Direct measurement of the built-in potential in a nanoscale heterostructure

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We combine transmission electron microscopy with electrostatic force microscopy to determine the built-in potential across individual isolated Cu2S-CdS heterostructured nanorods. We observe a variation of potentials for different bicomponent nanorods, ranging from 100 to 920 mV with an average of 250 mV. Nanorods of a uniform composition with no heterojunction do not show a built-in potential, as expected. The results are particularly relevant for applications of colloidal nanocrystals in optoelectronic devices such as photovoltaics.

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The electronic structure of nanocrystals is an intriguing basic science topic and of great importance for applications. However, few experimental techniques exist to directly characterize on a nanometer scale the electronic properties of structurally well-characterized heterogeneous materials. In fact, one of the most important characteristics of a semiconductor-semiconductor interface, the built-in potential, which determines the suitability of the interface for charge rectifying applications such as photovoltaics, has not previously been directly measured for an isolated bicomponent nanorod (NR). As colloidal grown nanocrystals typically display a distribution of properties, single-particle measurements are invaluable for observing individual differences.1 In the bicomponent cuprous sulfide—cadmium sulfide (Cu2S-CdS) heterojunction NRs examined in this work, there is significant variability in the relative fraction of the two materials among individual NRs, even within a given batch. Ideally, one would like to correlate the internal chemical structure of the NR with an independent mapping of the electronic structure of the same NR.

We report such a correlation experiment here. We use high-resolution transmission electron microscopy (TEM) to characterize Cu2S-CdS NRs and then employ electrostatic force microscopy (EFM), an adaptation of atomic force microscopy (AFM), to determine the electrostatic potential gradient associated with the same NRs. This is the first such application of EFM. EFM has previously been successfully employed to characterize semiconductors and nanomaterials including the charging of nanoscale systems,2–4 polarization in the tip-sample direction,5 and resolving surface potential distributions on thin films.6,7 Another technique for classifying nanomaterials, scanning tunneling spectroscopy, has been used to measure the band offsets of heterogeneous nanocrystals.8–10 In this study we find that homogeneous, single-component NRs with no heterojunction display no built-in potential, while bicomponent NRs have a built-in potential ranging from 100 to 920 mV. For comparison, a Cu2S-CdS thin film has a built-in potential of 840 mV and exhibits photovoltaic behavior.11,12 Additionally, the polarity of the built-in voltage for all bicomponent NRs studied is consistent with a Cu2S-CdS thin film, that is, the CdS side is negative and the Cu2S side is positive.

Cu2S-CdS NRs were synthesized using partial cation exchange to substitute Cu+ for Cd2+ ions within CdS NRs, as described previously.13 The exchange reaction leads to separate regions of Cu2S and CdS connected by well-defined,

FIG. 1. (a) A schematic of the experiment. The rods are examined in the TEM on an electron transparent silicon nitride window with a thin rear coating of conducting amorphous carbon. This substrate enables the same rods to be imaged with both the TEM for heterojunction identification and electrostatic force microscopy, which requires a conducting back plane. (b) High-resolution TEM image of CdS-Cu2S nanorods on a carbon film substrate. In the high magnification inset, lattice planes of both materials are visible, and the two materials induce a contrast difference over the length of the rod. Note that not all rods display a heterojunction.
epitaxial interfaces.\textsuperscript{14} The NRs used in this study have an average length of 29±4 nm and an average diameter of 9±4 nm; there is little change in the NR dimensions upon the partial transformation to Cu\textsubscript{2}S.

The Cu\textsubscript{2}S-CdS NRs were spin coated under argon upon a silicon nitride substrate with alignment marks and 20-nm-thick windows with 10 nm of amorphous carbon on the backside. This carbon layer provides a grounding plane for the EFM measurements while maintaining electron transparency. A control sample batch with homogeneous CdS rods that had not undergone exchange was prepared in the same fashion. TEM images were obtained with a JEOL 2010 TEM operated at 100 keV and AFM/EFM measurements were obtained with an Asylum Research MFP-3D AFM with platinum coated silicon probes (Olympus OMCL-AC240TM) under continuous argon flow at 1.5 sccm/s.

Figure 1 a shows schematically the experimental sample measurement configuration. Figure 1(b) shows TEM images for bicomponent Cu\textsubscript{2}S-CdS NRs and the inset shows a high-resolution image of a single NR heterostructure. The bicomponent nature of this NR is dramatically evident with contrasting lattice planes clearly defining a heterojunction approximately halfway across the length of the rod. At lower resolution the bicomponent nature of most of the NRs is still evident, as shown by the TEM contrast differential across the NRs in the main panel of Fig. 1(b). Importantly, not all of the rods examined display a heterojunction.

