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A polymer electrolyte with high luminous transmittance and low solar throughput: Polyethyleneimine-lithium bis(trifluoromethylsulfonyl) imide with In_2O_3:Sn nanocrystals

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Chemically prepared ~13-nm-diameter nanocrystals of In_2O_3:Sn were included in a polyethyleneimine-lithium bis(trifluoromethylsulfonyl) imide electrolyte and yielded high haze-free luminous transmittance and strong near-infrared absorption without deteriorated ionic conductivity. The optical properties could be reconciled with effective medium theory, representing the In_2O_3:Sn as a free electron plasma with tin ions screened according to the random phase approximation corrected for electron exchange. This type of polymer electrolyte is of large interest for opto-ionic devices such as laminated electrochromic smart windows. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4728994]

This Letter introduces a polymer electrolyte based on polyethyleneimine and lithium bis(trifluoromethylsulfonyl) imide (PEI-LiTFSI) and containing nanocrystals of tin-doped indium oxide (i.e., In_2O_3:Sn or ITO). This electrolyte combines high luminous transmittance T_{lum} with low solar transmittance T_{sol} and is of much interest for opto-ionic devices such as laminated electrochromic smart windows for energy efficient buildings.[1–3]

Electrochromic smart windows typically comprise a multilayer structure with a centrally positioned electrolyte usually being an inorganic thin film or a polymer electrolyte layer.[4] The latter option allows long open-circuit memory and uniform color changes and is also preferable for manufacturing.[3] Our prior work considered a PEI-LiTFSI model electrolyte and embraced ion relaxation mechanisms,[5,6] mechanical properties,[7] and SiO_2 nanoparticles to boost the ionic conductivity without sacrificing optical performance.[8]

In some applications of smart windows, it is preferable to minimize the near-infrared solar transmittance (in the $700 < \lambda < 3000$ nm wavelength range) irrespectively of T_{lum} (at $400 < \lambda < 700$ nm). As shown here, this functionality can be obtained by dispersing ITO nanocrystals in a PEI-LiTFSI electrolyte. ITO is a transparent conductor; the In_2O_3 semiconductor host has a wide band gap, and substitutional doping of Sn atoms on In sites yields free electrons whose density can be sufficient for plasmon absorption in the near-infrared.[9,10]

PEI-LiTFSI was prepared by mixing branched PEI (molecular weight 10 000) and $LiN(CF_3SO_2)_2$ in methanol and proceeding as previously described.[5] The PEI:LiTFSI molar ratio—defined as the number of moles of the PEI repeating units, $–(CH_2CH_2NH)–$, divided by the number of moles of LiTFSI—was 50:1, which yields maximum ionic conductivity.[6] ITO nanocrystals with an Sn/In ratio of 5 at. % were prepared by standard Schlenk-line techniques as reported elsewhere,[11] and their oleylamine and oleic acid ligands were stripped using $NOBF_4$.[12,13] The resulting bare, hydrophilic nanocrystals were stabilized by BF_4^- anions in a dimethylformamide (DMF) solution. Finally, known quantities of PEI-LiTFSI and ITO-DMF solutions were mixed and kept at 65 °C and 10^{-1} mbar for 48 h to remove methanol and DMF. Nanocomposite electrolytes of (PEI-ITO)-LiTFSI were made with up to 7 wt. % of ITO (counted as a fraction of the total weight of ITO and PEI). The transmission electron microscope (TEM) image in Fig. 1 shows colloidal ITO nanocrystals, prior to ligand exchange, with diameters D of 13 ± 3 nm; high-resolution TEM and x-ray diffraction (not shown) indicated that the nanocrystals are highly crystalline with the In_2O_3 bixbyite phase. Figure 1 also reports an absorbance spectrum for such colloidal ITO nanocrystals and demonstrates a strong absorption peak at $\lambda \approx 1830$ nm.

