Electrochromic devices operating in the near infrared are being developed as a part of smart windows that can dynamically modulate visible light and heat transmittance of solar irradiation, dependent on weather conditions and personal preferences. Here, doped metal oxide nanocrystals are used to obtain the desired effect in the infrared spectral region. Specifically, the infrared transmittance is electrochemically modulated by control of the carrier concentration in the nanocrystals. While indium tin oxide nanocrystals are already known to provide this effect, the consequence of ligand treatment during preparation of the nanocrystal electrode on the electrochromic properties is studied. The type of ligand treatment is shown to affect the surface morphology, as well as the localized plasmon resonance energy of the nanocrystal films. A short and convenient treatment by ethanedithiol cross-linking ligands is shown to provide superior results as compared with the formic acid treatment used in the previous work. Future work combining windows based on optimized electrochromic effects in the near infrared combined with those in the visible spectral range will simultaneously improve building energy efficiency and indoor human comfort. 

1. Introduction

Electrochromic devices change their color, reflection, and absorption, in response to either an electron transfer process or application of an electrical potential. They are omnipresent in daily life, at least in the form of antidazzle rearview mirrors in cars, or as state-of-charge indicator strips of batteries. Currently, one of the most important goals of current research in electrochromic devices is the development of smart windows, applied in buildings to save air-conditioning costs and energy by controlling the incident sunlight, and heat radiation. While most electrochromic windows are designed to operate for light-dimming, Llóedes et al. introduced a nanocomposite material with tunable visible light and near-infrared transmittance. This composite enables the development of smart windows with several switchable states, including dimmed, transparent, cold, and hot. The heat radiation transmittance control was obtained in this composite by indium tin oxide (ITO) nanocrystals exhibiting a widely tunable localized surface plasmon resonance (LSPR). While metal oxide nanocrystals with plasmonic resonances represent an active field of present research, there are only a few reports on electrochromic device performance based on such materials. The device performance will depend not only on the nanocrystals’ plasmonic properties, but also on the morphology of the electrodes fabricated from the nanocrystals. Operating as electrodes, the nanocrystal films, on the one hand, have to be electrically conductive and, on the other, should also provide an effective interface to the electrolyte, enabling tuning
of the plasmon resonances. As it is known from numerous nanocrystal-based devices, including solar cells and light emitting diodes, surface morphology and electrical conduction crucially depend on the choice of the nanocrystal ligands and their post synthetic treatments. Here, we compare the results of an infrared electrochromic device based on ITO nanocrystals with two different ligand treatment procedures. The first one is performed with formic acid (FA) as reported previously in the literature to provide a shift of the localized surface plasmon over a wide range, and the second one is based on treatment by 1,2-ethanedithiol (EDT), representing a highly successful ligand in colloidal quantum dot-based devices. Both ligand treatments convert the insulating nanocrystal layer present after deposition into a conductive one, which is required for use as an electrode. As a result, we demonstrate a superior electrochromic switching behavior in the EDT-treated devices, as compared with the previously applied FA-treated ones. These superior switching attributes partially to the fortunate surface morphology, exhibiting in the case of EDT-treated electrodes etch pits, and higher surface roughness as compared with the FA-treated electrodes showing instead microcracks through the film.

2. The Device Concept

We investigated electrochromic devices based on the “battery type” as shown in Figure 1a. The components of the cells, working and counter electrodes as well as the electrolyte, are all transparent in the visible spectral region, so that the cell appears similar to a usual glass window. The electrochromic effects in the device are designed to modulate the transmittance solely in the infrared spectral region. Unlike conventional electrochromic devices based on metal oxide electrodes where the metal ions are reduced by intercalating cations from electrolyte solution leading to a change of the materials absorbance, in ITO nanocrystal-based devices presented here, tuning of LSPRs results in transmittance change of the devices. As suggested by Garcia et al., carrier accumulation/depletion close to the nanocrystal surface, by addition/removal of cations from the electrolyte (Figure 1c), results in modulation of the LSPR energy. For tuning the LSPR, the ITO nanocrystals have to be exposed directly to the electrolyte, despite being embedded within a film electrode of some thickness to guarantee sufficient light extinction. A porous film morphology therefore appears to be advantageous for optimized electrochromic effects. To obtain such porosity, different strategies have been reported including preparation of polymer/nanocrystal composites with thermal removal of the polymer or applications of methods providing porous films right after deposition. Hitherto, we show an alternative ligand treatment for electrode optimization, involving a short and simple process based on EDT to obtain high bright/dark near-infrared modulation of the devices.

