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Ethanol solvothermal method derives plasmonic Al doped ZnO nanocrystals suitable for advanced applications.
A straightforward and “green” solvothermal synthesis of Al doped zinc oxide plasmonic nanocrystals and piezoresistive elastomer nanocomposite

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Plasmonic oxide nanocrystals hold great promise in a wide range of applications, for which the availability of scalable and “green” synthesis methods is prerequisite, whereas until recently an excellent response has been demonstrated only for samples prepared through intricate synthesis paths. We report here a simple ethanol solvothermal synthesis route of Al doped ZnO plasmonic nanocrystals (Zn$_{1-x}$Al$_x$O) at doping levels $x$ up to 0.15. The obtained Al doped ZnO samples consisted of nanoparticles and short nanorods with a diameter around 10 nm at $x=0.15$ doping level while reaching aspect ratio levels of 50 for lower doping levels. Detailed structural studies by powder X-ray diffraction Rietveld refinement, X-ray absorption and photoelectron spectroscopies show that all samples maintain the structure of phase-pure zincite of space group $P\overline{6}mc$. The resulting powders exhibit strong infrared absorption, while remaining largely transparent for visible light, enabling the preparation of transparent colloidal dispersions. Furthermore, as a test of applicability in a practical device, the nanocrystals were used to prepare transparent piezoresistive Zn$_{1-x}$Al$_x$O - polydimethylsiloxane composites. The prepared sensor material exhibits excellent repeatable and reproducible piezoresistive behaviour.

Introduction

Plasmonic semiconductor oxide nanocrystals such as Al-doped ZnO (AZO),1-3 indium-doped ZnO (IZO),4,5 Ga-doped ZnO (GZO),6 Sn-doped In$_2$O$_3$ (ITO),6,7 Sb-doped SnO$_2$ (ATO)8,9 or others10-14 have attracted growing attention due to their applicability in many optoelectronic applications, such as near-infrared selective electrochromic devices,15 (flexible) displays11 and polymer light emitting diodes.4 They also demonstrate excellent bio-sensing and chemical sensing capabilities.16 These materials exhibit localised surface plasmon absorption (LSPA) features in the near-infrared and mid-infrared range due to resonance frequency of collective oscillations of excess electrons or holes.5 Historically, LSPA is better known for phenomena in nanostructures of noble metals for which the plasmonic band is located in visible range.17 For oxide semiconductors, LSPA has been most commonly observed in n-type materials with extra conduction band electrons.18 Extra electrons are introduced by aliovalent donor doping where the impurity atoms in a higher charge state replace some host cations in the lattice.1 According to the Drude-Lorentz theory, the absorption will increase and resonance peak will shift to higher energies with increasing free charge carrier concentration.19 The aliovalent doping is therefore expected to result in a reasonably high LSPA in oxide semiconductors at high doping levels when the host oxide becomes a degenerated semiconductor with high extrinsic electrical conductivity.3 In metals, the resonance frequency of collective oscillations of electrons is sensitive to particle size, shape and properties of the surrounding medium.20 Contrary to metallic nanoparticles, the plasmon resonance frequency of free electrons in doped oxide semiconductors can be varied by changing the dopant type and concentration, thus providing alternative opportunities for plasmonic tailoring of light absorption.21

Synthesis of high quality plasmonic semiconductor oxide nanocrystals is a considerable challenge. The LSPA effect has been observed in semiconductor oxide nanocrystals synthesised by intricate synthetic methods such as hot-injection, which requires metal-organic precursors consisting of an inorganic cluster and coordinating organic ligands.22 Hot-injection is capable of yielding high quality colloidal metal oxide semiconductor nanocrystals with a controlled shape and high doping level, where dopants substitute the targeted atoms in a crystal lattice. However, hot-injection is harsh and not scalable to the industrial level. To be able to utilise the effect of LSPA in applications, it is necessary to find ways to use alternative high yield and environmentally-friendly chemical synthesis methods. The hydrothermal or solvothermal methods are well known solution-based, low-cost synthesis processes that are scalable

