A Novel Buffering Technique for Aqueous Processing of Zinc Oxide Nanostructures and Interfaces, and Corresponding Improvement of Electrodeposited ZnO-Cu₂O Photovoltaics

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A novel buffering method is presented to improve the stability of zinc oxide processed in aqueous solutions. By buffering the aqueous solution with a suitable quantity of sacrificial zinc species, the dissolution of functional zinc oxide structures and the formation of unwanted impurities can be prevented. The method is demonstrated for ZnO films and nanowires processed in aqueous solutions used for the selective etching of mesoporous anodic alumina templates and the electrochemical deposition of Cu₂O. In both cases, improved ZnO stability is observed with the buffering method. ZnO-Cu₂O heterojunction solar cells (bilayer and nanowire cells) synthesized using both traditional and buffered deposition methods are characterized by impedance spectroscopy and solar simulation measurements. Buffering the Cu₂O deposition solution is found to reduce unwanted recombination at the heterojunction and improve the photovoltaic performance.

1. Introduction

ZnO is a wide-bandgap semiconductor ($E_g = 3.3$ eV) with a high electron mobility.^[1] It is an integral component of many emerging technologies in areas such as optoelectronics, energy harvesting, sensing, and catalysis. In photovoltaics for example, ZnO films have been used as charge blocking layers in organic solar cells,^[2,3] ZnO nanowires have been used to improve charge collection in dye-sensitized and hybrid solar cells,^[4–9] and

heterojunctions such as ZnO-CdSe-CuSCN and ZnO-Cu₂O have been employed in inexpensive inorganic solar cells.^[10–13]

While there has been much effort to synthesize functional ZnO structures by inexpensive, aqueous methods (e.g. electrodeposition, hydrothermal growth), the quality of the interfaces and nanostructures formed by the aqueous techniques has typically been overlooked. Consider the examples in Figure 1. In panel (a), a heterojunction is formed by electrochemical deposition onto a ZnO film or nanostructure from an aqueous solution, a technique used previously to synthesize photovoltaic devices.^[10–13] In panel (b), a surface treatment or coating is applied to a ZnO nanostructure using an aqueous solution. Plank et al. for example,

reported a hydrothermal method for producing MgO shell coatings on ZnO nanowires, which involved soaking them for approximately 40 min in heated aqueous solutions. For TiO₂, TiCl₄ post treatments in heated aqueous solutions have been developed to tailor the conduction band edge^[14] and similar surface treatments may be developed for ZnO. In Figure 1c, an aqueous etching solution is employed to remove a mesoporous template used for the formation of nanostructured ZnO. Arrays of vertically-aligned metal oxide nanorods or nanowires are commonly synthesized in anodic alumina templates, which are typically removed using a basic, aqueous NaOH solution.^[15–17] For all of these examples, it is absolutely critical to consider the influence of the aqueous treatment on the morphology of the ZnO structures and the interfaces that they form.

Figure 2 illustrates a simplified electrochemical stability diagram for zinc and its oxide in aqueous solutions, constructed following the method of Pourbaix.^[18] This diagram indicates the thermodynamic regions of stability of the solid compounds (solid line), as well as the regions of predominance of the various dissolved species (thick dashed lines) and their solubility levels (thin dotted lines) in terms of $\log(\text{mol L}^{-1})$. While the presence of other dissolved species in a particular aqueous solution may alter the equilibria of the zinc species from that expected for a pure aqueous solution, Figure 2 should nonetheless provide a good estimate of the stability of ZnO in various aqueous processing

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Figure 1. Common aqueous treatments applied to functional zinc oxide structures. a) Heterojunctions are formed by electrochemical deposition onto ZnO from aqueous solutions. b) Surface treatments and coatings are applied to ZnO in aqueous solutions. c) Aqueous etchants can be used to removed ZnO nanostructures from mesoporous templates.

solutions. In particular, it is noted that in basic solutions, dissolution of ZnO is expected according to the following reactions:

Figure 2. Simplified electrochemical stability diagram for ZnO in an aqueous solution at 25 °C.

and in acidic solutions, ZnO dissolution is expected according to:

In this work, the effect of typical aqueous processing solutions on the morphology of functional ZnO structures is examined. Aqueous treatments are shown to result in the dissolution of ZnO and the formation of unwanted precipitates on the ZnO surface. A novel buffering technique is introduced, whereby sacrificial zinc species are added to the aqueous processing solutions to establish electrochemical equilibrium and buffer the functional ZnO structures from unwanted dissolution. This method is found to dramatically improve the stability of functional ZnO under aqueous treatment.

