

Magnetoelectric Control of Superparamagnetism

Hyungsuk K. D. Kim,^{†,||} Laura T. Schelhas,^{‡,||} Scott Keller,[§] Joshua L. Hockel,[§] Sarah H. Tolbert,^{*,†,‡,#} and Gregory P. Carman^{*,†,§}

[†]Department of Materials Science and Engineering, UCLA, Los Angeles, California 90095, United States

[‡]Department of Chemistry and Biochemistry, UCLA, Los Angeles, California 90095, United States

[§]Department of Mechanical and Aerospace Engineering, UCLA, Los Angeles, California 90095, United States

[#]California NanoSystems Institute, University of California, Los Angeles, California 90095, United States

(5) Supporting Information

ABSTRACT: Here we demonstrate electric-field induced magnetic anisotropy in a multiferroic composite containing nickel nanocrystals strain coupled to a piezoelectric substrate. This system can be switched between a superparamagnetic state and a single-domain ferromagnetic state at room temperature. The nanocrystals show a shift in the blocking temperature of 40 K upon electric poling. We believe this is the first example of a system where an electric field can be used to switch on and off a permanent magnetic moment.



KEYWORDS: Magnetoelectric, superparamagnetic, multiferroic, PMN-PT, Ni nanocrystal

E lectromagnetic devices, including antennas, motors, and memory, rely on extrinsic coupling produced by passing an electrical current through a wire to generate a magnetic field, a discovery made by Oersted and further developed by Ampere in 1820.1 While extremely successful in the large scale, this approach suffers significant problems in the small scale where resistive losses are preventing further device miniaturization. Since Curie's first attempt in 1894,² researchers have searched for an intrinsic approach to electrically control magnetization, and some minor progress has been made during the past decade using electric field induced strain to modulate magnetization in multiferroic composite materials.³⁻⁵ While promising, these "bulk" multiferroic materials contain multidomain magnetic structures that produce marginal magnetization changes with the application of an electric field.⁶⁻¹⁰ During the last five years, a handful of researchers have focused on nanoscale elements, using electric field induced strain to control a single magnetic domain. $^{11-15}$ These studies show more dramatic magnetization changes, but the electric fields only reorient the magnetization state and do not change its magnitude. Therefore, what is critically needed is an approach to intrinsically control the net observed magnetization state. Superparamagnetism, which occurs in nanoscale ferromagnetic crystals when the ambient thermal noise is larger than the magnetic ansisotropy resulting in a zero magnetization state, may hold the solution to this problem.¹⁶⁻¹⁸ Here we report experimental results demonstrating that an electric-fieldinduced anisotropy in a multiferroic system is capable of electrically switching between a superparamagnetic state and a single-domain ferromagnetic state at constant temperature and thus represents an intrinsic approach to turn on and off a net magnetic field. This electrical modulation of magnetism is achieved via an electric-field-induced strain in a magnetoelectric composite composed of Ni nanocrystals mechanically coupled to a (011) oriented PMN-PT single crystal. To our knowledge, this is the first example of a system where an electric field is used to turn on and off a permanent magnetic moment, and thus this work marks a significant advance in the field of electromagnetic devices.

The magnetoelectric composites used in this work were composed of ferromagnetic 16 nm diameter Ni nanocrystals mechanically coupled to (011) $[Pb(Mg_{1/3}Nb_{2/3})O_3]_{(1-x)}$ - $[PbTiO_3]_r$ (PMN-PT, $x \approx 0.32$) ferroelectric single crystal substrates. Nickel was chosen for its superior magnetoelastic properties as well as its stability in comparison to other pure metal nanocrystals. The nanocrystals were synthesized via thermal decomposition of 1 mmol nickel acetylacetonate in the presence of oleyamine (7 mL), oleic acid (2 mmol), and triocylphosphine (2 mmol).¹⁹ For this work, optimized conditions for the synthesis varied slightly from ref 19 and are thus summarized here. The solution was stirred at room temperature for 20 min under gentle Ar flow before heating first to 130 °C for 30 min and then to 240 °C (reflux) for 30 min. The solution was then cooled, and the particles were precipitated with ethanol and centrifuged. Two further washings were done with ethanol and hexane followed by

```
Received:September 17, 2012Revised:February 1, 2013Published:February 11, 2013
```

Nano Letters

centrifugation to remove any unbound ligands. The particles were stored dissolved in hexane under argon.