3. ITO Nanocrystal Electrodes

The ITO nanocrystals, synthesized via a hot injection method developed by Gilstrap et al., with a size of 5.5 nm ± 1 nm and a Sn concentration of 10%, demonstrate a green blue color in concentrated solution(Figure 1b), and become transparent when diluted. After spin casting on a glass substrate, the obtained films with a thickness of 148 ± 5 nm appear glass like and transparent. Measured by 4-probe technique the films are electrically insulating, owing to the myristic acid (MA) ligands, which have to be either removed or exchanged with a smaller species to obtain any electrical conduction. This is done in two ways following optimized procedures, the first was demonstrated for ITO nanocrystal electrodes in ref. and the second for PbS quantum dot-based solar cells in ref. In PbS quantum dot solar cells, an EDT treatment is applied to a thin interface layer of quantum dots to operate as hole transport and extraction layer, on top of the quantum dot-based active layer. EDT treatment was also shown to convert an insulating PbS quantum dot layer into a highly photoconducting one. The procedures how to exchange the two different ligand species chosen here for the ITO nanocrystal-based electrodes are completely different (Figure 2). While in the first case, the ITO nanocrystal films are immersed for 45 min in a solution containing the FA ligands to replace the MA, in the second procedure the fatty acid ligands are removed and replaced by EDT species much more aggressively, within 30 s. In PbS and other semiconductor quantum dot materials, small organic ligands are known also to etch the quantum dots, which can severely damage the devices after longer treatment time. On the contrary, the EDT treatment is very convenient because it is performed directly after ITO film deposition by spin casting, without removing the samples from the chuck. In addition, rinsing and drying of the samples after EDT treatment is achieved by keeping the sample on the spin coater.
When the ligand exchange procedures are applied as described earlier, for both cases after ligand exchange the nanocrystalline structure of the films is retained. The X-ray diffraction (XRD) spectra obtained for the films (Figure 3a), as deposited and after the two different ligand treatments, show the same peak positions and peak width, which are characteristics for ITO nanocrystals with a size of 5.5 nm. Moreover, the peaks of ITO nanocrystals before and after processing coincide with the peaks of the ITO powder material. The intensities of the individual peaks are different, which we attribute to variations in film thickness. The optical properties of the films after the different ligand treatment procedures are, however, clearly different (Figure 3b). The nanocrystals kept in solution exhibit a pronounced LSPR with a peak at a wavelength of 1800 nm (Figure 3b). In the spin casted film, this resonance is broadened and the peak is red shifted to 2200 nm. Ligand exchange results in a further red shift, with respect to the nanocrystals covered by MA ligands. The plasmon resonance energy is known to sensitively depend on various parameters, such as carrier concentration, particle shape, or dielectric function of the matrix. Here, the red shift attributes to a change of the nanocrystals environment. The environment of the nanocrystals changes by going from solution to film to ligand exchanged film. The exchange from long to short species results in an increasing fraction of solid ITO material within the film volume. It was determined by assuming that the nanocrystals are spheres arranged in a highest density packaging provided by a face-centered cubic arrangement, considering the experimental nanocrystal size (5.5 nm) and the theoretical sizes of the different ligand species (which we found to be in close agreement with statistical measurements of nanoparticle distances from the scanning electron microscope images in Figure 4). The ligand exchange results in a densification of the nanocrystals after ligand exchange, from \( f = 0.35 \) in the as-deposited film containing long chain MA ligands, to 0.43/0.47 for the EDT and FA-treated films. A higher volume fraction provides a lower contrast of the dielectric function between nanocrystals and its environment, providing a decrease in the localized surface plasmon energy, being in line with the observed red shift.