Temperature dependent ionic conductivity $\sigma(\tau)$ was recorded by impedance spectroscopy in the frequency range of 10^{-1} to 10^7 Hz for $23 < \tau < 70$ °C as described elsewhere.[5–8] Figure 2 reports σ at six temperatures for samples with 0, 1, 3, 5, and 7 wt. % ITO and shows that σ is rather independent of the ITO content and rises monotonically from $\sim 1 \times 10^{-6}$ S/cm at 23 °C to $\sim 2 \times 10^{-5}$ at 70 °C; $\sigma(\tau)$ obeys an Arrhenius behavior with activation energy of ~52.5 kJ/mol.

Spectral total and diffuse transmittance and reflectance were measured at $300 < \lambda < 2500$ nm for (PEI-ITO)-LiTFSI layers sandwiched between microscope glass slides using a metal foil as a spacer; the layer thickness was 70 ± 10 μm as determined mechanically. The diffuse components in the optical spectra were <1% in transmittance and <0.3% in reflectance and hence negligible. Solid curves in Fig. 3 show spectral transmittance. Without ITO, the transmittance is large for $\lambda < 1500$ nm while there are absorption bands due to PEI at $\lambda > 1500$ nm. When ITO is added, the transmittance remains high in the luminous range but decreases sharply in the near-infrared. Reflectance (not shown) was 7 to 8% in the luminous range and ~4% in the near-infrared. Hence, the

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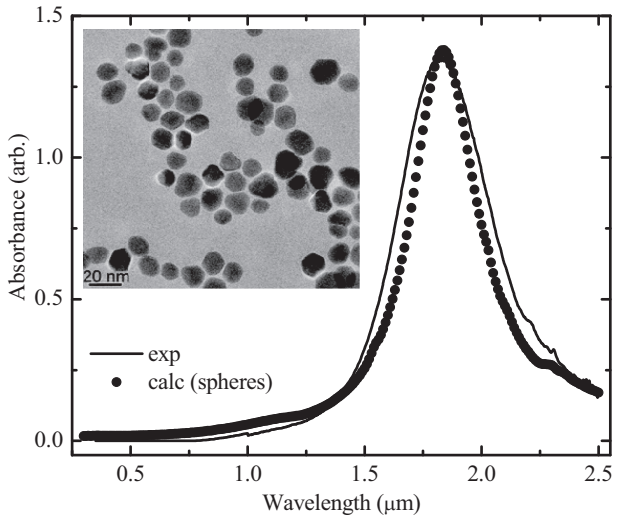

FIG. 1. Main figure shows spectral absorbance as measured using an ASD Quality Spec Pro VIS/NIR spectrometer for an as-synthesized (non-ligand exchanged) dilute suspension of colloidal ITO nanocrystals (solid curve) and as computed from a model described in the main text (symbols; the vertical scale was adjusted to coincide with the measurement at the peak). Inset depicts a TEM image of ITO nanocrystals; data were obtained with a JEOL 2100 operated at 200 kV.

low transmittance in Fig. 3 is caused by an absorption band whose intensity depends on the ITO content. Table I shows T_{lum} and T_{sol} obtained from

$$T_{\text{lum,sol}} = \int d\lambda \varphi_{\text{lum,sol}}(\lambda) T(\lambda) / \int d\lambda \varphi_{\text{lum,sol}}(\lambda), \qquad (1)$$

where φ_{lum} is the sensitivity of the light-adapted human eye[14] and φ_{sol} is solar irradiance for air mass 1.5 (the sun at 37° above the horizon).[15]

The optical data in Fig. 3 are theoretically addressed next. We assume that ITO nanoparticles with $D \ll \lambda$ are embedded in a continuous matrix, which implies that a Maxwell-Garnett effective medium treatment is appropriate.[16,17] Following established notation,[18–20] the effective dielectric function ε^{MG} is

$$\varepsilon^{MG} = \varepsilon_m (1 + {}^2/_3 f\alpha)/(1 - {}^1/_3 f\alpha), \qquad (2)$$

where ε_m is the dielectric permeability for the matrix and f is the "filling factor," i.e., the particles' volume fraction. For reasons given below, we consider a random distribution of ellipsoidal particles so that

$$\alpha = \frac{1}{3}\sum_{i=1}^{3} \frac{\varepsilon_p - \varepsilon_m}{\varepsilon_m + L_i(\varepsilon_p - \varepsilon_m)}, \qquad (3)$$

where ε_p is the dielectric function of the nanocrystals and the L_is are a triplet of depolarization factors given by the nanocrystals' shape. Spheres have $L_i = {}^1/_3$. Refinements of the theoretical model encapsulated in Eqs. (2) and (3) are possible.[21]