To demonstrate the efficacy of this method, the buffering technique is applied to the electrochemical synthesis of Cu_2O -ZnO heterojunction solar cells from aqueous solutions. Inorganic solar cells electrodeposited from solutions near room temperature are extremely promising as ultra-low-cost, stable, non-toxic photovoltaics. Cu_2O is a p-type semiconductor with a direct bandgap of approximately 2.0 eV and a theoretical maximum power conversion efficiency of approximately 20%, assuming only radiative recombination.^[19,20] Difficulty in doping Cu_2O n-type has necessitated heterojunction architectures and ZnO been shown to be a suitable n-type counterpart.

In recent work, we showed that a nanowire (NW) architecture can be used to improve the minority carrier collection efficiency in electrodeposited Cu_2O -ZnO heterojunction solar cells.^[13] Although enhanced carrier collection was observed, the open-circuit voltage V_{OC} measured for the NW cells was approximately 0.2 V. While this represented a significant improvement from most previous Cu_2O -ZnO nanowire cells,^[12,21] it is well below the built-in potential of around 0.7 V expected from the band offset of the materials. In this work, the low open-circuit voltage is attributed, at least in part, to a high density of interface states at the Cu_2O -ZnO heterojunction resulting from the aqueous synthesis. Such states facilitate unwanted recombination currents that oppose the photogenerated current. Impedance spectroscopy analysis of Cu_2O -ZnO heterojunctions synthesized with and without the buffering method indicate that the homogeneity of the interface and resistance to recombination are increased with the buffering method. The improved interface is shown to improve the V_{OC} and power conversion efficiency PCE of both bilayer and NW Cu_2O -ZnO solar cells.

2. A Novel Buffering Method for Processing ZnO in Aqueous Solutions

Following from the electrochemical stability calculations of Pourbaix,^[18] the approximate solubility levels of the aqueous zinc species shown in Figure 2 are given in Table 1 as a function of the pH level. For ZnO immersed in an aqueous solution with a pH of 12.5 for example, Figure 2 indicates that HZnO_2^- is the predominant dissolved species, although a smaller quantity of ZnO_2^{2-} will also be present. Table 1 indicates that HZnO_2^- should be produced via Equation 1 to attain an equilibrium concentration of approximately $10^{-4.2} \text{ mol L}^{-1}$. Two

Table 1. Solubility levels of zinc species in aqueous solutions at 25 °C.^[18]

Aqueous species	Solubility Level [mol L ⁻¹]
Zn ²⁺	$\log(\text{Zn}^{2+}) = 10.96 - 2 \text{ pH}$
HZnO ₂ ⁻	$\log(\text{HZnO}_2^-) = -16.68 + \text{pH}$
ZnO ₂ ²⁻	$\log(\text{ZnO}_2^{2-}) = -29.78 + 2 \text{ pH}$

aqueous processing solutions with pH levels of approximately 12.5 are studied as examples in this work: a NaOH solution for etching anodic alumina membranes and a CuSO₄/lactic acid/NaOH solution for the electrodeposition of Cu₂O.

To prevent the unwanted dissolution of ZnO, a suitable quantity of sacrificial ZnO powder was added to the aqueous processing solutions, which were then stirred and heated at 40 °C for several hours, prior to the insertion of the functional ZnO material. For example, for 40 mL of aqueous solution with a pH of 12.5, approximately 8 mg of ZnO powder was typically added, which corresponds to a ZnO concentration greater than 10⁻³ mol L⁻¹. This should ensure that an equilibrium concentration of aqueous zinc species (particularly HZnO₂⁻) is achieved prior to insertion of the functional ZnO, such that no further ZnO dissolution should occur.

For aqueous processing solutions with other pH levels, an appropriate quantity of ZnO powder with which to buffer the solution can be determined by selecting the predominant dissolved species from Figure 2 and its solubility level from Table 1. After heating and stirring the buffered solution, a small quantity of ZnO powder should remain, indicating that electrochemical equilibrium has been reached and further ZnO dissolution will be inhibited.

2.1. Buffering of NaOH Etching Solution

As illustrated in Figure 1c, aqueous NaOH etching solutions are typically used to selectively remove anodic alumina templates to leave free-standing nanostructures.^[16,17] In the basic etching solution, there is a strong affinity for the following reaction:

resulting in dissolution of the anodic alumina template. For ZnO nanostructures synthesized using such templates, dissolution of the ZnO is also expected in the basic etching solution, according to Equations 1 and 2.

To examine the influence of the etching solution on ZnO nanostructures, free-standing ZnO nanowire arrays electrochemically-synthesized from a zinc chloride solution were soaked in both a typical 0.1 M NaOH etching solution and a buffered equivalent at room temperature. Approximately 35 mL of etching solution was used in both cases and approximately 9.5 mg of ZnO powder was added to the buffered solution. The nanowire arrays

were examined with scanning electron microscopy (SEM) before deposition, as well as after soaking for 2 h, 4 h, and 8 h in the etching solutions. The etching solutions were replaced after 4 h.