Figure 1a shows TEM images of the as-synthesized Ni nanocrystals indicating that they are both spherical and fairly



Figure 1. Characterization of Ni nanocrystals. Part a shows a TEM image of several as-synthesized Ni nanocrystals. The average nanocrystal diameter is ~ 16 nm, and particles are approximately spherical and nonagglomerated. Part b shows an SEM micrograph of the nanocrystals after deposition onto the piezoelectric substrate. Submonolayer coverage of nonagglomerated nanocrystals is observed.

monodisperse in size. X-ray diffraction data obtained on the Ni nanocrystals (Figure S1) shows an FCC structure (JCPDS #4-850), consistent with literature reports. Magnetoelectric composites were produced by slowly evaporating a dilute solution of the Ni nanocrystals dissolved in hexane onto an unpoled PMN-PT substrate coated with a thin titanium adhesion layer.²⁰ The (011) oriented PMN-PT single crystal ferroelectrics were manufactured by Atom Optics Co., Ltd. (Shanghai, China). The substrate was angled between 60 and 70° in a vial containing a dilute solution of Ni nanocrystals dispersed in hexanes. Gentle heat of approximately 80 °C was applied to facilitate evaporation along with a gentle Ar flow to prevent oxidation of the Ni nanocrystals. An SEM image of the particles deposited onto the substrate is shown in Figure 1b, demonstrating that a homogeneous submonolayer distribution is produced.

After nanocrystal deposition, the organic ligands on the particles were removed in an inert atmosphere using a two minute argon plasma etch. Without breaking vacuum, a 30 nm thick Pt layer was deposited onto the PMN-PT substrate to fully encase the Ni particles and protect them from oxidation (see Figure 2a). Both the argon plasma etching and the Pt sputtering were performed using a Hummer 6.2 from Anatech. In addition to preventing oxidation, the Pt layer also helps provide a load transfer path from the PMN-PT substrate to the Ni nanocrystals. A schematic of the complete magnetoelectric architecture is shown in Figure 2A.

XPS depth profiling analysis (Figure S2) of the magnetoelectric composite indicates that the Ni nanoparticles are wellpreserved throughout this process and that only a small amount of oxidation occurs (XPS Ni 2p peak analysis shows 95% Ni, 5% NiO). The NiO likely arises from reaction of the Ni nanocrystals with the oxidized surface of the Ti electrode. Importantly, this slight oxidation of the Ni nanocrystals appears to be a critical component for producing good adhesion of the nanocrystals to the substrate, which is required to facilitate strain transfer from the piezoelectric substrate to the particles. Indeed, when the nanocrystals are deposited on oxide-free Pt substrates rather than the Ti/TiO_x substrates used here, the effects reported in this manuscript are not observed, suggesting that interfacial bond formation coupled with the Pt overlayer are both critical components of the strain transfer process between the piezoelectric substrate and the nanocrystals. A more detailed schematic of the device structure, including all interfacial layers can be found in the SI in Figure S3.

Magnetic measurements on the magnetoelectric sample were performed before and after poling the PMN-PT substrate at room temperature. Figure 2b shows the anisotropic in-plane (x-y plane) strains generated as a function of applied electric field measured using a bidirectional strain gauge attached to the sample. In the unpoled state, the Ni particles in the magnetoelectric sample are subjected to negligible strains (ε_x = ε_v = 0). During poling (i.e., E = 0.4 MV/m), compressive strains up to $\varepsilon_x = -1200 \ \mu\varepsilon$ and $\varepsilon_y = -800 \ \mu\varepsilon$ are produced. Upon removal of the electric field, large anisotropic compressive strains of $\varepsilon_x = -300 \ \mu \varepsilon$ and $\varepsilon_y = -1000 \ \mu \varepsilon$ are present in the poled state. Since Ni has a negative magnetostriction coefficient, any induced magnetoelastic anisotropy causes the magnetic dipoles in the single domain Ni nanocrystals to align along the dominant compressive strain direction (which corresponds to the deeper energy well).^{13,21}



Figure 2. Magnetoelectric device characteristics. Part a shows a schematic representation of the full device. 1: 30 nm thickness Pt layer (drawn partially transparent for clarity). 2: 16 nm diameter Ni nanocrystal. 3: 10 nm thick Ti electrodes evaporated on the top and bottom of the PMN-PT. 4: 500 μ m thick (011) oriented PMN-PT single crystal substrate. Arrows indicate the direction of induced anisotropic strain. Part b shows the strain induced in PMN-PT via an electric field applied along the (011) direction. Red triangles indicate strain along the *y*-axis, black circles along the *x*-axis.