The different ligand treatments not only result in different volume ratios of the ITO in the film, but also in different surface morphologies (Figure 4). The ITO nanocrystals covered by MA ligands exhibit after deposition a smooth surface and a homogeneous surface coverage. After immersion in FA, which results in an increase in the ITO nanocrystal packaging throughout the film volume, numerous nanosized cracks are formed throughout the film (Figure 4a), to compensate for the volume loss of ligand material during exchange of bulky to small ligand. These cracks form an irregular pattern throughout the sample surface; however, within the cracks, the film is rather smooth and of low roughness (Figure 4b). The surface treatment by EDT, in contrast, does not result in any cracks, but instead forms indications of surficial etch pits (Figure 4d). These etch pits have an approximate depths of 13 nm and a width in the order of 2 \( \mu m \), as is estimated from the profile in Figure 4e. Between the etch pits a pattern of walls is formed contributing to an increased surface roughness of the EDT-treated films, as compared with the FA-treated ones. In addition, within the etch pits, a lower surface density of nanoparticles as in the case of FA-treated nanocrystals is observed (Figure 4c,f). This higher surface roughness eventually also contributes to a difference in the electrochromic behavior of the electrodes.
4. Electrochromic Device Properties

The most important feature of an electrochromic device is the alteration of the optical density upon application of an electric potential.\textsuperscript{[14,33]} The optical density of the complete electrochromic devices (0 V lines in Figure 5) are affected not only by the plasmonic resonance features of the ITO nanocrystal electrodes (shown in Figure 3), but also by the absorption of the glass substrates, the sputtered ITO contact layers, and the electrolyte. While the glass substrates are virtually transparent up to a wavelength of 2500 nm, special care has to be taken in respect to the sputtered ITO electrodes. Standard ITO electrodes have a resistivity of $10 \, \Omega \text{cm}$ and they are partly opaque in the near-infrared spectral region of interest. Thus, here electrodes with a resistance of $100 \, \Omega \text{cm}$ were used, to obtain optical transparency in this spectral range. These sputtered ITO electrodes did not show any electrochromic effect, in contrast to the ITO nanocrystal films. The propylene carbonate (PC) solutions containing a Li$^+$ salt, acting as an electrolyte, showed a series of distinct absorption peaks in the near-infrared region. These peaks are superimposed on top of the plasmonic absorption of the ITO nanoparticle electrode displayed in between 1100 and 2200 nm in Figure 5. At longer wavelengths almost no electrochromic effects are observed, due to the strong absorbance by the electrolyte. The absorption of the PC also limits the thickness of the electrochromic devices to the millimeter range. The device characteristics were measured for a thickness of the electrolyte of 2 mm. The devices based on the FA-treated ITO nanocrystal electrodes show the basic operation of an electrochromic infrared smart window (Figure 5a). Application of a positive voltage between working and counter electrode results in a bleach of the device, whereas application in the opposite direction results in an increase in its absorbance. As discussed in refs., \textsuperscript{[1,15,33]} these effects are associated with a shift of the plasmonic resonances. Increasing the density of free electrons in the ITO conduction band provides a blue shift, which, in turn, increases the optical density in the near-infrared spectral range up to 2000 nm, whereas removal of electrons results in a red shift and thus decrease in absorbance in the monitored spectral region. The change of the electron concentration in the ITO nanocrystals is caused by the formation of a depletion or an accumulation layer, located close to the nanocrystal surfaces. These
layers form upon enrichment or dilution of the nanocrystals surfaces with Li$^+$ ions from the electrolyte, under an applied bias. By changing the bias between ±4 V, at a wavelength of 1800 nm the ratio of the optical density measured between amounts to ±250% (turquoise line in Figure 5). At this wavelength, the optical density varies in between 0.35 and 0.9. To observe such an effect, first a bias of −4 V was applied for 40 min, and then the switching of the bias between the individual values was performed. For each value the bias was kept for 15 min before the spectra were measured, to allow for full change of optical absorbance. In comparison with the sample with FA-treated electrodes, devices with electrodes based on EDT-treated films showed a higher absorbance within the desired wavelength range, as shown in Figure 5b. This higher absorbance is caused by the plasmon resonance energy of the EDT-treated film. As shown in Figure 3, the plasmon resonance of EDT-treated ITO electrode is found at 2200 nm, whereas that of the FA-treated electrode is found at 2500 nm (further red shifted in respect to the wavelength region of interest). However, by applying a voltage of +4 V the electrochromic devices based on EDT-treated electrodes becomes at least as transparent as that based on FA-treated electrodes. When an opposite voltage is applied (−4 V), the optical density measured at 1800 nm increased to 1.1, resulting in a transparent/dark transmittance ratio of 310%. This value is superior to the 250% observed with the devices based on FA-treated electrodes. This superior modulation capability of the EDT-treated electrodes ascribes to the advantageous micro- and nanostructure of these nanocrystal films. Cracks in the films as observed for the FA-treated electrodes, for instance, act as short circuit through the nanocrystal electrode, which do not contribute to the electrochromic effect. The lower volume fraction of solid ITO material in the EDT electrode also facilitates intercalation with Li$^+$ ions, which cause the electrochromic effect in the ITO nanocrystals. The higher surface area observed for EDT-treated electrodes due to the formed etch pits exposes more ITO nanocrystals directly to the electrolyte than a flat nanocrystal film. Thus, clearly the morphology plays an important role for the electrochromic effect, and it is the reason for the more advantageous property of the EDT-treated film as compared with the FA-treated ones.