No change was visible by SEM in the nanowire array soaked in the buffered etching solution. Figure 3a and c display the nanowire array after 4 h and 8 h in the buffered solution respectively. Smooth, straight nanowires are observed, typical of electrochemical growth. A considerable change in ZnO nanowire morphology, however, was observed for the nanowires soaked in the regular etching solution. Figure 3b and d display the nanowire array after 4 h and 8 h in the buffered solution respectively. A clear decrease in nanowire uniformity is observed. The wires are rougher and notable variations in diameter are seen along their lengths. A reduction in typical nanowire diameter and increase in film porosity is observed with soaking in the regular solution, clearly indicating that dissolution of the ZnO nanowires occurs.

Depending on the thickness of the anodic alumina template, etching times of several hours may be necessary, such that significant damage to ZnO nanostructures can result. This novel buffering technique can be used to maintain the integrity of ZnO nanostructures during removal from anodic alumina templates. A pH of approximately 12.5 was measured for both solutions, and anodic alumina templates synthesized on indium-tin oxide (ITO)/glass substrates by a previously reported method^[17] were found to be efficiently etched by the buffered solution. This encouraging result suggests that the buffering technique should likewise improve the stability of ZnO in aqueous solutions used for treating or coating its surface.

2.2. Buffering of Cu₂O Electrodeposition Solution

Similar improvements in stability were found for ZnO exposed to an aqueous Cu₂O electrochemical deposition solution

Figure 3. SEM images of ZnO NWs after soaking in a buffered 0.1 M aqueous NaOH solution for 4 h (a) and 8 h (c), and after soaking in a regular 0.1 M aqueous NaOH solution for 4 h (b) and 8 h (d). Buffering of the NaOH solution with ZnO powder was found to dramatically reduce the dissolution of the NWs.

(pH approximately 12.5) when the buffering technique was employed. Electrochemically grown ZnO nanowires were again exposed to the regular and buffered solutions, as were continuous ZnO films electrodeposited from zinc nitrate solutions. The etching of a ZnO film is demonstrated clearly in Figure 4. A SEM image of an as-deposited ZnO layer is shown in (a), and image (b) shows the same film after sitting in the regular Cu₂O deposition solution for 1 h. A typical Cu₂O deposition takes approximately 30 min, such that considerable etching of the ZnO films and nanowires will occur during device fabrication. Significant concentrations of the aqueous species (HZnO₂⁻, ZnO₂²⁻, H⁺) are thus likely to be present on the ZnO surface and are liable to introduce a high concentration of interface states at the Cu₂O–ZnO heterojunction. These effects are expected to be much more significant for Cu₂O deposition on NWs, where a larger ZnO surface area will result in more dissolution and a greater concentration of the aqueous species at the interface.

Etching of the ZnO cannot be avoided by instead depositing ZnO onto Cu₂O, as the electrochemical potential at which ZnO is deposited (approximately –1 V versus Ag/AgCl) is liable to reduce Cu₂O to Cu.^[18] To limit ZnO dissolution and the formation of undesirable interface states during device fabrication, the buffering technique was employed. For every 100 mL of CuSO₄/lactic acid/NaOH solution, approximately 25 mg of ZnO powder was added.

Figure 4c shows a SEM image of a ZnO film after soaking for 1 h in this buffered solution. The ZnO powder was found to drastically reduce the ZnO etching in the Cu₂O solution. Figure 4d shows a bright-field transmission electron microscopy (TEM) image of ZnO nanowires that were etched for 15 min

in regular Cu₂O electrodeposition solution then scraped off the sample surface. A high-resolution TEM (HRTEM) image of one of the nanowire tips in Figure 4d (highlighted by a dashed rectangle) is shown in Figure 4e. HRTEM imaging indicated that the wires were single crystalline. The dark rims in Figure 4e indicate the presence of surface steps on the wire, which may correspond to the etching of the wire surface. Figure 4f shows a similar HRTEM image of a nanowire scraped from a sample that was instead soaked for 15 min in a buffered Cu₂O electrodeposition solution. A single crystal structure is again evident. No surface step features are observed for this nanowire, indicating that dissolution of the ZnO was inhibited by buffering the Cu₂O deposition solution. It should be noted that the removal of material from the nanowires may be due in part to TEM beam damage. Damage was noted for both samples after extended study in the TEM. However, the surface steps of the sample etched in the regular solution were present from the beginning, strongly suggesting that they were due to the chemical treatment.