Alignment marks on the sample substrate allow individual NRs characterized by TEM to be subsequently located and characterized by AFM/EFM. Figure 2 shows an example of the dual-measurement and correlation method. The lower portion of the figure shows a TEM image of ion-exchanged Cu\textsubscript{2}S-CdS NRs with the outer perimeters highlighted for clarity (red online). In the upper portion of Fig. 2, similar TEM data exist, but only the perimeters of the NRs have been drawn. The upper portion of Fig. 2 represents AFM topography data. Because of small thermal drift during the relatively slow AFM scan the AFM topography image is registered by an affine transformation using three landmark points.

The low-resolution AFM topography data shown in Fig. 2 serve only to register the AFM instrument to predetermined NR locations. At specific locations of TEM-characterized NRs, EFM data were collected. For EFM measurements, a conducting AFM tip was used to scan each line of the sample twice, first near the surface for topography, and then raised 20 nm above the surface with a bias dc voltage applied to the tip. During the raised scan, the electrostatic interaction be-
NR 3, on the other hand, has relatively uniform TEM con-
tact of forces in the tip-sample-substrate system. To correctly ex-
tended that induces a built-in voltage across the NRs. The-
oretical work has shown that on the scale of tens of nanom-
profile to extract the built-in potential across the NRs.

Figure 3 shows, for three independent NRs, the raw TEM
image (upper row images) along with the TEM opacity, ob-
tained by measuring the contrast level along a central axis
line scan of the NR. The TEM opacity is shown in the second
row of Fig. 3. The TEM images and opacity line scans clearly
indicate a nonhomogeneous nature to NRs 1 and 2. The darker region (on the right side of NR 1, and on the left
side of NR 2) is identified with Cu$_2$S while the lighter region is identified with CdS. Hence, NRs 1 and 2 are bicompo-
nent NRs (though apparently not with 50/50 composition
distributions) with expected built-in electrostatic potentials.

Figure 3 shows, in the third row, the experimentally de-
termined EFM data for NRs 1, 2, and 3. The solid lines
represent the phase shift response to a set of expected built-in potential magnitudes, 400 mV and 100 mV ,
respectively. As expected, the polarity of the built-in poten-
tial differences across the structure. We then performed
EFM measurements on this system, and verified that our
model, adjusted to reflect the geometry of this control sys-
tem, accurately reproduced the phase shift response to a

\[
\Delta \Theta = \arcsin \left( \frac{Q \ dF}{k \ dz} \right),
\]

where $Q$ is the quality factor of the cantilever, $k$ is the spring constant, and $dF/dz$ is the derivative of the force with re-
spect to the tip-sample distance.

Using the model, the electrostatic force between the tip
and the sample was calculated for a series of tip positions
along the NR axis and at three different tip heights above the
sample, at 19, 20, and 21 nm. To obtain the force gradient at
each position along the NR, we used a finite difference ap-
proach. With the forces from the three different tip heights
we calculated two gradients and ensured that they converge to better than 10%. Using the measured values for
$Q$ and $k$, and Eq. (1), we generated the expected phase shift.

Table I. Statistical analysis of EFM data. Shown are the slope of the phase shift trend over the rod, normalized to the length of the rod, $V_{bi}$, and the reduced $\chi^2$ goodness of fit parameter for this $V_{bi}$. The first three rows present the results for rods (1), (2), and (3) shown in Fig. 3. The fourth row gives the averages of the results for all rods. In the fifth row, all phase profiles were averaged before they were analyzed as a single data set. The last row shows the average results for the single material CdS control rods.

| Rod(1) | 12 | 400 | 0.96 |
| Rod(2) | 9  | 100 | 0.5  |
| Rod(3) | 1.4| 0   | 0.64 |
| Averaged results | 14±9 | 250 | 0.96 |
| Averaged data for each position | 15 | 100 | 1.4 |
| Control CdS rods | 3.2±2.8 | 0 | 1.04 |

AFM tip was modeled as a cone with a spherical apex with
dimensions given by the manufacturer and was positioned above a single NR. We did not include the cantilever in the
model, as it has been shown to have negligible influence on
the phase shift profile. The NR on the substrate surface was
modeled as two separate, adjoining strips with dielectric con-
stants $\varepsilon_1$ and $\varepsilon_2$ set to the bulk values for CdS and Cu$_2$S. The model strips were separated by a 1 nm gap and kept at
$-V_{bi,\text{sim}}/2$ and $V_{bi,\text{sim}}/2$, respectively, where $V_{bi,\text{sim}}$ was varied from 0 to 1 V. The gap avoids divergence during compu-
tation and is expected to have negligible influence on the
result. For simplicity, we modeled the two component sides
equal in length.

Using the model, the electrostatic force between the tip
and the sample was calculated for a series of tip positions
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known potential difference, equivalent to the built-in voltage in a NR.