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Hydrothermal or solvothermal crystal growth is performed in aqueous or non-aqueous hot solutions under high pressure in an autoclave. These synthesis processes are often used to obtain well-ordered crystal structure metal-doped ZnO diluted magnetic semiconductors, photocatalysts, photoanodes and photodetectors. Although these routes for synthesis of AZO nanomaterials have been studied in a number of earlier reports, to the best of our knowledge, the availability of the LSPA effect in the produced samples has not been previously demonstrated for solvothermally or hydrothermally derived doped ZnO nanocrystals. Meanwhile, high electrical conductivity and LSPA absorption in the infrared range has been observed for high quality AZO, GZO and IZO colloidal nanocrystals obtained by hot-injection synthesis. In the present article we demonstrate plasmonic properties of AZO degenerated semiconductor nanocrystals synthesised by a “green” ligand-free solvothermal method using simple Al and Zn salt precursors. AZO has several advantages over other conductive oxides due to Zn and Al abundance in nature, low production costs and low toxicity. To add to the versatility of the results, the obtained AZO nanocrystals were mixed into polydimethylsiloxane (PDMS) to create a hyperelastic piezoresistive composite sensor material. Hyperelastic piezoresistive composite materials can be used in currently less probable applications, which are out of reach for the mechanically rigid technology, such as biomedical devices, wearable strain and motion sensors, smart clothes, and sensory skin for a robotic system. By now the hyperelastic piezoresistive or tenoresistive sensors have been based on carbon-based or metallic filler polymer composites, but ferroelectric oxide nanofillers have been used in flexible piezoelectric polymer composites for strain sensing, acoustic sensing and energy harvesting. To the authors’ best knowledge, only Ishigure et al. have investigated oxide based (Sb-doped SnO and La$_{0.5}$Sr$_{0.5}$CoO$_3$) piezoresistive polymer composites and their electrical properties, but until now no plasmonic oxide nanocrystal based piezoresistive polymer composites have been reported that would exhibit optical transparency. Here we demonstrate plasmonic oxide nanocrystals to be used as alternative fillers in piezoresistive sensors. As compared to carbonaceous or metallic filler based analogue, this type of system potentially exhibits transmittance in the visible range due to a wide band gap, lower charge carrier concentration and consequent plasmon resonance shift to infrared spectral range.

**Experimental details**

ZnO and Al doped ZnO powders were synthesised using a solvothermal method. Zinc acetate dihydrate (Zn(CH$_3$CO$_2$)$_2$-2H$_2$O) (98%, Sigma Aldrich) was dissolved in 15 ml ethanol (99%, Merck) to obtain 0.1 M solution. Simultaneously, 30 ml of 0.5M NaOH (98%, Sigma Aldrich) solution in ethanol was prepared. Both solutions were heated to 80 °C and vigorously stirred in a closed glass vial until clear solutions were obtained. The two solutions were mixed and left under stirring at 80 °C for the next 10 h. The mixture was transferred into a 50 ml Teflon-lined stainless steel autoclave, sealed and heated at 150 °C for 24 h. The obtained precipitates were filtered, washed with methanol, and dried in air at 60 °C for 5 h. For doped ZnO synthesis a proportionate amount of Zn(CH$_3$CO$_2$)$_2$-2H$_2$O in ethanol was replaced with Al(NO$_3$)$_3$·9H$_2$O (98%, Sigma Aldrich) to obtain Zn$_{1-x}$Al$_x$O (where x = 0, 0.025, 0.050, 0.075, 0.100 and 0.150).

The phase composition of the as-synthesised powders was analysed by powder X-ray diffraction (XRD) and Rietveld refinement. The powders were hand-milled in acetone for 5 minutes using an agate mortar and pestle. After drying, some of the material was transferred into a glass capillary of 500 μm in diameter (Mark tube No. 4007805, glass no. 10, Hilgenberg, Malsfeld, Germany) and measured on a Bruker D8 Advance diffractometer (Bruker, Karlsruhe, Germany). The 2θ scan range was 25°–120° (step size of 0.0122°) using (Ni- and digitally filtered) Cu Kα X-radiation. The counting time of 6.5 seconds per step resulted in a total measurement time of approximately 14 hours per dataset. Rietveld refinement was carried out with the software BGMN version 4.2.2243 and was compared with a wurtzite structure of ZnO published by Kisi and Elcombe. Refined parameters included the scale factor, unit cell dimensions a and c, and anisotropic peak broadening. The latter parameter was used by the refinement software to calculate mean crystallite domain sizes.