The ZnO dissolution resulting from exposure to the Cu₂O deposition solutions was also examined using X-ray diffraction (XRD). A pristine ZnO film was first analyzed; other than peaks corresponding to the ITO substrate, only ZnO reflections were observed. The sample was then cleaved in two. One half was soaked for 45 min in regular Cu₂O deposition solution, and the other for the same duration in a buffered solution. Following this, the samples were thoroughly rinsed with distilled water, dried with nitrogen gas, and re-examined using XRD. Figure 5a shows the XRD data for the two samples. The sample soaked in the buffered solution was unchanged, whereas a significant decrease in the relative intensities of the ZnO peaks is observed for the film soaked in the regular Cu₂O deposition solution, clearly indicating the dissolution of ZnO.

Several small, additional peaks were also noted in the XRD data for the film soaked in the regular Cu₂O deposition solution. These peaks are attributable to a number of species that may precipitate from the solution, including sodium hydroxide, copper sulfate, copper oxide sulfate, and copper (II) oxide. Figure 5b shows a SEM image of precipitates formed on the ZnO surface. Energy-dispersive X-ray (EDX) analysis of these precipitates indicated a 1:1 atomic ratio of Cu:O, in agreement with the copper (II) oxide peak observed in the XRD. It is likely that the roughened film surface that results from ZnO etching inhibits the removal of these precipitates during rinsing. It is also possible that the aqueous species formed by the dissolution of the ZnO may mediate the precipitation of these impurities. In any case, no such precipitates were detected for the ZnO samples soaked in the buffered solution.

Cyclic voltammetry measurements were performed on both the regular and buffered Cu₂O deposition solutions and were found to be identical, indicating that the small

Figure 4. SEM images of ZnO films as-deposited (a), and after sitting for 1 h in a regular Cu₂O deposition solution (b) and buffered Cu₂O deposition solution (c). Buffering of the Cu₂O solution with ZnO powder was found to dramatically reduce the etching of the underlying ZnO during Cu₂O deposition. d) Bright-field TEM and (e) HRTEM images of ZnO nanowires that were etched in a regular Cu₂O electrodeposition solution for 15 min. Surface steps are visible on the wire surface in (e), suggesting that etching of the ZnO takes place. f) A similar HRTEM image of a nanowire tip that was etched in a buffered Cu₂O solution for 15 min shows no surface step features.

Figure 5. (a) XRD data of ZnO films soaked for 45 min in a regular and buffered Cu_2O electrodeposition solution. Buffering with ZnO powder is seen to prevent the dissolution of ZnO in the basic solution and the formation of unwanted impurities. (b) SEM image of impurities (highlighted with arrows) formed on the ZnO film surface when it was soaked in regular Cu_2O deposition solution.

concentration of zinc species has little influence on the Cu_2O deposition dynamics. Furthermore, no zinc impurities were detected by EDX in Cu_2O films synthesized using the buffered solution, indicating negligible incorporation of zinc impurities.

3. Cu_2O –ZnO Heterojunctions Synthesized Using Buffered Cu_2O Deposition Solutions

The importance of the buffering method presented in this work has been further demonstrated by employing it in the electrochemical synthesis of Cu_2O –ZnO solar cells. Both simple bilayer and NW Cu_2O –ZnO heterojunctions were fabricated by electrodeposition of ZnO and Cu_2O onto commercial ITO/glass substrates. The device structures are shown in Figure 6. ZnO films and nanowires were deposited using zinc nitrate^[22] and zinc chloride^[23] solutions respectively. The ZnO films were polycrystalline, with a hexagonal wurtzite structure. The ZnO nanowire arrays were grown on a 50 nm Zn seed layer. The wires were disordered but highly crystalline, again with a wurtzite structure. The light-absorbing Cu_2O layer was electrodeposited

Figure 6. Schematic illustrations of bilayer and NW Cu_2O –ZnO heterojunction solar cells studied in this work.

on the ZnO films and NW arrays using a CuSO_4 (0.4 M)/lactic acid (3 M) solution, to which a similar amount of 4 M NaOH was added to adjust the pH to approximately 12.5.^[19,20,24] Both regular and buffered versions of the Cu_2O deposition solution were employed. The Cu_2O and ZnO layers used were typically 3 μm and 550 nm thick respectively, and the ZnO nanowires had lengths up to approximately 1 μm and diameters ranging from 20 nm to over 200 nm. Typical deposition times were 10 and 45 min for the ZnO films and nanowires, and 30 min for the Cu_2O layers.

The influence of buffering the Cu_2O deposition solution on the properties of the electrochemically synthesized heterojunctions was examined using impedance spectroscopy and related to solar simulation measurements.

3.1. Impedance Spectroscopy

Impedance spectroscopy is a powerful tool for the electrical characterization of interfaces and composite structures, and has been used extensively to characterize the properties of solid state solar cells.^[25–27] Impedance measurements were conducted in the dark under different applied biases ranging from 0 V to 0.5 V and the frequency was swept from 40 Hz to 1 MHz with a 20 mV AC voltage perturbation.