Our calculations assumed ITO nanocrystals in a polymer host, and f was calculated from weight percentages. We obtained ε_m from handbook values of the refractive index together with spectrophotometric measurements of the absorption coefficient.[22] The nanocrystal dielectric function ε_p was taken as ε_{ITO} and was computed as in earlier work,[9] assuming a free electron plasma with singly charged tin impurities screened according to the random phase approximation with exchange represented by Hubbard's model.[23]

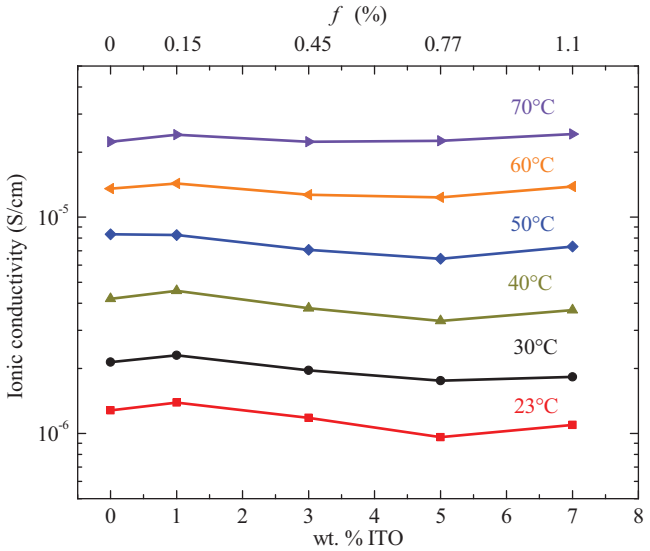

FIG. 2. Ionic conductivity vs ITO content in wt. % as well as volume fraction (filling factor, f) at the shown temperatures. Data points are indicated by symbols, which are joined by straight lines for convenience. The data were taken by use of a Novocontrol BDC-N dielectric interface together with a Solartron 1260 frequency analyzer; the applied ac voltage was 1 V.

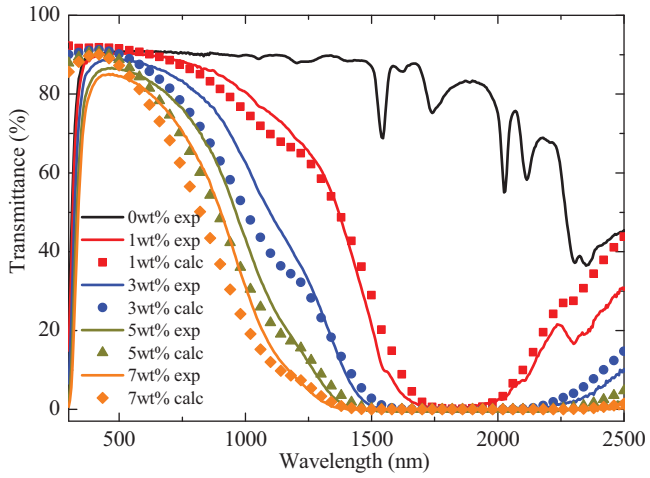

FIG. 3. Spectral transmittance for the shown ITO contents as measured (solid curves) and calculated (symbols) for ~70-μm-thick (PEI-ITO)-LiTFSI. The measurement used a Perkin Elmer 900 spectrophotometer with a barium-sulphate-coated integrating sphere. The sharp drops at the shortest wavelengths are dominated by absorption in the glass slides.

TABLE I. Luminous and solar transmittance, T_{lum} and T_{sol}, for ~70-μm-thick (PEI-ITO)-LiTFSI layers with different ITO content.