Finally, the stability of the electrochromic devices was tested. Cycling the bias voltage between ±4 V resulted in an initial decrease in the bright/dark transmittance change by 7%; however, after that initial decrease the bright/darkness contrast stabilized after more than 40 switching cycles.

5. Discussion

The aforementioned results show that the EDT treatment provides a slightly better result with respect to optical density ratio between applied electrical potentials with opposite signs, as compared with FA treatment. Of course, such a comparison also depends on other parameters, for instance, the number of deposited nanocrystal layers, which controls the thickness of the electrochromic layer. While a single nanocrystal layer, after one spin casting step, provided a thickness of 150 nm, a double layer showed twice that thickness, and triple layered samples were ±410 nm thick. With increasing total thickness, the optical density in the infrared blocking state was almost the same for both ligand treatment methods. However, in the transparent state the triple layered samples were not clear but showed scattering effects. Even at short wavelengths, where no plasmonic peak is observed, the transmittance was considerably decreased. This undesired effect was more pronounced for the FA-treated sample than for the EDT ones, underlying the suitability of EDT for nanocrystal treatment.

In the work of Llordes et al., the tin-doped indium oxide nanocrystals were covered by niobium oxide (NbO)x clusters, forming a glass matrix, resulting in distinct electrochromic effects in two separate spectral regions, in the visible and in the infrared. Similar effects could be obtained with our indium-tin-oxide electrodes by assembling them to a smart window with a second electrochromic electrode operating in a complementary spectral range. To obtain several switchable states from one device, it would be important that the complementary electrodes show its switching transitions at different applied potentials than the ITO electrode, which should not be too difficult to achieve, considering the large range of electrochromic materials known to operate in the visible spectral region.[1]