The X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS) experiments were carried out at beamline D1011 of MAX II synchrotron storage ring (Lund, Sweden). The beamline is equipped with a modified SX-700 plane grating monochromator. XPS spectra were measured by an electron energy analyser SCIENTA SES-200 in a fixed analyser transmission (FAT) mode with 200 eV pass energy. The sample was positioned at a normal emission with 40° incident angle for the incoming photon beam. XPS spectra were normalised to the synchrotron ring current to account for the variations in the photon beam intensity. The binding energy scales for XPS experiments were referenced to the C 1s transitions. Zn 2p and Al 2p photoelectron peaks were fitted by asymmetric Gaussian-Lorentzian line shapes after subtracting a Shirley background. The XAS was measured in total electron yield mode, with a spectral resolution of 0.12 eV at the O 1s and 0.33 eV at the Zn 2p threshold regions.

To measure the diffuse light absorbance of powder samples and transmittance of AZO colloids, a UV-Visible Shimadzu UV-3700 spectrophotometer (Shimadzu Scientific Instruments Kyoto, Japan) was used. Piezoresistive properties were measured for AZO-PDMS thin films. AZO nanocrystals (15 mg/ml) were ultrasonically dispersed in a butylamine (20%) and dichloromethane (80%) solution. The desired amount of PDMS (Sylgard 184; Dow Corning, Midland, MI) solution in hexane (10 mg/ml) and curing agent (Sylgard 184) solution in hexane (1 mg/ml) were added to the dispersion of AZO nanocrystals. The weight ratio of PDMS to curing agent was 10:1. Before spin coating, 90% by volume of solvents were evaporated out from the mixture under continuous shaking at room temperature. At the end, 50
μl of the final mixture was spin-coated on the rotating (1500 rpm) glass substrate (2.5x2.5 cm), coated by ITO finger electrodes. After spin coating the sample was left at 70 °C for 6 h for curing. After curing AZO-PDMS film in thickness 5 μm was obtained. ITO electrodes were produced by immersing ITO-covered glass (Rs = 15 Ω/sq; Kintec, Hong Kong, China) together with a mask into 36.5–38% HCl aqueous solution (Sigma-Aldrich) for 10 min. After etching, the substrate was rinsed with distilled water and the distance between fingers was 350 μm. Electrical resistance change in the cured AZO-PDMS film was measured under applied load as it underwent cyclic loading, applied by tapping the top of the film with a small rubber stack (6 mm in diameter).

Results and discussion

According to X-ray diffraction data (see Figure 1) all the samples have phase-pure zincite crystal structure of space group P63mc (no. 186). Substitution of up to 15% of Zn with Al during the synthesis is not observed to lead to separate Al (oxide) phases. We therefore conclude from the XRD that Al doping causes lattice shrinkage along c, but the elongation along c remained. The shape of the broadened peaks could be approximated, but not accurately modelled by the Rietveld software’s algorithms for crystallite size and micro-strain related peak broadening, which indicated the presence of abundant complex lattice distortions (substitutions and vacancies) in samples with Al substitution. The reduced quality of these datasets rendered a full structure refinement unfeasible, preventing us from more precise localisation and quantification of substitutions and vacancies. A marginal effect of Al doping on the unit cell dimensions was observed. The lattice constant c was approximately 0.1% shorter at 15% Al than the pure ZnO phase.