Nyquist plots of bilayer heterojunctions synthesized using regular and buffered Cu_2O deposition solutions are shown in Figure 7a and b, respectively, at various applied biases. The corresponding Bode plots are included in Figure S1 of the Supporting Information. The Nyquist plots consist of a large, low-frequency arc, typical of p–n junctions. Such junctions are traditionally modeled by an equivalent circuit consisting of a resistor in series with a parallel combination of a resistor and a capacitor.^[25–27] The series resistor describes the resistance of the collection electrodes and the parallel resistor characterizes leakage and recombination paths through the cell. The parallel capacitor represents the capacitance resulting from the depletion region of the p–n junction.

Figure 7d shows a magnified view of the high-frequency data for the buffered device from Figure 7b. A second, high-frequency arc is observed. This additional arc was likewise observed for the device synthesized using the regular Cu_2O deposition solution. Impedance spectra consisting of two arcs have been observed previously for CdTe solar cells, where the

Figure 7. Impedance spectra for bilayer heterojunctions synthesized with regular (a) and buffered (b) Cu_2O deposition solutions. (c) The equivalent circuit used to fit the data, where constant phase elements are used to account for surface inhomogeneities resulting from roughness and interfacial states. Data fits to impedance spectra are indicated by solid lines. (d) High-frequency impedance data for the buffered cell indicates a second arc due to a Schottky barrier at the ITO–ZnO interface.

high-frequency feature was attributed to a Schottky contact at one of the electrodes.^[28,25,27] The high-frequency feature observed here was likewise attributed to a Schottky barrier at the ZnO–ITO interface. Figure S2 in the Supporting Information shows Nyquist plots of electrodeposited ZnO films on ITO with Ag and Au top contacts, without a Cu_2O layer. While the low-frequency arc corresponding to the Cu_2O –ZnO heterojunction is no longer present, the high-frequency arc remains, confirming that it originates from the interface between the ZnO and contact electrode. No such features were observed when Cu_2O films deposited on ITO with Au or Ag top contacts were measured.

The impedance spectra in Figure 7 are not perfect semicircles. The arcs are compressed, with centers of radius below the $\text{Re}(Z)$ axis. This behavior is known to result from inhomogeneities in the electrical properties of the measured interface.^[29] Such inhomogeneities include roughness and interface states (charge trap levels near the interface) induced by defects and impurities.^[30,27] In previous impedance studies of solar cells, additional circuit elements have been included to account for discrete trap levels at heterojunctions.^[31,32,27] In the simplest case, the presence of one trap level can be represented in an equivalent circuit by a series RC component associated with the

charging and discharging time characteristic for the given trap level, as shown in Figure 8a where R_{IS} and C_{IS} are the resistance and capacitance associated with the trap level. Typically there may be multiple trapping states at the heterojunction interface with a significant spread in time constants, which give rise to multiple circuit elements as shown in Figure 8b. To account for this distribution in electrical properties at the interface, a Constant Phase Element (CPE) can be used in lieu of a simple capacitor, as shown in Figure 8c.^[33,29,34,27] The impedance of the CPE is defined as:

$$\tilde{Z}(\omega) = \frac{1}{(Q\omega t)^\varphi} \quad (5)$$

where ω is the frequency and φ is a fitting parameter with a value between 0 and 1. When φ is 1, the element is an ideal capacitor with the capacitance equal to Q . As the homogeneity of the interface decreases, φ is expected to deviate further from 1.

Figure 7c shows the equivalent circuit to which the impedance data was fit. The fits are indicated by solid lines in the plots and showed good agreement with the data, confirming the suitability of the equivalent circuit model used. Circuit

Figure 8. Equivalent circuits for (a) a heterojunction with a single trapping state of time constant $R_{1S}C_{1S}$ and (b) a heterojunction with a distribution of trap states of varying time characteristic. (c) A constant phase element can be used to describe the distributed nature of a heterojunction with a variety of interfacial states.

parameters obtained from a complex nonlinear least-squares fitting program^[35] are summarized in Table S1 in the Supporting Information. Fitted R_{series} values were negligible for the bilayer heterojunctions and thus have not been included in the table.

The fitted values of R_{rec} are plotted in Figure 9 as a function of the bias voltage for both the buffered and regular bilayer heterojunctions. For a solar cell under bias, a dark current results, which flows in a direction opposing the photogenerated current. For a lattice-mismatched heterojunction such as Cu_2O -ZnO, this dark current is expected to result from recombination at the interface (holes from the Cu_2O recombine with electrons from the ZnO).^[36] R_{rec} provides a measure of the resistance to this recombination at the Cu_2O -ZnO interface. R_{rec} was found to decrease with bias voltage as expected, as the potential barrier to tunnelling or carrier injection at the interface is reduced. Notably, a larger resistance to recombination was observed for

Figure 9. R_{rec} values obtained by complex nonlinear least-squares fitting of bilayer Cu_2O -ZnO heterojunction impedance data. The buffered device displayed larger values for the recombination resistance, suggesting a smaller density of defect states, which act as recombination centers at the Cu_2O -ZnO interface.

the bilayer device synthesized using the buffered solution. This suggests that a smaller density of defect states, which act as recombination centers, exist at the buffered interface. Correspondingly, the characteristic frequencies of the low-frequency impedance arcs in Figure 7 are lower for the buffered cell, indicating a slower recombination rate at the buffered Cu_2O -ZnO interface.

