Air-stable n-type colloidal quantum dots solids

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Table S1 Soft and hard acids and bases.1
Figure S1 Absorption spectra of the CQDs in toluene solution before and after the addition of halides. The addition of halides red-shifts the excitonic absorption peak. Iodide passivation offers a minor improvement to the absorption below 800 nm.

Figure S2 Photoluminescence spectra of CQDs before and after the addition of halide ligands at 640 nm excitation wavelength. Minor differences in the luminescence intensity is observed between the varying halide ligands, implying that similar quantities of ligands are bound to the CQD surface for each halide treatment. The iodide treatment shows a slightly higher emission intensity due to the increase in absorbance in the visible region, as shown in Figure S1.
Figure S3 Absorption spectra after the ethanol precipitation and redispersion in octane of solution-phase halide-treated CQDs. Chloride processed dots show broadening of the exciton peak.

Figure S4 Schematic depicting the ligand exchange process. Method 1: protic solvent wash before iodide treatment (top); Method 2: protic solvent wash following iodide treatment (bottom). In method 1, a fraction of oleic acid ligands previously protecting the surface were removed and enabled surface oxidation and the formation of defects. In method 2, the oxidation of the surface is effectively prohibited.
Table S2 Performance of the quantum junction devices before and after air exposure employing the CQDs with incomplete iodide passivation, i.e., when halide solution-phase treatment is performed after the protic solvent wash (Method 1). The PCE drops from 5.7 % to 4.5 %, primarily as a result of the loss in V_{oc}.

<table>
<thead>
<tr>
<th></th>
<th>V_{oc} (V)</th>
<th>J_{sc} (mA/cm²)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before air exposure</td>
<td>0.54</td>
<td>20.7</td>
<td>0.51</td>
<td>5.7</td>
</tr>
<tr>
<td>After air exposure</td>
<td>0.46</td>
<td>20.5</td>
<td>0.48</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Figure S5 XPS analysis of oxygen and iodide amount in films prepared by CQDs that treated by Method 1 (iodide treatment after protic solvent wash) and Method 2 (iodide treatment before protic solvent wash). Films processed using Method 1 show higher oxygen levels and smaller iodide content compared with Method 2.
Figure S6 Transient photovoltage measurements of the films that fabricated by Method 1 and Method 2 treated CQDs. The defects state density of the film for CQDs treated using Method 2 is notably smaller.
Figure S7 Current-voltage curves of the quantum junction devices tested in nitrogen with different halide ligands used in solid state ligand exchange. Data are summarized in Table S3. The CQDs used for all devices are processed via pre-iodide solution treatment.

<table>
<thead>
<tr>
<th></th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>iodide</td>
<td>0.56</td>
<td>21.6</td>
<td>0.47</td>
<td>5.6</td>
</tr>
<tr>
<td>bromide</td>
<td>0.48</td>
<td>22.6</td>
<td>0.46</td>
<td>4.9</td>
</tr>
<tr>
<td>chloride</td>
<td>0.44</td>
<td>22.5</td>
<td>0.44</td>
<td>4.4</td>
</tr>
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</table>

Table S3 Performance data for quantum junction devices based on CQDs employing the complete iodide passivation, i.e. performing the iodide solution-phase treatment before the protic solvent washing (Method 2) and using different halides in the solid state ligand exchange. Iodide solid-state exchanged CQDs result in the highest power conversion efficiency, predominantly as a result of sustaining the highest $V_{oc}$. 
Figure S8 Stability curves of $V_{OC}$, $J_{SC}$, FF, shunt resistance, and series resistance of the iodide solid state exchanged device. The device was stored and tested in air. No significant changes are observed in key device performance parameters.
Figure S9 Capacitance-voltage measurement of the iodide processed film before and after exposure to air. No obvious change of the curves was observed, indicating that there is no substantial change of the doping density of the film after air exposure.
Figure S10 Field effect transistor measurement of the iodide solid exchanged film. Al₂O₃ was used as the gate dielectric, and Ti as the source and drain electrodes. N-type behavior is consistently observed, even following prolonged air exposure.

Figure S11 UPS data of a secondary electron cut-off and valence band for CQD films with different halide ligands.
Figure S12 Stability curves of Voc, Jsc, FF, shunt resistance, and series resistance of the bromide-treated device. All parameters deteriorate with increased air exposure.
Figure S13 Capacitance-voltage curve of the quantum junction device with a top bromide-treated n-type film and bottom hydroxide-treated p-type film, prior to air exposure.

Figure S14 Field effect transistor measurement of the bromide treated film. Al₂O₃ was used as the gate dielectric, and Ti as the source and drain electrodes. The electron density of the film is ~10¹⁶. No n-type channel is observed following exposure to air.
Figure S15 Capacitance-voltage curve of the quantum junction device based on chloride-treated n-type film on hydroxide-treated p-type film before air exposure.

Figure S16 Field effect transistor measurement of the chloride treated film. Al₂O₃ was used as the gate dielectric, and Ti as the source and drain electrodes. The electron density of the film is ~10¹⁶ cm⁻³. No n-type channel is observed following exposure to air.
Figure S17 Field effect transistor measurement of the chloride solid exchanged film. Al₂O₃ was used as the gate dielectric, and Au as the source and drain electrodes. P-type behavior is observed after air exposure.

Figure S18 Relative Fermi level position of different halide ligands exchanged films relative to the Kelvin probe tip after air exposure.
Figure S19 XPS results of the oxide content in the film after air exposure for 4 days. The oxide amount in the bromide and chloride solid state exchanged film are significantly higher than for iodide, consistent with the RBS measurement results.