<table>
<thead>
<tr>
<th>x (Zn$<em>x$Al$</em>{1-x}$O)</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>Crystallite size &lt;1,0,0&gt; (nm)</th>
<th>Crystallite size &lt;0,0,1&gt; (nm)</th>
</tr>
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<tr>
<td>0</td>
<td>3.2496</td>
<td>5.20683</td>
<td>69.6 (0.9)</td>
<td>140.6 (5.1)</td>
</tr>
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<td>0.025</td>
<td>3.25066</td>
<td>5.20185</td>
<td>20.8 (0.3)</td>
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<tr>
<td>0.050</td>
<td>3.25040</td>
<td>5.20161</td>
<td>20.5 (0.3)</td>
<td>75.8 (3.3)</td>
</tr>
<tr>
<td>0.075</td>
<td>3.25017</td>
<td>5.20317</td>
<td>19.1 (0.3)</td>
<td>67.3 (3.0)</td>
</tr>
<tr>
<td>0.100</td>
<td>3.24993</td>
<td>5.20119</td>
<td>15.2 (0.3)</td>
<td>51.0 (1.8)</td>
</tr>
<tr>
<td>0.150</td>
<td>3.24904</td>
<td>5.20113</td>
<td>11.9 (0.2)</td>
<td>38.3 (1.2)</td>
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</tbody>
</table>

Table 1. Crystallographic parameters determined from XRD data by Rietveld refinement. 3σ intervals reported by the Rietveld refinement software are given in parentheses. Microstructural features of solvothermally synthesised pristine ZnO and AZO powders were studied by SEM and TEM (Figure 2). Pristine ZnO sample powder consists of hexagonal single crystalline nanowires with a diameter from 20 to 70 nm, length from 0.2 μm to 1 μm and aspect ratio up to 50. The addition of Al dopant decreased the aspect ratio to the extent that the sample with composition Zn$_{0.85}$Al$_{0.15}$O consisted of nanoparticles and short nanorods only (Figure 2 (b) and (d)). The length of the Zn$_{0.85}$Al$_{0.15}$O nanorods is below 50 nm with a diameter around 10 nm. Average sizes of nanocrystals of Zn$_{0.85}$Al$_{0.15}$O and other compositions were in good agreement with Rietveld calculations results given in Table 1. The increasing Al loading-related reduction in shape anisotropy can be rationalised via two mechanisms. First, according to Rietveld analysis, the Al doping causes lattice shrinkage along c attributed to the smaller Al$^{3+}$ (radius 0.53 Å) replacing the larger Zn$^{2+}$ (radius 0.74 Å), which further leads to a variation of the crystal aspect ratio due to ion diameter effects. Second, the replacement of Zn$^{2+}$ by Al$^{3+}$ increases charge density during nanocrystal growth due to the formation of free electrons, which compensates an excess positive charge from Al$^{3+}$. During hydrothermal synthesis ZnO crystal growth is facilitated by zinicate ion (Zn(OH)$_4^{2-}$) growth units, which may form at high pH values above 12 in accordance with reaction:

$$\text{Zn(OH)}_2 + 2\text{OH}^- \xrightarrow{pH \geq 12} \text{Zn(OH)}_4^{2-}$$ (1)

Free electrons formed by Zn$^{2+}$ substitution with Al$^{3+}$ make it difficult for the zinicate ions to diffuse to the crystal surface because of charge repulsion. The ZnO and the Zn$_{0.925}$Al$_{0.075}$O samples were further characterised using XPS and XAS. Figure 3 shows the Zn 2p, O 1s, Al 2p and valence band XPS of the ZnO and the Zn$_{0.925}$Al$_{0.075}$O nanocrystals. The Zn 2p XPS (Figure 4 (a))
contains the spin-orbit split 2p\textsubscript{3/2} and 2p\textsubscript{1/2} component bands, with a mutual energy difference of 23.2 (± 0.1) eV, with the Zn 2p\textsubscript{3/2} binding energy at 1022.0 (± 0.2) eV in ZnO and 1021.8 (± 0.2) eV in Zn\textsubscript{0.925}Al\textsubscript{0.075}O, indicating that Zn is in the 2\textsuperscript{+} charge state in both samples.\textsuperscript{36} The O1s XPS (Figure 3 (b)) contains two partially resolved components at approximately 530 eV and 531.5 eV binding energy. The component at 530 eV corresponds to the O\textsuperscript{2-} ions in the wurzite structure of ZnO, surrounded by Zn\textsuperscript{2+} ions (or Zn\textsuperscript{2+} substituted by Al\textsuperscript{3+} ions). Photoelectron peak at 531.5 eV is attributed either to the presence of loosely bound oxygen on the surface of the films or it belongs to hydrated oxides. It can also be associated with O\textsuperscript{2-} ions in the oxygen deficient regions within the matrix of ZnO.\textsuperscript{44} We have observed that the latter component becomes relatively higher for the Zn\textsubscript{0.925}Al\textsubscript{0.075}O sample as compared to the undoped ZnO nanowires. The Al 2p (Figure 3 (c)) XPS of the Zn\textsubscript{0.925}Al\textsubscript{0.075}O sample contains a single photoelectron peak positioned at 74 eV, indicating that only the Al\textsuperscript{3+} charge state is present (the metallic Al 2p line at 72.7 eV binding energy is not observed).