Figure 3. Magnetic hysteresis curves obtained on nickel nanocrystals embedded in Pt thin film on top of (011) PMN-PT at 298 K. Parts a and b show data measured with the magnetic field applied parallel to the x- and y-axes, respectively, on the unpoled sample. Parts c and d show data measured with the magnetic field applied parallel to the x- and y-axes, respectively, on the poled sample.



Figure 4. Zero field cooled (ZFC) magnetization curves as a function of temperature for Ni nanocrystals embedded in Pt on (011) PMN-PT before and after electrical poling. All data is normalized to 1 at the peak magnetization. Parts a and b show data on the unpoled sample, measured in the xand y-directions, respectively. Parts c and d show data on the poled sample, again measured in x- and y-directions, respectively. All curves were measured using a 50 Oe applied field. The line drawn at 300 K is intended as a guide to the eye.

For the poled state, the larger anisotropic strain along the *y*-axis direction produces this deeper energy well.

Figure 3a and b shows room temperature magnetic moment (M) measurements as a function of the applied magnetic field (H) for the unpoled (i.e., $\varepsilon_x = \varepsilon_y = 0$) magnetoelectric composites measured in x- and y-directions, respectively. Measurements were conducted using a superconducting

quantum interference device (SQUID) magnetometer (Quantum Design, MPMS XL-5). Similar, small coercive fields, $H_c <$ 20 Oe, are observed in both directions indicating that the sample is both magnetically isotropic in-plane and dominantly superparamagnetic (i.e., they show near zero net magnetization). The small measured coercive fields likely result from the inhomogeneous size distribution of the nanocrystals within the sample, resulting in a few ferromagnetic nanocrystals distributed among a sample containing dominantly superparamagnetic nanocrystals. The small differences in the x and y data are attributed to small variations in the spatial distribution of the nanocrystals produced during the evaporative deposition process used to manufacture the magnetoelectric composite and are typical of magnetic measurements on arrays of superparamagnetic nanocrystals.

Figure 3c and d shows similar magnetic measurements after the sample has been poled ($\varepsilon_x = -300 \ \mu \varepsilon$, $\varepsilon_y = -1000 \ \mu \varepsilon$). The data in Figure 3c show that a hard magnetic axis is created parallel to the x-direction for the poled sample with a magnetic anisotropy (H_a) of 600 Oe. The ratio of the remanent magnetization (M_r) to the saturation magnetization (M_s) is very low, suggesting that domains tend to orient in an off-axis direction. In contrast, Figure 3d shows that a magnetic easy axis is created along the y-direction for the poled sample. In this direction, $M_{\rm r}$ is approximately equal to $M_{\rm s}$, indicating that the sample consists of essentially single domain Ni nanocrystals that are aligned along the y-axis. Furthermore, $H_c = 80$ Oe measured along this direction confirms a deeper potential well for spin alignment is present in the *y*-direction after application of an electric field. This result thus demonstrates that the application of an electric field stabilized the y-axis aligned spin state, resulting in a net magnetization equivalent to the saturation magnetization of Ni (i.e., 485 emu/cc). Rephrased, this result shows that we can use an applied electric field to "turn on" a net magnetization.

Figure 4a and b shows normalized magnetic moments as a function of temperature for the unpoled magnetoelectric sample. Samples were initially cooled to 10 K in the absence of a magnetic field (zero field cooling, ZFC) followed by measurement of the magnetic moment as a function of temperature in a 50 Oe applied field. The temperature corresponding to the highest magnetic moment is typically defined as the blocking temperature (T_b) , above which magnetic dipoles begin to lose their directionality due to thermal randomization and the sample becomes superparamagnetic.²² There are some small differences in the data measured in the *x*- and *y*-directions, which are attributed to the evaporative deposition process, as discussed previously. Nonetheless, similar blocking temperatures of ~300 K are found in the unpoled state in both directions. We again note that this blocking temperature corresponds to the average sized nanoparticle in the sample, and a small but finite distribution of nanoparticle sizes and environments exists within the sample, resulting in a fairly broad peak in the ZFC curve.

By contrast, Figure 4c and d show ZFC curves for the poled magnetoelectric sample measured along the *x*- and *y*-directions, respectively. The data measurements in the *x*-direction (hard axis) show a peak at 280 K, which represents a decrease of 20 K compared to the peak observed in the unpoled samples (Figure 4a and c). More dramatically, for the *y*-direction (easy-axis) the peak of the magnetization curve (or $T_{\rm B}$) increases to 340 K or a change of 40 K when compared to the peak in the unpoled samples.

The shifts in the maximum of the ZFC curves can be explained by considering how the potential landscape for spin alignment is changed in an anisotropically strained sample. In the unpoled sample, the magnitude of the barrier for spin flip is on the order of the available thermal energy at room temperature and so the spins begin to hop between magnetic easy axes as the blocking temperature of 300 K is approached. When the sample is anisotropically strained by the PMN-PT substrate, however, the potential well for spin alignment in the y-direction is deepened. It thus requires significantly more thermal energy for the spins to hop out of this deeper well, and so the blocking temperature shifts to well above room temperature (340 K) after electric poling. In the x-direction, the blocking temperature appears to decrease, but this is not a true blocking temperature, as the falloff in magnetization at 280 K is not thermal randomization of magnetic moments, but rather magnetization transfer from the x-direction to the ydirection as the system obtains sufficient thermal energy to free the spins from the metastable potential minima where they were trapped. Because spins are directionally transferring from a high energy configuration to a lower energy configuration, the process occurs at a lower temperature than the thermal randomization observed in the unpoled sample. The true blocking temperatures in the unpoled and poled system are thus 300 and 340 K respectively. This result thus confirms the experimental results shown in Figure 3, which indicate that the electric field can be used to stabilize the ferromagnetic spin state at room temperature. This is accomplished by moving the blocking temperature from a value very near room temperature, to a value well above room temperature

The above conclusions can be validated using the Arrhenius-Neel equation, $1/\tau = 1/\tau_0 e^{(-KV)/(k_BT)}$, where τ is the magnetization switching time, K is the total anisotropy energy density, V is the particle volume, $k_{\rm B}$ is Boltzmann's constant, T is the temperature, and $1/\tau_0$ is the attempt frequency. $^{6-8}$ Using $1/\tau_0 = 10^9$ /s and $\tau = 100$ s produces the familiar $KV = 25k_{\rm B}T$ relation.^{23,24} For this system, the electric-field-induced change in the magnetoelastic anisotropy is approximated by $3/2\lambda Y \Delta \varepsilon_{a}$ where $\lambda = -34 \ \mu \varepsilon$ is the Ni magnetostrictive constant, Y =213.7 GPa is the Ni Young's modulus, and $\Delta \varepsilon_{\rm a}$ = -700 $\mu \varepsilon$ is the residual strain induced in the Ni nanocrystal after electric poling (see Figure 2b).^{13,21} Incorporating this anisotropy term into the Arrhunius-Neel equation produces $3/2\lambda Y \Delta \varepsilon_a =$ $25k_{\rm B}\Delta T_{\rm B}$, which provides an estimate of the blocking temperature change $\Delta T_{\rm B}$ that should result from the additional magnetoelastic energy added during electric poling. The calculated value of 46 K is in excellent agreement with the measured value of ~40 K.

While the primary impact of this work lies in the fundamental ability to control not only the direction, but also the magnitude of a spin state using an electric field, it also has significant ramifications to the miniaturization of a wide class of electromagnetic devices. Consider, for example, magnetic random access memory (MRAM), which currently faces two major engineering challenges to reduce size: overcoming the thermal instability associated with nanoscale magnetic elements and reducing the write energy to encode a bit of information.²⁵⁻²⁸ In the former case, the superparamagnetic transition behavior defines the smallest bit size, ^{16-18,29} while for the latter case, larger write energies require larger fields and thus larger write heads or other routes to reduce fields.³⁰ The multiferroic system discussed here offers a solution to both of these problems, which would yield further miniaturization. By electrically increasing the magnetic anisotropy, as demonstrated in this paper, the minimum size of a stable bit of information can be reduced. Furthermore, since the magnetic anisotropy is electrically generated, the anisotropy can be modulated using an electrical field, thus providing an avenue to create bits that are magnetically hard and thus thermally stable when written but can be electrically switched to a magnetically soft state that