The CPE parameter ϕ_2 characterizes the dispersion of time constants at the Cu_2O -ZnO interface, as described in Equation 5. ϕ_2 values obtained from spectra with prominent low-frequency impedance arcs well suited for fitting are given in Table 2. Standard deviations determined by the fitting routine are given in the table as error bounds. The lower ϕ_2 values observed for the unbuffered device indicate a more inhomogeneous interface, which may be attributed to both a rougher heterojunction resulting from ZnO dissolution and a greater density of interface states with varying energy levels.

Interface states are known to influence the built-in potential (V_{bi}) of a diode and hence its photovoltaic properties.^[37] Figure 10a illustrates the approximate energy levels of a Cu_2O -ZnO heterojunction. For typical majority carrier concentrations of 10^{14} cm^{-3} and 10^{18} cm^{-3} in electrodeposited Cu_2O ^[24] and ZnO^[22] films respectively, a V_{bi} of approximately 0.7 V is expected at the heterojunction, which corresponds to the difference in Fermi energies of the two materials and provides an estimate of the achievable open-circuit voltage. The reported open-circuit voltages of electrodeposited bilayer Cu_2O -ZnO solar cells, however, vary widely (i.e., 0.19 to 0.59 V), which may be due in part to varying concentrations of interface states.^[11,22,38]

If a significant number of states exist at the interface and act as acceptors, electrons may be removed from the depletion region, bending the energy bands upwards, as shown in Figure 10b. As the carrier concentration is much higher in the electrodeposited ZnO, the built-in potential is expected to be formed predominantly in the Cu_2O ($V_{bi}(p) > V_{bi}(n)$). Upward band bending in the Cu_2O near the interface would therefore drastically reduce the built-in potential of the diode. Holes from the Cu_2O could more easily reach the interface and recombine, reducing the achievable V_{OC} . Trap levels near the interface could likewise facilitate carrier tunneling to the interface for recombination. The increased resistance to recombination at the Cu_2O -ZnO interface that was observed here for the buffered heterojunction has been attributed to a reduction in the interface state density. The influence of this reduction in interface state density on the photovoltaic performance of the heterojunctions is examined in the following section.

Table 2. Fitted ϕ_2 values for bilayer heterojunctions (standard deviations from the fitting routine indicated by error bounds).

Bias [V]	ϕ_2	
	Regular heterojunction	Buffered Heterojunction
0.00	0.75 ± 0.01	0.82 ± 0.01
0.05	0.75 ± 0.01	0.81 ± 0.01
0.10	0.78 ± 0.01	0.81 ± 0.01
0.25		0.87 ± 0.01

Figure 10. (a) Cu_2O - ZnO heterojunction at equilibrium. $V_{bi}(p)$ and $V_{bi}(n)$ represent the portions of the diode built-in potential formed in the Cu_2O and ZnO respectively. The achievable V_{OC} is expected to increase with the total built-in potential of the diode ($V_{bi} = V_{bi}(p) + V_{bi}(n)$), which acts as a barrier to recombination currents in a heterojunction solar cell. (b) Interface states can influence the distribution of charges at the interface, reducing the built-in potential and limiting the achievable V_{OC} .

3.2. Solar Cell Performance

To examine the influence of the buffering method on the performance of electrochemically-synthesized Cu_2O - ZnO photovoltaics, the current density-voltage J - V characteristics of bilayer and NW Cu_2O - ZnO solar cells synthesized using both the traditional and buffered Cu_2O deposition methods were examined under simulated AM 1.5G solar illumination (100 mW cm^{-2}). For both geometries, device performance was found to improve when the buffering technique was used.

Figure 11 displays solar simulator data for the bilayer heterojunctions. The devices were measured as-deposited, one week after their synthesis. The buffered solution is seen to increase both the V_{OC} and the fill factor FF of the bilayer device, while the short-circuit current density J_{SC} is relatively unchanged, resulting in an increase in the PCE from 0.50% to 0.65%. This result is consistent with a decrease in the interface state density at the heterojunction. Following from Figure 10b, it is expected that a reduction in interface state density should limit unwanted band bending and carrier recombination, resulting in a higher V_{OC} , while leaving the J_{SC} relatively unchanged. Dark J - V measurements of the bilayer cells are included in Figure S3a of the Supporting Information. A reduction in the reverse bias current is observed with buffering, consistent with the increased recombination resistance observed by impedance spectroscopy. The reduced reverse saturation current and increased recombination resistance measured in the dark are also consistent with the observed increase in V_{OC} . However, it is difficult to directly correlate these measurements performed in the dark with device properties under illumination, due to the photoconductive nature of the materials. The photoconductivity of Cu_2O , for example, has been attributed to deep minority carrier trapping centers that become filled

during illumination.^[39] Transport properties of the devices will therefore vary with illumination. Future impedance and J - V studies of the devices after illumination will permit more detailed comparison.