Figure S20 Capacitance-voltage curve of the heterojunction device with an mercaptopropionic acid (MPA) treated p-type film deposited in inert atmosphere on TiO₂. The calculated doping density of the MPA treated film is only 3*10¹⁵ cm⁻³.
Figure 21 Current-Voltage curves of depleted heterojunction (TiO$_2$/CQD) device with MPA ligand exchanged CQD layer deposited in air or in inert atmosphere. The device prepared in inert atmosphere show much lower voltage compared to that prepared in air.

<table>
<thead>
<tr>
<th>Device</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Device 1</td>
<td>0.49</td>
<td>23.0</td>
<td>0.50</td>
<td>5.63</td>
</tr>
<tr>
<td>Device 2</td>
<td>0.50</td>
<td>24.0</td>
<td>0.49</td>
<td>5.88</td>
</tr>
<tr>
<td>Device 3</td>
<td>0.51</td>
<td>22.9</td>
<td>0.46</td>
<td>5.37</td>
</tr>
</tbody>
</table>

Figure S22 Best current-voltage curves and performance parameters of devices made completely inside an N$_2$ glovebox. Similar device fabrication procedures were followed compared to the inverted quantum junction device. Device 1: iodide layer 120 nm/bromide layer 300 nm/MPA layer 30 nm. Device 2: iodide layer 120 nm/bromide layer 210 nm/MPA layer 120 nm. Device 3: Iodide layer 60 nm/bromide layer 360 nm/MPA layer 30 nm.
Figure S23 Capacitance-voltage curve of the heterojunction device (TiO$_2$/CQD) with bromide and MPA treated p-type film that prepared in air. The doping density of the MPA treated layer is $\sim 10^{17}$ cm$^{-3}$, which is one order of magnitude higher than that prepared in glovebox.

Figure S24 The transmittance spectra of 450 nm and 300 nm thick films (double pass). The absorbance of the thicker film near the exciton peak region (970 nm) reaches 80% compared to $\sim 50\%$ for the thinner film.
Figure S25 Power conversion efficiency statistics for inverted quantum junction devices (24 in total).

<table>
<thead>
<tr>
<th>Device type</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inverted Quantum junction</td>
<td>0.50 ± 0.02</td>
<td>25.8 ± 0.9</td>
<td>0.59 ± 0.03</td>
<td>7.6 ± 0.4</td>
</tr>
<tr>
<td>Quantum junction</td>
<td>0.49 ± 0.03</td>
<td>23.5 ± 1.1</td>
<td>0.52 ± 0.04</td>
<td>6.3 ± 0.5</td>
</tr>
<tr>
<td>Heterojunction</td>
<td>0.48 ± 0.02</td>
<td>23.3 ± 1.0</td>
<td>0.56 ± 0.03</td>
<td>6.5 ± 0.4</td>
</tr>
</tbody>
</table>

Table S4 Mean values for the key parameters of different types of devices.
Figure S26 Dark current-voltage curves of the heterojunction and inverted quantum junction devices. The built-in voltage of the inverted quantum junction device is similar to the heterojunction device, indicative of good rectification.

Figure S27 EQE curves of the inverted quantum junction devices with different iodide treated layer thicknesses. When the thickness is increased, the EQE value in a 400-600 nm range reduces, indicating the increase of the quasi-neutral region in this layer.
**Gas Sensor Fabrication:** CQD films were fabricated on gold (Au) or silver (Ag) interdigitated electrodes. The film spin coating procedure is the same as that for solar cells, but only 2 layers were deposited. Iodide and chloride were used as the ligand for the solid state ligand exchange.

**Gas-Sensing Measurement:** The gas sensor measurement was performed using a custom designed characterization instrument. The samples were mounted in a testing chamber of 0.7 L volume and connected in series with a single resistor. 5 V bias was applied across the channel of 2.5 μm length during the measurement. The measurement was conducted under atmospheric pressure in air to test the film response to NO$_2$ gas in the concentration range of 10 ppm to 100 ppm.

Figure S28 NO$_2$ sensor response curve of films made using chloride and iodide treated CQD films on gold or silver electrodes. Iodide treated film show much higher sensor response compared chloride treated film. This is consistent with the n-type character of the iodide treated film. Higher sensor response was found when the film was prepared on gold substrate compared to silver, which could be caused by the higher Schottky barrier between gold and the n-type CQD film.
Figure S29 NO₂ sensor response curves toward NO₂ of different concentrations. The sensor response depends linearly on NO₂ concentration, indicating the stable performance of the sensor.

Figure S30 Sensor response curve to different NO₂ gas concentration. We measured 175 data points of the baseline film before NO₂ exposure. The points were averaged and a standard deviation (S) of 4.4E-3 was measured. NO₂ sensor detection limit is calculated by the following equation:

\[ \text{RMS}_{\text{noise}} = \sqrt{\frac{S^2}{N}} = 3.3\text{E}-4 \]

\[ \text{DL}(\text{ppm}) = 3 \times \frac{\text{RMS}}{\text{Slope}} = 3 \times \frac{(3.3\text{E}-4)}{(8.93\text{E}-3)} = 0.1 \text{ppm} \]
Figure S31: Solar cell stability performance under continuous light illumination in 100 ppb NO₂ atmosphere. No obvious decay of device efficiency was found after 48 hours. The normal NO₂ concentration in air is below 10 ppb, hence the normal concentration of NO₂ in air will not affect the device performance.

Scheme S1: Chemical equation between tetrabutylammonium iodide and oleylamine at 200 °C.
Figure S32 $^1$H NMR spectroscopy of the iodide precursor.
Figure S33 $^{13}$C NMR spectroscopy of the iodide precursor.

Figure S34 Mass spectroscopy of the iodide precursor.
References: