#### Arrays of Sealed Silicon Nanotubes As Anodes for Lithium Ion Batteries

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**ABSTRACT** Silicon is a promising candidate for electrodes in lithium ion batteries due to its large theoretical energy density. Poor capacity retention, caused by pulverization of Si during cycling, frustrates its practical application. We have developed a nanostructured form of silicon, consisting of arrays of sealed, tubular geometries that is capable of accommodating large volume changes associated with lithiation in battery applications. Such electrodes exhibit high initial Coulombic efficiencies (i.e., >85%) and stable capacity-retention (>80% after 50 cycles), due to an unusual, underlying mechanics that is dominated by free surfaces. This physics is manifested by a strongly anisotropic expansion in which 400% volumetric increases are accomplished with only relatively small (<35%) changes in the axial dimension. These experimental results and associated theoretical mechanics models demonstrate the extent to which nanoscale engineering of electrode geometry can be used to advantage in the design of rechargeable batteries with highly reversible capacity and long-term cycle stability.

KEYWORDS Lithium ion battery, silicon, nanotubes, anisotropic expansion

dvanced energy storage technologies are critically important for the operation of electric vehicles and for the practical use of many types of renewable sources of energy.<sup>1-4</sup> Lithium ion batteries are valuable for portable electronics, but they cannot meet requirements for more demanding applications due to limitations in energy capacity and reliable operation. Silicon is a promising candidate for electrodes in these devices due to its large theoretical energy density (about 4200 mAhg<sup>-1</sup>, ten times higher than graphite (372 mAhg<sup>-1</sup>)) and relatively low working potential ( $\sim$ 0.5 V vs Li/Li<sup>+</sup>).<sup>5</sup> Currently, its use is frustrated by comparatively poor capacity retention and irreversible morphological change due to mechanical degradation caused by large changes in volume associated with lithiation/ delithiation ( $\sim$ 400%) during cycling. In previous studies, nanophase forms of Si,<sup>6,7</sup> including nanocrystals,<sup>8</sup> nanocomposites with either carbon<sup>9</sup> or other phases inactive<sup>10</sup> to lithium, nanoporous materials,<sup>11,12</sup> nanowires<sup>13–17</sup> (NW), bundled Si nanotubes,<sup>18</sup> and thin films<sup>19</sup> as candidate anode materials in lithium ion battery show promise. The work

forts, focuses on purely silicon anodes and the effect of nanostructure on their underlying behavior. In the simplest geometry (i.e., thin films), silicon shows irreversible morphological changes such as cracking during operation, especially under cycling. This response, which arises from an enormous increase in the thickness of Si layer, and the low capacity per unit area due to limited thickness, represent significant disadvantages. In the Si NWs case, devices achieve discharge capacities of >3000 mAhg<sup>-1</sup> and little fading of capacity up to 10 cycles, without mechanical damage to the Si NWs. The geometry of the Si NWs and their sparse coverage were postulated to facilitate expansion/ contraction. Although promising, this system has disadvantages, including a loss of nearly half of the capacity after 50 cycles at a 0.2 C rate, perhaps due to high internal stresses associated with lithiation and/or accelerated electrolyte decomposition reactions<sup>20</sup> through formation of solid electrolyte interface (SEI) films on the large exposed surface areas provided by the Si NWs.

presented here, and benchmark comparisons to other ef-

An alternative electrode configuration with nanostructured geometries optimized based on a quantitative understanding of the underlying mechanics could enable improvements. Sealed nanotube (NT) layouts, in particular, can be expected to improve electrochemical performance and reversible morphological changes via more favorable me-

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# NANOLETTERS

chanics during lithiation. In this paper we demonstrate that this intuition is accurate, as supported by detailed experimental results and theoretical analysis of the mechanics. Despite tremendous stresses and volume changes associated with intercalation of lithium, Si NT arrays exhibit robust performances such as stable cycle retention and reversible morphology change. In particular, the axial void spaces of the Si NTs provide additional free surfaces to benefit the mechanics, without creating additional surfaces for accelerated SEI formation. These results suggest a general capacity to use nanostructures with theoretically guided layouts to improve the performance of anodes in lithium ion batteries. The key contributions presented in the following include (1) the optimized use of nanostructure geometry for silicon anodes, in the form of organized arrays of nanotubes, (2) the experimental demonstration of performance in such systems that exceeds that of other reported approaches for using silicon, and (3) theoretical analysis of the mechanics, to reveal aspects of the underlying physics, to account for experimental observations and to derive optimized dimensions in the tubes.

