

Effect of Rare-Earth Metal Oxide Nanoparticles on the Conductivity of Nanocrystalline Titanium Dioxide: An Electrical and Electrochemical Approach

Pom L. Kharel,¹ Paul M. Cuillier,² Kasun Fernando,³ Francis P. Zamborini,^{1*} and Bruce W. Alphenaar^{3*}

¹Department of Chemistry, University of Louisville, Louisville, Kentucky 40292, United States

²University of Arizona, Tucson, Arizona 85721, United States

³Electrical and Computer Engineering Department, University of Louisville, Louisville Kentucky 40292, United States

*Corresponding Authors: f.zamborini@louisville.edu and bruce.alphenaar@louisville.edu

SUPPORTING INFORMATION

Derivation of $e^{-qV_{peak}/kT} = \nu/\nu_0$

The following derivation is based on the work of Bisquert *et al.*¹ The change in the probability f that a trap state is occupied as a function of time is given by:

$$\frac{df(t)}{dt} = \frac{1}{\tau_{tr}(t)}[1 - f] - \frac{1}{\tau_{dtr}}f \quad (1)$$

where $1/\tau_{tr}$ is the trapping rate and $1/\tau_{dtr}$ is the de-trapping rate. For deep level traps, assuming that the rate of capture is proportional to the number of electrons in the conduction band, the de-trapping rate is assumed to be zero, while the trapping rate is given by:

$$\frac{1}{\tau_{tr}(t)} = \beta_n n_c = \frac{1}{\tau_0} e^{(E_{Fn}(t) - E_{FO})/kT} \quad (2)$$

where n_c is the density of electrons in the conduction band and β_n is the time constant per unit volume for electron capture.

The time dependence comes about because the Fermi energy changes as a function of time with potential:

$$-(E_{Fn}(t) - E_{F0})/q = V_0 - vt \quad (3)$$

Here, V_0 is the starting bias, and v is the bias scan rate.

The trapping rate can then be re-written as:

$$\frac{1}{\tau_{tr}(t)} = (1/\tau_0) e^{-q(V_0 - vt)/kT} = g(t) \quad (4)$$

The function $g(t)$ is introduced to make the mathematics easier to follow. Taking the derivative of Eq. (4) gives:

$$\frac{dg(t)}{dt} = \frac{qv}{kT} g(t) = \frac{1}{\tau_v} g(t)$$

where $\tau_v = kT/qv$ is introduced. Solving the differential equation (1), the occupation probability $f(t)$ should be given as:

$$f(t) = 1 - e^{(\tau_v g(0) - \tau_v g(t))} \quad (5)$$

Taking the derivative of Eq. (5),

$$\frac{df(t)}{dt} = \tau_v e^{(\tau_v g(0) - \tau_v g(t))} \frac{dg(t)}{dt} = g(t) e^{(\tau_v g(0) - \tau_v g(t))}$$

Re-writing Eq. (1) using our definition for $g(t)$ and taking $1/\tau_{dtr} = 0$ gives:

$$\frac{df(t)}{dt} = g(t)(1 - f(t)) \quad (6)$$

so clearly the function in (5) is a solution to the differential equation (6).

Finally, the peak position occurs at the potential where there is maximum change in the trap occupation probability, or at the point where $d^2f/dt^2 = 0$. Taking the second derivative of the occupation probability gives:

$$\frac{d^2f}{dt^2} = e^{\tau_v g(0)} \left[-g^2(t) e^{-\tau_v g(t)} + \frac{g(t)}{\tau_v} e^{-\tau_v g(t)} \right]$$

For this to equal zero, $g(t) = 1/\tau_v$, or $\tau_{tr} = kT/qv$. Plugging this into Eq. (4) then gives:

$$\frac{qv}{kT} = 1/\tau_0 e^{-qV_{peak}/kT} \Rightarrow e^{-qV_{peak}/kT} = v/v_0$$

Adding rare earth oxide (REO) nanoparticles causes the peak position to have a stronger sweep rate dependence and appear at more negative potentials than in the pristine TiO_2

material. This would occur if the probability for trapping an electron from the conduction band goes down because there are fewer low lying deep trap states.

Conductivity of Pure REO nanoparticles

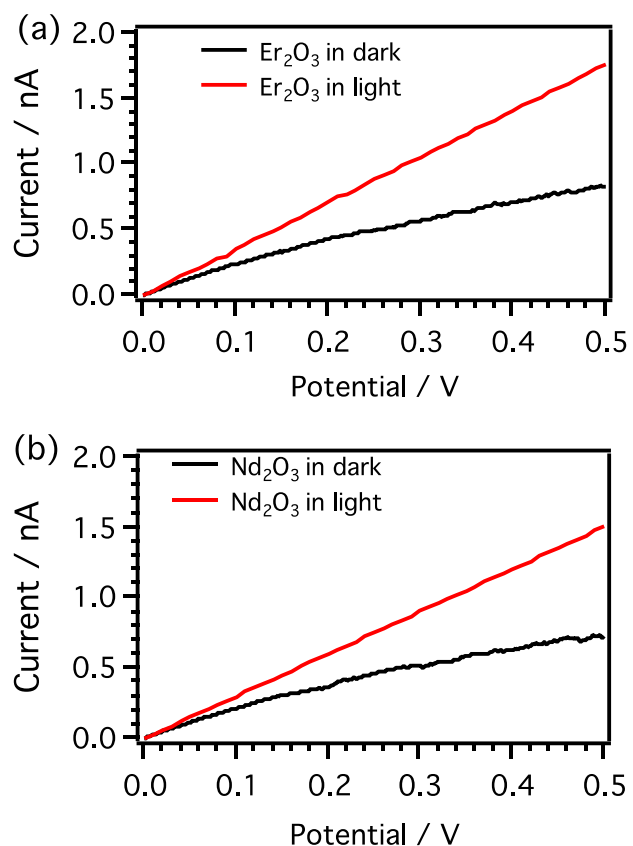


Figure S1. Conductivity measurements of films of pure (a) Er_2O_3 and (b) Nd_2O_3 nanoparticles. The films of rare earth oxide (REO) nanoparticles are less conductive than undoped titania.