The O 1s and Zn 2p XAS results are presented in Figure 4. The Zn 2p edge absorption is virtually identical for the two samples, indicating that the Zn ligand coordination (and sublattice) remains unaffected by Al-doping. The O 1s edge absorption aligns well with previous reports for ZnO\textsuperscript{48,49} and is overall very similar to the two samples, which indicates a quite perfect preservation of local symmetry and ligand configuration, with a minimal gain in intensity for the Al-doped sample in the energy region; this coincides with the relatively structureless broad band of alumina absorption,\textsuperscript{50} as a result of the presence of Al 3p–O 2p hybridised states. However, we further notice that the Al 2p XAS (not shown) of the Zn\textsubscript{0.925}Al\textsubscript{0.075}O sample contained only a baseline, with the intense and structured alumina (α-Al\textsubscript{2}O\textsubscript{3}) features\textsuperscript{50} absent, indicating that no segregation of alumina occurred in the sample.

Figure S (left panel) shows the UV-NIR absorption spectra of ZnO and AZO samples. The AZO nanopowders with different Al content show strong absorption in the NIR region, while pristine ZnO exhibits a sharp absorption edge below 400 nm, while it is transparent in visible and IR. The appearance of absorption in the NIR region for AZO samples is a clear indication of the LSPA effect.\textsuperscript{51} The observed LSPA in the AZO samples can be regarded as an indication that the increase of free electron density upon Zn\textsuperscript{3+} substitution by Al\textsuperscript{3+} can be directly assessed from the optical properties. Zinc substitution by Al\textsuperscript{3+} can be expected to give rise to the formation of various point defects of which the majority would be zinc vacancies (V\textsubscript{Zn}), Al\textsuperscript{3+} on Zn\textsuperscript{2+} sites (Al\textsuperscript{3+}\textsubscript{Zn}), oxygen interstitials (O\textsuperscript{2+}i) or freestanding electrons trapped at an anion lattice vacancy (e\textsuperscript{-}). In AZO materials obtained under oxidising conditions, an Al\textsuperscript{3+}\textsubscript{Zn} defect is compensated either by a V\textsubscript{Zn}\textsuperscript{2-} or an O\textsuperscript{2+}i in accordance to eq. (2) and eq. (3), respectively:

\begin{equation}
\text{Al}_2\text{O}_3 \rightarrow 2\text{Al}^{3+} + 3\text{O}_2^{-}
\end{equation}

(2)

\begin{equation}
\text{Al}_2\text{O}_3 \rightarrow 2\text{Al}^{3+} + 2\text{O}_2^{-} + \text{O}_2^{2-}
\end{equation}

(3)

where O\textsubscript{2} stands for a regular oxygen site. Since these pathways will not give the (detached, trapped electron) e\textsuperscript{-} defects, it appears that in order to increase the density of (quasi) free charge carriers in the AZO, the synthesis...
should be carried out under non-oxidising conditions,\textsuperscript{52} where
generation of the e’ defects proceeds according to
\begin{equation}
A_2O + ZnO \rightarrow 2Zn + 2ZnO + \frac{1}{2}O_2 + 3O
\end{equation}
and becomes preferable. This will have a bearing on the LSPA
behaviour and related plasmonic of the material.