It is noted that the PCE s measured for the bilayer heterojunctions here are less than the highest value previously reported in the literature (1.28%), due to a higher V_{OC} (0.59 V) measured in that work.^[11] Thus while the reduction in interface states resulting from aqueous processing is an important step in improving the performance of electrochemically-synthesized solar cells, other interfacial properties such as roughness and crystallographic orientation certainly influence the V_{OC} of the Cu_2O - ZnO heterojunctions in this study and warrant further optimization.

Figure 11b displays solar simulator data for NW heterojunctions synthesized using both the traditional and buffered Cu_2O deposition solutions. The heterojunctions synthesized using the traditional Cu_2O deposition solution typically demonstrated a negligible photovoltaic effect in their as-deposited form. Post-deposition annealing at 100°C on a hotplate was required for several hours in order to observe rectification and a photovoltaic effect in these cells. The unbuffered NW cell in Figure 11b was annealed for 5 h at 100°C .

NW cells fabricated using the buffering technique, on the other hand, did not typically require annealing. The NW cell in Figure 11b that was synthesized using the buffering method was measured after sitting in air for approximately 2 weeks, with no thermal treatment. This suggests that annealing is required in the traditional devices to accelerate the passivation of a high density of interface states. As these heterojunctions are intended as ultra-low-cost cells to be fabricated on various conducting substrates, the elimination of the annealing requirement is a considerable advantage of the buffering method presented there.

As a greater density of interface states is expected for the large-area nanowire heterojunction, more significant improvement is expected with the buffering technique. The V_{OC} and FF of the nanowire cells increased by 27% and 18%, respectively, with buffering, compared to 16% and 15% increases in the bilayer devices. Likewise, the reduction in the reverse bias current for the buffered NW cell was larger than that observed for the buffered bilayer cell, even though the buffered NW device was annealed for a shorter duration than the equivalent unbuffered cell (see Figure S3b of the Supporting Information).

A slight reduction in J_{SC} is observed for the buffered NW cell. This can be attributed to the fact that the NW heterojunction synthesized from the traditional solution required annealing for 5 h, whereas the buffered device could be measured as deposited. In previous work on Cu_2O - ZnO NW heterojunctions, it was found that annealing the cells at 100°C improves the incident-photon-to-electron conversion efficiency slightly, which was attributed to improved crystallinity of the electrodeposited Cu_2O and better charge collection.^[13] An efficiency of 0.47% was measured for the buffered NW cell, higher than that observed for any NW cell synthesized using the traditional solution. However, it is noted that this PCE is still less than those of the equivalent bilayer cells reported in this work and elsewhere.^[11] Thus while this novel buffering method effectively reduces the interface state density and increases the efficiency of electrochemically

(a) bilayer heterojunction

(b) nanowire heterojunction

Figure 11. Current density-voltage measurements under AM 1.5G illumination for bilayer (a) and NW (b) Cu_2O -ZnO heterojunctions synthesized using regular and buffered Cu_2O deposition methods.

deposited Cu_2O -ZnO NW heterojunctions, further investigation of limitations in these NW cells is necessary.

4. Conclusions

A novel buffering technique has been presented to improve the stability of ZnO in aqueous processing solutions. A suitable quantity of sacrificial ZnO powder is added to the aqueous solution to attain electrochemical equilibria of dissolved zinc species. Buffering of solutions used for (i) releasing ZnO nanostructures from mesoporous anodic alumina templates and (ii) the electrochemical deposition of Cu_2O onto ZnO films and nanowires was found to prevent the dissolution of the ZnO structures and the formation of unwanted precipitates on their surfaces. Cu_2O -ZnO bilayer and NW solar cells electrochemically synthesized using buffered Cu_2O deposition solutions were found to have a greater resistance to unwanted recombination at their interfaces, which was attributed to a reduction in the interface state density. Enhanced open-circuit voltages and power conversion efficiencies were measured for the buffered cells under solar illumination, consistent with the larger recombination resistance observed by impedance spectroscopy.

