Size-dependent Phononic Properties of PdO Nanocrystals Probed by Nanoscale Optical Thermometry

Rizia Bardhan1*, Holly F. Zarick1, Adam Schwartzberg2, Cary L. Pint3
1 Department of Chemical and Biomolecular Engineering, Vanderbilt University, Nashville, TN 37215, USA
2 The Molecular Foundry, Material Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA
3 Department of Mechanical Engineering, Vanderbilt University, Nashville, TN 37235, USA

* corresponding author: rizia.bardhan@vanderbilt.edu

Figures

Figure S1. X-ray diffraction patterns of (a) 4 nm and (b) 10 nm PdO nanocrystals demonstrating the complete oxidation of Pd nanocrystals to PdO during the synthesis process. Aliquots of the reaction mixture were examined before and after air exposure.
Figure S2. (a) TEM image showing polydisperse PdO nanocrystals when 0.15 g of Pd(acac)$_2$ was used. The solvent was also changed from trioctylphosphine to oleylamine and oleic acid but the size could not modified beyond 10 nm without high degree of polydispersity. A different approach was therefore used to obtain larger particles, however cubic nanocrystals were obtained instead of spherical nanoparticles. (b) SEM image of ~ 25 nm Pd@PdO nanocubes obtained by reduction of Pd(acac)$_2$ in the presence of dimethylformamide and polyvinylpyrrolidone and exposure to O$_2$ at 180 °C.
Figure S3. X-ray diffraction patterns of pristine Pd foil (red) and Pd foil after oxidation for 2 hours with heat treatment at 350 °C. Since the Pd foil is relatively thick (0.025 mm), metallic Pd remains. However a strong PdO peak corresponding to (101) crystal plane demonstrates the oxidation of Pd foil to PdO.

**Grain Size Determination of Bulk PdO Foil**

Grain Size of bulk PdO foil was determined from the XRD-profile shown in Figure S4 by using the Scherrer’s equation given by:

\[ d = \frac{0.9 \lambda}{\beta \cos \theta} \]

where \( d \) is the size of the crystallite in Å, \( \beta \) is the full width at half maximum of the XRD peak in radians, \( \lambda \) is wavelength of Cu K\( \alpha \) line \( \lambda = 1.5418 \) Å, and \( \theta \) is half of the 2\( \theta \) value of the peak of PdO observed at (101) in radians.

Using \( \beta = 0.001745 \) radians and \( \theta = 0.2917 \) radians, we calculated \( d = 273 \text{ nm} \). Therefore, it is evident, that PdO foil had grain sizes equivalent to bulk.
**Figure S4.** SEM images of pristine Pd foil at (a) low magnification, and (b) high magnification and SEM images of foil oxidized to PdO after 2 hours of oxygen plasma and heat treatment at (c) low magnification and (d) high magnification. The SEM images clearly show that microstructuring occurs on the surface of Pd foil after oxidation to PdO.

**Figure S5.** Hysteresis observed in the (a) peak broadening, and (b) peak shifts when the power density is increased and then immediately decreased. The hysteresis in the forward and backward experiments indicates that heating (and melting) induced structural and electronic changes results in variations in the phonon energies and hence the FWHM and peak positions do
not match when the power is decreased. After one cycle, however, the results are no longer reversible due to sample damage caused by complete nanocrystal melting.

**Figure S6.** 10 nm PdO nanocrystals on quartz substrate (a) pristine, and (b) after laser-induced melting. The scale bar is 100 nm. The nanocrystals undergo irreversible structural transformation with an effective increase in grain size after intense light mediated heating.

**Figure S7.** The melting temperature of nanocrystals, \( T_m \), and bulk, \( T_B \), correlated to the size of the nanocrystals and to the grain size of the bulk. The solid line is a theoretical fit using the equation shown in inset. The blue dotted line indicates the nanocrystal size (~ 25 nm) beyond which bulk melting behaviors is observed.

We used the value of \( \Delta S_B = 6.426 \text{ J/g-atomK} \).\(^1\) To obtain this theoretical fit, we assumed that at \( R \geq 25 \text{ nm} \) bulk melting temperatures are obtained. This is a reasonable assumption as it has been demonstrated with other semiconductor and oxide nanocrystals (see ref. 30-34 main text)
that phonon confinement effects no longer play a role when nanocrystal sizes are $\geq 25$ nm. While this theoretical fit provides semi-quantitative information for our experimental results, the model is robust and can be generalized to a range of semiconductor nanocrystal systems to obtain size-dependent melting behaviors.