In order to probe the effect of synthesis environment on the
plasmonic behaviour of the obtained samples, the samples
were tested using UV-Vis absorption. First, the Zn\textsubscript{0.85}Al\textsubscript{0.15}O nanocrystals were used to produce visible light transparent
colloidal dispersions. Figure 5 (right panel) shows the
transmittance spectrum and photography of the Zn\textsubscript{0.85}Al\textsubscript{0.15}O colloidal solution in a mixture of butylamine (20%) and
dichloromethane (80%). Colloid of Zn\textsubscript{0.85}Al\textsubscript{0.15}O nanocrystals
shows strong absorption in the near-infrared region.

The optical absorption behaviour of the synthesised samples
shows that free electron formation in AZO materials is
favoured in ethanol solvothermal synthesis. The NIR
absorption initially increases with increasing Al dopant
concentration until it attains the strongest NIR absorption for
the Zn\textsubscript{0.925}Al\textsubscript{0.075}O sample. At even higher dopant levels,
however, the NIR absorption instead decreases again. The
possible causes for this latter decrease at higher Al
concentration probably stem from the lowered sample
definition at high Al concentrations, which can favour the
formation of non-reducible defect clusters that would act as
recombination centres and cause loss of produced charge
carriers.\textsuperscript{53}

In order to test the overall applicability of our results in case of
practical devices, the obtained Zn\textsubscript{0.925}Al\textsubscript{0.075}O nanocrystals
were mixed into PDMS to create hyperelastic piezoresistive
sensor composite material. According to percolation theory,
conductive fillers in insulating matrix, above a critical volume
fraction (percolation threshold) form a conductive network in
polymer matrix. The highest piezoresistive effect is expected
at filler concentrations slightly above the percolation threshold
where the electric resistance changes most abruptly with filler
concentration.\textsuperscript{54} Figure 6(a) shows percolation behaviour for
Zn\textsubscript{0.925}Al\textsubscript{0.075}O/PDMS composite. The percolation threshold is
comparatively high (ϕ~20%), which is attributed to a low
aspect ratio of the nanofillers as well as a weak tendency to
build aggregate and subsequently conductive channels in
polymer matrix. Most well-known piezoresistive hyperelastic
sensors are carbon black filled elastomers, which have
percolation thresholds above 10%.\textsuperscript{55} At the same time, the
graphene filled composites have a percolation threshold below
1%, attributed to graphene high aspect ratio \textasciitilde{}1000.\textsuperscript{57}

In piezoresistive elastomer composites with low aspect ratio fillers the
divergence of adjacent particles and the destruction of existing
networks is more probable.\textsuperscript{57} Our sensor material shows fast
response-recovery behaviour as well, with the resistance
either rapidly decreasing or restored to the initial value after
applying or removing the external mechanical load. The output
signals were highly repeatable and reproducible over multiple
cycle tests, indicating their potential for applications in real-
time monitoring. The produced sensor device shows (limited)
transparency even in the visible range (see inset of Figure 6
(a)).

Overall, the obtained AZO/PDMS composites can be spin
coated on transparent flexible electrodes to further produce
transparent and flexible pressure sensors. This appears to be
in line with the presently growing demand to replace in
numerous applications the presently essentially brittle and
rigid devices by lightweight, mechanically flexible and
transparent next generation electronic appliances.\textsuperscript{56} From a
different aspect, thin films made of such conductive wide band
gap semiconductor oxides will probably exhibit higher
transmittance in visible range as compared to metal or carbon
based counterparts.

Conclusions

Zn\textsubscript{1-x}Al\textsubscript{x}O nanocrystals with excellent plasmonic response were produced using a “green” ethanol-based solvothermal
synthesis route. The synthesis of undoped ZnO yields
nanowires. The Al content was observed to have an effect on
the shape and aspect ratio of the produced nanoparticles;
while the synthesis of undoped ZnO yielded long nanowires
with aspect ratios up to 50, the increasing Al content gradually
decreases the aspect ratio to slightly above 1 (almost isotropic growth) at Al content x=0.15. Powder XRD Rietveld refinement, XAS and XPS reveal all samples to exhibit phase-pure zincite crystal structure of space group \( P6_3/mc \). Diffuse reflectance measurements showed the appearance of localized surface plasmon absorption in the NIR region for all with a maximum at \( x=0.075 \) Al-loaded samples. 

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