The need for annealing of the NW devices was eliminated with the buffering method, allowing the synthesis of nanostructured heterojunction solar cells entirely from solutions near room temperature. While this work has emphasized the use of this buffering technique in the treatment of ZnO in basic aqueous solutions, it is equally applicable to ZnO in acidic mixtures and to other oxides that are unstable in aqueous solutions such as BaO, Al_2O_3 , V_2O_5 , and MoO_3 .^[18] The buffering method developed in this work is a powerful technique applicable to a wide variety of functional oxides synthesized and processed in aqueous solutions.

5. Experimental Section

ZnO Film and Nanowire Synthesis: Commercial ITO/glass substrates (Prazisions Glas & Optik, 14 mm × 14 mm × 0.7 mm) were used for synthesis of the ZnO films and nanowire arrays and consisted of an approximately 200 nm ITO layer (sheet resistance less than $10 \Omega \text{ sq}^{-1}$) on soda glass. All substrates were thoroughly cleaned in an ultrasonic bath with acetone and iso-propanol for 20 min prior to use. For the growth of ZnO nanowires, a Zn seed layer approximately 50 nm thick was sputtered onto the substrates using an Emitech sputter coater.

Electrodepositions were performed using a standard three-electrode system in aqueous electrolytes of dissolved precursors. A Princeton Applied Research Model 363 Potentiostat/Galvanostat was used to supply a constant deposition potential or current. The substrates were electrically connected with an insulated wire and Ag paste, which was masked using Kapton polyimide tape. A Ag/AgCl reference electrode in a saturated aqueous KCl solution was employed, with a 6.25 cm² inert platinum counter electrode. The sample and platinum electrodes were placed approximately 1 cm apart in the deposition solution and the reference electrode was placed immediately adjacent to the sample surface. The depositions were performed under computer control and the amount of charge collected at the working electrode was used to estimate the nominal thickness of material deposited. All chemicals used were reagent grade, and the water purified (resistivity greater than $16 \text{ M}\Omega \text{ cm}$).

Approximately 550-nm thick ZnO layers were potentiostatically deposited at -0.85 V versus Ag/AgCl from a simple $\text{Zn}(\text{NO}_3)_2$ (0.08 M) solution (75% H_2O ; 25% ethanol by volume) at 70°C , following from previous reports.^[22,40] The nanowires were electrodeposited at -1.0 V versus Ag/AgCl from a ZnCl_2 ($5 \times 10^{-4} \text{ M}$)/KCl (0.1 M) solution at 78°C , in a similar manner to previous work.^[23] Oxygen was bubbled in the NW deposition solution throughout the deposition to ensure oxygen saturation.

Cu_2O Electrodeposition and NaOH Etching Solutions: The standard Cu_2O deposition solution consisted of CuSO_4 (0.4 M)/lactic acid (3 M) at 40°C to which NaOH (4 M) was added to adjust the pH to approximately 12.5. The NaOH (0.1 M) etching solution was used at room temperature. pH levels were measured using an Oakton Benchtop pH 510 meter. For the buffered solutions, ZnO powder was added then the solutions were heated at 40°C and stirred for several hours. A suitably large beaker was used for the stirring to ensure a shallow solution depth (less than approximately 5 cm) during mixing. Again, all chemicals used were reagent grade, and the water purified (resistivity greater than $16 \text{ M}\Omega \text{ cm}$).

Heterojunction Synthesis: Cu_2O was deposited galvanostatically at -1.0 mA cm^{-2} following the method of Izaki.^[11] Gold or silver contacts (0.125 cm^2 illuminated area) were evaporated onto the Cu_2O using a BOC Edwards resistance evaporator to form an ohmic contact.

Materials Characterization: SEM images were obtained using a LEO VP-1530 field-emission scanning electron microscope equipped with an EDX detector. TEM images were obtained with a Jeol JEM-2011 transmission electron microscope operated at 200 kV acceleration voltage and with a FEI Titan TEM operated at an acceleration voltage of 300 kV. XRD measurements were performed using a Bruker D8 theta/theta XRD system with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) and a LynxEye position sensitive detector. Cyclic voltammetry measurements were

performed using the same three-electrode cell used for depositions and custom-made LabView software.

Device Characterization: Impedance measurements were performed in the dark using an Agilent 4294 Precision Impedance Analyser. For each frequency scan, 201 data points were taken on a logarithmic scale and recorded using custom-made LabView software. The impedance data was fit to relevant circuit models using LEVMW complex nonlinear least-squares fitting software.^[35]

Current density-voltage measurements were performed using a Keithley 2400 SourceMeter with a custom-made LabView program. A solar simulator equipped with AM 1.5G filters was used at 100 mW cm⁻² intensity. The illumination intensity was calibrated using an ISE Fraunhofer institute certified silicon reference diode equipped with a KG5 filter to minimize spectral mismatch errors.

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Note: This article was amended on February 8, 2011 to update Figure 4f from the one originally published online, which showed an incorrect scale bar.

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