To compare electrochromic devices from different materials or fabricated by various methods, a suitable parameter is the coloration efficiency. It relates the change of the optical density per electrical charge required to induce that change. The charge was obtained by integration of the cyclic voltammograms measured at different scan rates. For a wavelength of 1970 nm, where we observe the largest change of optical density, we obtained a coloration efficiency of $368 \pm 58 \text{cm}^2 \text{C}^{-1}$ which is in close agreement with the value reported in ref. [14] for plasmonic ITO nanoparticle-based smart windows of $375 \text{m}^2 \text{C}^{-1}$. For the EDT-treated electrodes, a considerable higher value of $499 \pm 47 \text{cm}^2 \text{C}^{-1}$ was achieved. This comparison shows that the EDT treatment of the ITO nanocrystals results in improved electrochromic performance, not only in comparison to own reference samples but also in comparison to accepted values in literature. Thus, the ligand treatment procedure introduced by us results in improved electrochromic response for electrochromic devices, which can find applications eventually in windows, to control the transparency of heat radiation.

6. Conclusions

Electrochromic devices operating in the infrared spectral region are developed to control heat radiation through smart windows in addition to the visible sun light. In the battery type of electrochemical devices, the electrochromic effect is related to the tuning of the LSPRs in transparent metal oxide nanocrystal film electrodes. Application of an electric field controls the nanocrystal surface coverage with cations from the electrolyte, affecting the free carrier concentration in the nanocrystals. Here, the effectiveness of this process is investigated in dependence on the surface treatment of the nanocrystal films, performed during deposition. The highest transmittance contrast upon voltage switching was found by making use of a ligand treatment procedure based on EDT ligands. As compared with the FA ligand treatment, the EDT procedure avoids the formation of cracks

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in the film, possibly due to its cross-linking nature proven for other nanocrystal systems. Furthermore, it results in a more moderate red shift of the localized plasmon resonance energy so that the transmittance modulation is observed at wavelengths for which the glass substrates and the electrolyte are transparent. Together with its short treatment time, the EDT treatment is thus a good candidate for scaling up the fabrication processes to sizes, which are required for applications in windows, used to control the heat radiation into buildings.

7. Experimental Section

Synthesis of ITO Nanocrystals: The tin-doped indium oxide nanocrystals were synthesized according to a method developed by Gilstrap et al.\textsuperscript{[14]} however, with a fourfold amount of materials. First, a carboxylate precursor solution was prepared by adding 0.045 mM indium acetate, In(OAc)\textsubscript{3}, 0.005 mM tin acetate, Sn(OAc)\textsubscript{2}, and 0.15 mM MA in 80 mL of 1-octadecene (ODE) and filled in a three-necked flask. This carboxylate solution was connected to a Schlenk line, rinsed several times with argon, and then degassed under vacuum at 110 °C for 2 h. During this time the indium acetate and the tin acetate reacted with MA to form indium myristate and tin myristate. Then the myristate solution was heated to 295 °C. Meanwhile, an amine precursor solution was prepared from 3 mmol oleylamine (OAm) in 4 mL of ODE. This amine solution was quickly injected into the myristate solution using a syringe. Immediately afterward, the temperature of the solution was reduced from 295 to 280 °C and kept at this temperature for 1 h. Within 2–3 min after injection, the solution turned slightly yellow, indicating initial oxide formation by hydrolysis. The color of the solution changed in the next 5 min as the reaction progressed further to orange, and finally to dark green. The temperature was further reduced to 240 °C and kept at this temperature for a further 60 min. After cooling down to room temperature, the material was separated from solution (using acetone as antisolvent for this step) by centrifugation and washed with toluene/acetonitrile (4:1) anhydrous. Finally, the nanocrystals were dispersed in hexane–octane mixture (1:1).