Additional NRs were examined in a manner similar to that described for the three specimens in Fig. 3. EFM analysis of a control batch of 27 nonion-exchanged CdS NRs resulted in flat electrostatic potentials, i.e., \( V_{bi} = 0 \). TEM and EFM measurements were performed on 18 additional bicomponent Cu2S-CdS NR specimens which showed a single junction in TEM analysis and had random physical orientations. The results for these additional samples, together with those for NRs 1, 2, and 3, and the control CdS set, are summarized in Table I.

Table I shows that the phase gradient \( \frac{d\phi}{dx} \) (and thus the built-in potential) has the same polarity for all 20 bistructure NRs; using TEM opacity measurements, we determined that the phase gradient increases from the CdS side to the Cu2S side. The average slope is 0.014°/nm with a standard deviation of 0.0097. For comparison, the average of the absolute slopes is 0.0097. For comparison, the average of the absolute slopes is 0.014°/nm, indicating that the measured gradients of the bicomponent rods are within our measurement resolution.

The average built-in potential for the NRs is \( \langle V_{bi} \rangle \approx 250 \) mV. Excluded from this set are 3 NRs which had poor fits to the model (reduced \( \chi^2 > 1.6 \)). For the \( \chi^2 \) analysis, we use the EFM error of 0.1°, based on measurements over the empty substrate. The average goodness of fit for this set is \( \langle \chi^2 \rangle = 0.96 \), and the average \( \chi^2 \) for all 20 rods is 1.1, indicating good consistency between the model and the experiment. We estimate the error of determining the built-in voltage with our method to be \( \pm 100 \) mV, an interval within which the \( \chi^2 \) goodness of fit values do not clearly favor a specific value for \( V_{bi} \).

In addition to analyzing individual rods, we also analyzed the average phase profile of all NRs, by aligning orientationally all 20 EFM profiles and averaging. Table I (fifth row) shows the results for this averaged profile, which compares well with taking the average of the individually fitted NRs: the slopes are similar and \( V_{bi} \) is within the expected error margin.

Table II gives the distribution of built-in potentials associated with the NRs. Ten of the twenty NRs have a \( V_{bi} \) in the range 100 ± 100 mV while seven have a larger \( V_{bi} \) of up to 920 mV. No NR has a potential greater than 920 mV. The voltage variation within the set may arise from: the presence of different crystalline phases of Cu2S (high chalcolite, low chalcolite, or djuerlite); lattice plane orientation at the CdS-Cu2S interface; or the presence of a small Cu2S cap at the end of the CdS portion of the rod. Despite clearly identifying NRs with a junction, the TEM images do not reveal these small variations that can cause the observed variability in the phase profile and the resulting built-in potential.

In summary, we measured electrostatic potential gradients in nanorods with a technique that is sensitive to the individual variability in the built-in potentials of the rods. Most rods examined showed a built-in potential in the range of 100–400 mV, with some as high as 920 ± 100 mV, indicating that these rods show promise for applications such as photovoltaics. The characterization technique is generally useful to electronically quantify new nanostructured materials.

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**TABLE II.** The number of rods associated with each \( V_{bi} \) interval, as determined by a \( \chi^2 \) analysis of the fit of the measured phase profiles to the model. For three of the twenty NRs, \( \chi^2 \) values did not indicate a good fit.

<table>
<thead>
<tr>
<th>( V_{bi} )</th>
<th>Number of rods</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;200 mV</td>
<td>10</td>
</tr>
<tr>
<td>200–400 mV</td>
<td>2</td>
</tr>
<tr>
<td>400–600 mV</td>
<td>2</td>
</tr>
<tr>
<td>600–920 mV</td>
<td>3</td>
</tr>
<tr>
<td>Min ( \chi^2 &gt; 1.6 ) (poor fit)</td>
<td>3</td>
</tr>
</tbody>
</table>

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The average fraction of Cu$_2$S depends on the number of Cu$^+$ cations added to the batch. The relative fraction of Cu$_2$S varies among individuals within a sample. The growth of Cu$_2$S into the CdS NRs via cation exchange preferentially occurs at the end facets leading to Cu$_2$S segments at one or both ends. The interface between the segments, though not apparent in Fig. 3, can be studied with high-resolution TEM and is discussed in detail in Ref. 13.


We find that this approximation, which is obviously not precisely correct for NRs 1 and 2, introduces only a modest deviation within an estimated range of ±100 mV in the determination of $V_{bi}$; the limited EFM resolution on this scale does not justify a more complex component distribution.

The phase profile trends for these rods are similar to the trend in all other rods but the fits are poor because these NRs include statistical variations that are larger than average. For normal statistical fluctuations, the probability of measuring three or more rods with a $\chi^2$ value greater than 1.6 is 32%, given our sample size of 20. Thus, the presence of three rods with a poor fit to the model is indicative of expected statistical variations.