ITO content (wt. %)	0	1	3	5	7
T_{lum} (%)	91.7	90.7	88.7	85.7	83.3
T_{sol} (%)	88.9	77.3	68.8	61.1	56.3

We first modeled the absorbance data in Fig. 1 using a free electron density n_e of $9.8 \times 10^{20}\,\mathrm{cm}^{-3}$,[24] and this value was then employed to represent the data in Fig. 3. It is seen that theory and experiment are in good semi-quantitative agreement for all samples. The calculated data display a weak "shoulder" at $\lambda \approx 1200\,\mathrm{nm}$; its origin is unknown, but it is striking that this feature lies close to a wavelength where the real part of ITO's dielectric function crosses zero and the real part of the corresponding dynamic resistivity has a "knee."[9] Some other minor discrepancies can also be found between experimental and theoretical data, and nanocrystal aggregation deserves consideration as a possible source of those. Dipole-dipole interaction due to clustering can be included in an effective medium treatment via *effective* depolarization factors, denoted L_i*, in Eq. (3). Specifically aggregates in the form of chains and fcc clusters are represented by triplets of L_i*s being (0.133, 0.435, 0.435) and (0.0865, 0.0865, 0.827), respectively.[25] Figure 4 illustrates the effect of including aggregates in the model for a sample with 1 wt. % ITO and again using $n_e = 9.8 \times 10^{20}\,\mathrm{cm}^{-3}$. In this case, the model clearly diverges, which lends additional credence to our conclusion that the optical data in Fig. 3 are consistent with essentially well-dispersed ITO nanocrystals. Non-spherical shapes of the ITO nanocrystals, evident from Fig. 1, may add some broadening of the transmittance minimum in Fig. 3, though.[26]

In summary, we have incorporated ITO nanocrystals in a transparent polymer electrolyte and demonstrated that high haze-free luminous transmittance can be combined with strong near-infrared absorption without compromising ionic conductivity. An effective medium treatment for well-separated nanocrystals could be reconciled with the optical data. Our material is of large interest for opto-ionic devices such as laminated electrochromic smart windows. We note that our work is a proof-of-principle, and there are innumerable ways for development by using alternative polymer electrolyte hosts[27] and other kinds of transparent conducting nanoparticles such as ZnO:Al,[28] SnO_2:Sb,[29] M_xWO_3 (M being Na, K, or Cs),[30,31] or LaB_6.[32,33] There are also numerous routes to nanoparticle and nanowire fabrication, as recently surveyed for ITO.[34] An interesting development of the present work would be to use VO_2-based nanoparticles[20] to enable devices with joint electro- and thermochromism.

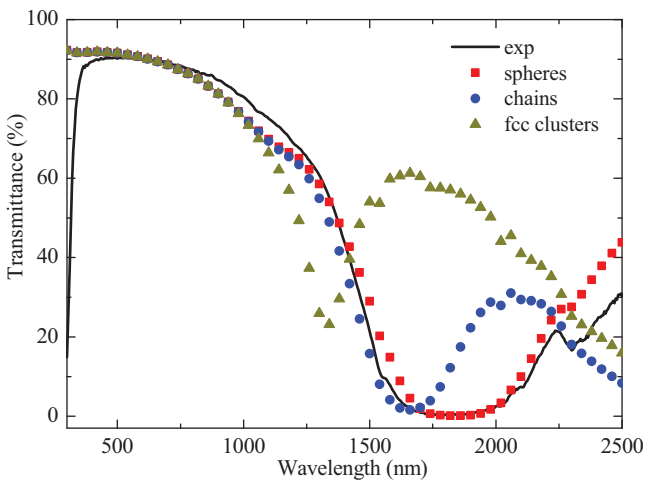

FIG. 4. Spectral transmittance for ~70-μm-thick (PEI-ITO)-LiTFSI with 1 wt. % ITO as measured (solid curve, also shown in Fig. 3) and computed (symbols) using (effective) depolarization factors appropriate to spheres, chains, and fcc clusters.

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