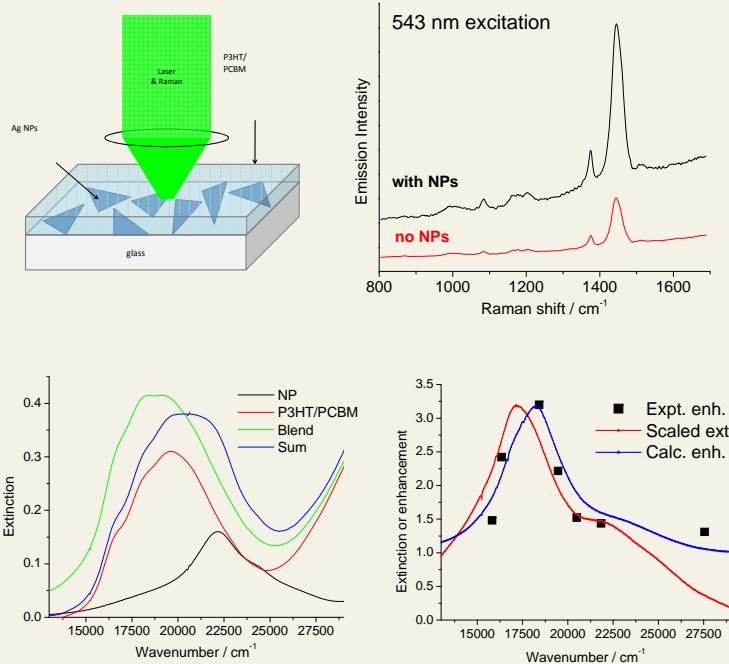
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Plasmonic Enhancement in P3HT/PCBM by Silver Nanoprisms

Plasmonically active metal nanostructures show promise for enhancing the power conversion efficiencies of photovoltaic cells for solar energy applications.[1] Enhancement has been observed in many device configurations including those based on organic polymers,[2,3] which have great promise because of their low cost and processability. Metal nanostructures could influence device efficiency in a variety of ways, prompting experiments designed to probe the mechanism(s) of the enhancement. Recently, plasmonically active triangular silver nanoprisms (NPs) were shown to increase the yield of photoinduced charge in the organic polymer blend poly(3-hexylthiophene):[6,6]-phenyl C₆₁-butyric acid methyl ester (P3HT:PCBM).[4] We are exploring the accompanying enhancement of Raman scattering (SERS)[5] to explore the metal-organic interaction at the molecular scale.

Bare NPs of different sizes exhibited plasmon resonances ranging from 440 to 550 nm, while the pure P3HT/PCBM films had an absorption maximum near 510 nm. Raman spectra were obtained on a microscope-based system at excitation wavelengths from 351 to 633 nm. In our earlier work on the hole transport material PEDOT:PSS,[6] both Raman intensity enhancement and chemical changes were observed in the presence of metal nanoparticles. Here we find that the NPs have no apparent effect on the P3HT/PCBM spectra beyond an overall intensity enhancement that ranges from nearly unity to about a factor of 20 depending upon excitation wavelength and NP characteristics. There is no evidence that the NPs affect the chemistry or morphology of P3HT or PCBM. The average SERS enhancement is small because most of the organic material is tens of nm from the metal surface. The P3HT fluorescence is weak in the presence of PCBM, but it is enhanced by approximately the same factor as the Raman scattering. This result is also consistent with most of the P3HT chromophores being sufficiently far from the metal that they experience some electromagnetic field enhancement but undergo minimal excited-state quenching by the metal.

The extinction spectra of the P3HT/PCBM/NP composites are significantly different from the sum of the separate P3HT/PCBM and NP spectra. Subtraction of the pure P3HT/PCBM spectrum from the composite spectrum yields a modified plasmon spectrum red-shifted by 4000-5000 cm⁻¹ from that of the bare NPs. The shape of the theoretical SERS enhancement profile calculated from this modified plasmon extinction[7] agrees quite well with the measured enhancement profile. This result further suggests that plasmonic enhancement of the local electromagnetic field is the dominant interaction between P3HT/PCBM and silver NPs.



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