Cyclic voltammograms of undoped and REO-doped nanocrystalline titanium dioxide (NTD)

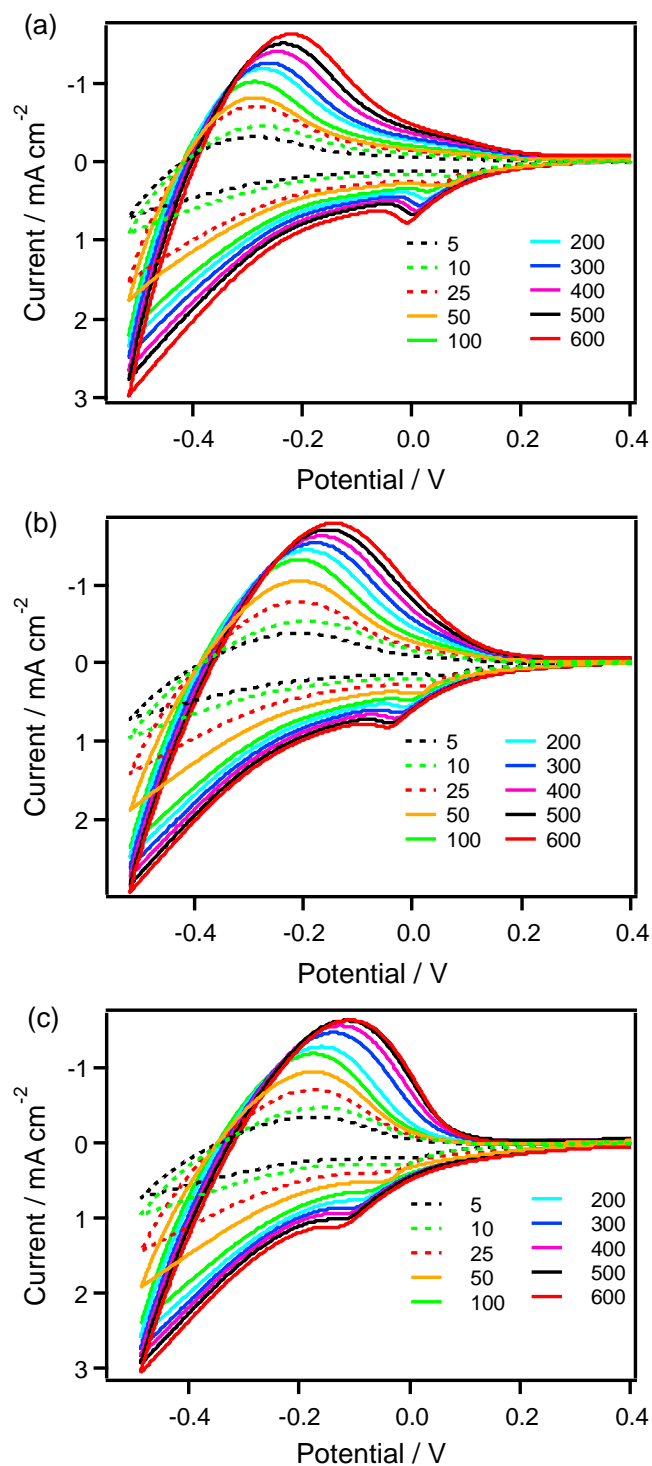


Figure S2. Cyclic voltammograms of (a) undoped, (b) ErNPs-Solid and (c) NdNPs-Solid at different scan rates as shown in the keys. The scan rates are in mV/s.

Table S1. Peak potentials at different scan rates for the different films.

Scan Rates (mV/s)	Peak potential (V) vs RHE		
	Undoped	ErNPs-Solid	NdNPs-Solid
5	0.123	0.073	0.018
10	0.109	0.058	0.003
25	0.078	0.033	-0.025
50	0.065	0.019	-0.038
100	0.042	-0.001	-0.065
200	0.040	-0.018	-0.075
300	0.024	-0.028	-0.093
400	0.012	-0.032	-0.099
500	0.005	-0.038	-0.104
600	0.001	-0.048	-0.126

Table S2. Calculation of τ_0 from Figure 4b.

Samples	$y - intercept = \frac{kT}{q} \ln(v_0)$	v_0 (mV/s)	τ_0 (ms)
Undoped	0.16756	629.3	42
ErNPs-Solid	0.11946	98.95	263
NdNPs-Solid	0.057258	9.045	2874

1. Bertoluzzi, L.; Cardona, I. H.; Gottesman, R.; Zaban, A.; Bisquert, J. Relaxation of Electron Carriers in the Density of States of Nanocrystalline TiO₂. *J. Phys. Chem. Lett.* **2014**, 5, 689-694.