is relatively easy to reorient for the write process. To see this process more concretely, consider the data in Figure 3d, which shows a coercive field of the poled sample is $H_c = 80$ Oe, corresponding to the stabilized nanoscale bit. Examination of Figure 2b indicates that application of a 0.24 MV/m electric field reduces the magnetoelectric anisotropy to zero (i.e., $\varepsilon_x = \varepsilon_y$ or $\Delta \varepsilon_a = 0$), returning the sample to near the superparamanetic state ($H_c < 20$ Oe). A transient bias can thus be used to reduce anisotropy during the write step. In this way, this fundamental research provides an electrical mechanism to both increase the blocking temperature and decrease magnetic write energies, a combination that is simply not possible in conventional magnetic systems.

By applying electric-field-induced strain to the ferromagnetic nanocrystals, we demonstrate that superparamagnetic Ni nanocrystal without a permanent magnetic moment at room temperature can be converted to strong single-domain ferromagnets, again at room temperature, through application of an electric field. This work thus provides a revolutionary new approach for controling magnetizim at the small scale and is a sharp departure from Oersted and Ampere's original work running current through a wire. The intrinsic control of magnetization demonstrated in this paper manifests itself as an electric field induced shift in the blocking temperature of approximately 40 K for 16 nm Ni nanocrystals. Such control in a nanoscale magnetic material may provide exciting opportunities to explore new types of electromagnetic devices as well as allowing researchers to transition conventional devices down to length scales too small to effectivly exploit standard electromagnetic coupling.

ASSOCIATED CONTENT

S Supporting Information

Instrumentation details, as well as XPS, XRD, and a more detailed device schematic. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: carman@seas.ucla.edu, tolbert@chem.ucla.edu.

Author Contributions

^{II}These authors contributed equally to this work.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank Kyle Wetzlar, Dr. Tao Wu, and Prof. Indrani Banerjee for helpful discussion. We also thank Drs. Ignacio Martini and Sergey Prikhodko, UCLA, for their assistance with SQuID magnetometry and electron microscopy. This work was supported by the Air Force Office of Scientific Research (AFOSR) under Grant No. FA9550-09-1-0677 managed by Byung-Lip (Les) Lee (G.P.C.) and by the NSF under grants CHE-1112569 (S.H.T.) and the Cooperative Agreement Award EEC-1160504 (G.P.C. and S.H.T.). Instrumentation was supported by NSF grant CHE-0840531. We acknowledge the use of instruments at the Electron Imaging Center for NanoMachines supported by NIH (1S10RR23057 to ZHZ) at the California NanoSystems Institute, UCLA.

REFERENCES

(1) Ampere, A.-M. Ann. Chim. Phys. 1820, 15, 170-218.