Preparation of the Electrochromic Devices: The electrochromic electrodes of the devices made use of indium tin oxide covered glass substrates (1 × 1 in.) with a resistivity of −100 Ω cm, providing a transparency >85% in the near-infrared spectral region. ITO nanocrystals were spin coated (1000 rpm, 30 s, spin coater from Ossila) on cleaned substrates (ultra sonicated in deionized water, acetone, and 40 °C hot isopropanol for 15 min each) from a 1:1 octane/hexane solution. After the spin coating a ligand exchange was performed followed by deposition of a second layer on top of the first one again with a ligand exchange treatment. For ligand exchange two methods were applied. 1) Immersion in solution of FA (1 M in acetonitrile) for 45 min, followed by a washing in acetonitrile and drying by compressed air. 2) EDT treatment, 0.01 vol.% EDT in acetonitrile was deposited over the entire surface of the ITO nanocrystal layer, where it reacted for 30 s, before being removed from the sample by spin coating (2500 rpm for 10 s). The EDT solution was removed by rinsing with ethanol (3 times). Afterward, the electrodes from both methods were heated to 250 °C (1 h in a nitrogen atmosphere).

The electrochemical devices were assembled by putting together the electrochromic electrode and a (100 Ω cm) ITO-covered glass substrate as counter electrode, via a 1 mm-thick spacer element (a ring of TitanX deposited by a 3D-printer, Ultimaker 2). The cavity formed by the spacer element and the two adjacent electrodes was filled by liquid electrolyte (1 M Lithium perchlorate (LiClO\textsubscript{4}) in PC) via a small hole in the spacer by a syringe. This was done in nitrogen atmosphere and finally the hole was sealed by a cyanoacrylate-based glue (Pattex Ultra Gel PSMG3), so that all following experiments could be performed in ambient conditions.

Visible/Infrared Spectroscopy and Photoelectrochemical Experiments: The absorbance on the electrodes was measured by a Perkin Elmer spectrometer (LAMBDa 950) with operating from the UV up to 2700 nm. To obtain photoelectrochromic spectra, a home-built setup was used. Illumination source was a 12 V halogen lamp, passing first an Acton SP2150i monochromator and then via a light chopper (100 Hz) the electrochromic cell. The signal was measured by a photoconductive PbSe infrared detector (Laser Components), amplified by a lock-in amplifier (Signal Recovery, 7265 DSP) and registered by a computer. The transmission of the cell was measured as a function of the applied potential between the working and counter electrode, provided by a Keithley 2612B SMU. Appropriate filters were used to avoid second-order diffraction light after the monochromator.

Electron Microscopy: Images were taken with a Schottky field-emission scanning electron microscope JSM-7610F from JEOL Ltd. at an acceleration voltage of 15 kV, a beam current of 6 nA, and a working distance of 6 mm.

Atomic Force Microscopy: A Veeco Dimension 3100 Microscope was used in tapping mode. The applied Bruker silicon probes had a spring constant of 12–10 \textsuperscript{−3} N m\textsuperscript{−1} and 320 kHz resonance frequency; 1024 × 1024 pixels were measured for surfaces of 1 × 1 or 5 × 5 μm\textsuperscript{2}. The data were processed with a Gwydion .54 S roughness values by the statistical quantities tool embedded in the Gwyddion SPM analysis software.

XRD: A D8 ADVANCED ECO diffractometer from Bruker was used for XRD measurements. ITO nanocrystal electrodes were recorded in a parallel beam geometry with an angle of incidence of 0.5°. The obtained data were compared with the indium oxide data published by International Center for Development and Decent Work (ICDD).

Electrochemical Experiments: A CAMRY Interface 1000 Potentiostat/ Galvanostat/Zero Resistance Ammeter was applied for taking electrochemical data. The devices were cycled at different scan rates (100, 10, and 1 mV s\textsuperscript{−1}) by using three electrode or two electrode setup, respectively.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

O.M. and J.K. performed the synthesis of the ITO nanocrystals, the ligand exchange procedures, and the electrochemical characterization of the devices. A.E. performed the AFM analysis of the electrodes. A.-A.Y.-A. developed the device fabrication. N.K. assisted performed optical absorbance measurements. A.B. performed electron microscopy. N.K. performed the XRD measurements. M.H., K.G.W., and W.H. contributed to the writing of the manuscript. W.H. coordinated the project.

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