- (2) Curie, P. J. Phys. Theor. Appl. 1894, 3, 393-415.
- (3) van Suchtelen, J. Phillips Res. Rep. 1972, 27, 28-37.
- (4) Ryu, J.; Priya, S.; Uchino, K.; Kim, H. J. Electroceram. 2002, 8, 107–119.
- (5) Ortega, N.; Kumar, A.; Katiyar, R. S.; Rinaldi, C. *Thin Solid Films* **2010**, *519*, 641–649.
- (6) Wan, J. G.; Liu, J.-M.; Wang, G. H.; Nan, C. W. Appl. Phys. Lett. 2006, 88, 182502.
- (7) Chung, T.-K.; Carman, G. P.; Mohanchandra, K. P. Appl. Phys. Lett. 2008, 92, 112509.
- (8) Murakami, M.; Chang, K.-S.; Aronova, M. A.; Lin, C.-L.; Yu, M. H.; Simpers, J. H.; Wuttig, M.; Takeuchi, I.; Gao, C.; Hu, B.; Lofland, S. E.; Knauss, L. A.; Bendersky, L. A. *Appl. Phys. Lett.* **2005**, *87*, 112901.
- (9) Yamasaki, Y.; Miyasaka, S.; Kaneko, Y.; He, J.-P.; Arima, T.; Tokura, Y. *Phys. Rev. Lett.* **2006**, *96*, 207204.
- (10) Yang, J. J.; Zhao, Y. G.; Tian, H. F.; Luo, L. B.; Zhang, H. Y.; He, Y. J.; Luo, H. S. *Appl. Phys. Lett.* **2009**, *94*, 212504.
- (11) Chu, Y.-H.; Martin, L. W.; Holcomb, M. B.; Gajek, M.; Han, S.-J.; He, Q.; Balke, N.; Yang, C.-H.; Lee, D.; Hu, W.; Zhan, Q.; Yang, P.-L.; Fraile-Rodríguez, A.; Scholl, A.; Wang, S. X.; Ramesh, R. *Nat. Mater.* **2008**, *7*, 478–82.
- (12) Chung, T.-K.; Keller, S.; Carman, G. P. Appl. Phys. Lett. 2009, 94, 132501.
- (13) Bur, A.; Wu, T.; Hockel, J.; Hsu, C.-J.; Kim, H. K. D.; Chung, T.-K.; Wong, K.; Wang, K. L.; Carman, G. P. *J. Appl. Phys.* **2011**, *109*, 123903.
- (14) Wu, T.; Bur, A.; Wong, K.; Zhao, P.; Lynch, C. S.; Amiri, P. K.; Wang, K. L.; Carman, G. P. *Appl. Phys. Lett.* **2011**, *98*, 262504.
- (15) Wu, T.; Zhao, P.; Bao, M.; Bur, A.; Hockel, J. L.; Wong, K.; Mohanchandra, K. P.; Lynch, C. S.; Carman, G. P. *J. Appl. Phys.* **2011**, *109*, 124101.
- (16) Bean, C.; Livingston, J. D. J. Appl. Phys. 1959, 30, S120-S129.
- (17) Leslie-Pelecky, D.; Rieke, R. D. Chem. Mater. 1996, 8, 1770–1783.
- (18) Cowburn, R. P. J. Appl. Phys. 2003, 93, 9310.
- (19) Chen, Y.; Peng, D.-L.; Lin, D.; Luo, X. Nanotechnology 2007, 18, 505703.
- (20) Shevchenko, E. V.; Talapin, D. V.; Murray, C. B.; O'Brien, S. J. Am. Chem. Soc. 2006, 128, 3620-37.
- (21) Weiler, M.; Brandlmaier, A.; Geprägs, S.; Althammer, M.; Opel, M.; Bihler, C.; Huebl, H.; Brandt, M. S.; Gross, R.; Goennenwein, S. T.
- B. New J. Phys. 2009, 11, 013021.
- (22) Hansen, M. F.; Mørup, S. J. Magn. Magn. Mater. 1999, 203, 214-216.
- (23) Knobel, M.; Nunes, W. C.; Socolovsky, M.; De Biasi, E.; Vargas, J. M.; Denardin, J. C. J. Nanosci. Nanotechnol. **2008**, *8*, 2836–2857.
- (24) Yoon, M.; Kim, Y.; Kim, Y. M.; Volkov, V.; Song, H. J.; Park, Y. J.; Park, I.-W. *Mater. Chem. Phys.* **2005**, *91*, 104–107.
- (25) Ramesh, R.; Spaldin, N. A. Nat. Mater. 2007, 6, 21–9.
- (26) Hu, J.-M.; Li, Z.; Wang, J.; Nan, C. W. J. Appl. Phys. 2010, 107, 093912
- (27) Lee, K.; Kang, S. H. IEEE Trans. Magn. 2011, 47, 131-136.
- (28) Lee, K.; Kang, S. H. IEEE Trans. Magn. 2010, 46, 1537-1540.
- (29) Skumryev, V.; Stoyanov, S.; Zhang, Y.; Hadjipanayis, G.; Givord,
- D.; Nogues, J. Nature 2003, 423, 850-853.
- (30) Kryder, M. H.; Gage, E. C.; McDaniel, T. W.; Challener, W. A.; Rottmayer, R. E.; Ju, G.; Hsia, Y.-T.; Erden, M. F. *IEEE Magn.* **2008**, *96*, 1810–1835.