To form vertically aligned tubular constructs with uniform and regular void space, we used a sacrificial template strategy<sup>21</sup> due to its advantages in simplicity and control compared to alternatives based on supercritical hydrothermal synthesis<sup>22</sup> and direct transformation of silicon substrates through plasma treatment.<sup>23</sup> The process, performed on a stainless steel substrate, involves three steps: (i) growth of arrays of dense ZnO nanorods as a sacrificial template using a hydrothermal process,<sup>24</sup> (ii) chemical vapor deposition (CVD) of Si onto these nanorods, and (iii) selective removal of ZnO via a high temperature reduction process<sup>25</sup> (Supporting Information, Figure S1). Figure 1 provides images and elemental analysis of the resulting array of Si NTs. We define the inner and outer radii as  $R_{in}$  and  $R_{out}$ , respectively, and the length as *h*. The structures have  $R_{out}$  of  $\sim 60$ nm, h of  $3-5 \,\mu$ m (Figure 1a), shell thicknesses of  $\sim 30$  nm, and  $R_{in}$  of ~30 nm (Figure 1, panels d and e). Precise control of R<sub>out</sub> is possible by adjusting the Si deposition time (Figure 1, panels b and c). The Si NTs are polycrystalline, as confirmed by X-ray diffraction analysis (Supporting Information, Figure S2). Compositional line profile analysis (Figure 1f) reveals that Zn, originally inside the tube structure, is completely absent, to within the detection limit. Interestingly,  $SiO_x$  layers are not observed on the inner surfaces of the tubes, even though oxygen is released during the decomposition of ZnO (Supporting Information, Figure S3).

Figure 2 shows the electrochemical performance of a representative Si NT array electrode. At a rate of 0.05 C, discharging (lithium insertion) and charging (lithium removal) occurs at 3860  $\pm$  20 and 3360  $\pm$  20 mAhg<sup>-1</sup>, respectively, both of which approach the theoretical capacity of Si, indicating that all Si NTs connect to the stainless steel substrate and fully react with lithium. The Coulombic efficiency at the first cycle is 87  $\pm$  0.5%. At a rate of 0.2 C, Si



FIGURE 1. Electron microscope images and elemental line profile analysis of Si NTs. SEM image of a vertically aligned Si NT array with (a)  $R_{out} \sim 60$  nm, (b)  $R_{out} \sim 80$  nm, (c)  $R_{out} \sim 110$  nm on a stainless steel substrate. Insets show high magnification TEM images of the sealed tip of a Si NT. (d) Low magnification TEM image of a bundle of Si NTs with  $R_{out} \sim 60$  nm. (e) High magnification TEM image of the closed tip of a Si NT. (f) Cross-sectional EDX elemental mapping along the yellow dotted line in (e).

NT array electrodes exhibit 2924  $\pm$  60 and 2645  $\pm$  60 mAhg<sup>-1</sup> for discharging and charging, respectively, and an initial Coulombic efficiency of 90.4  $\pm$  0.5 % . This efficiency is higher than that of Si NW electrodes ( $\sim$ 79%),<sup>26</sup> implying improved reversibility in electrochemical behavior. This performance might be due to the decreased potential for electrolyte decomposition and reduced SiO<sub>x</sub> coverage associated with the confined void spaces, both of which are known to have deleterious effects.<sup>27,28</sup> Recent reports describe impressive Coulombic efficiency and cycle performance using carbon-coated, bundled Si NT electrodes, with initial efficiencies of 89%, 3247 and 3648 mAhg<sup>-1</sup> for discharging and charging at rates of 0.2 C, respectively, and capacity retention of about 95% after 50 cycles.<sup>18</sup> Similarly, carbon-Si core-shell NW electrodes exhibited initial efficiencies of 90%, reversible capacities of  $\sim$ 2000 mAhg<sup>-1</sup> at rates of 0.2 C, and capacity retention of about 92% after 50 cycles.<sup>17</sup> In both cases, the coatings of carbon enhance the performance. The work reported here provides systematic experimental and theoretical studies of the bare Si NTs to reveal key aspects of the underyling mechanics, with strategies for optimization. Within five cycles, the Si NT array electrodes approach Coulombic efficiencies of more than 98% at rates of 0.05 and 0.2 C (Figure 2b). The nonideal Coulombic efficiencies likely result from repetitive SEI cracking and regeneration during cycling caused by huge volumetric changes in the Si. Compared to previous on Si

# NANO LETTERS



FIGURE 2. Electrochemical characteristics of Si NT array electrode ( $R_{\rm in} \sim 30$  nm and  $R_{\rm out} \sim 60$  nm). (a) Voltage profiles for the first cycle at a rate of 0.05 and 0.2 C. (b) Cycle performances at a rate of 0.05 and 0.2 C (square symbol: 0.05 C, circle symbol: 0.2 C) (c) Rate capabilities of Si NT array electrodes at various C rates.

NWs,13,16 our Si NTs exhibit comparable or improved efficiencies. More important, the Si NT arrays show stable performance over prolonged cycles without restricted voltage ranges to limit the extent of lithiation. In particular, capacity retention after 50 cycles is  ${\sim}81\pm0.5\,\%$  and 82  $\pm$ 2% at a rate of 0.05 and 0.2 C, respectively, significantly better than the corresponding Si NWs system ( $\sim$ 62%),<sup>26</sup> suggesting that the void spaces in the Si NTs improve the mechanics associated with cycling, as discussed in a theoretical treatment described subsequently. Furthermore, our Si NT electrodes show 3360, 3160, 2650, 2260, 1900, and 1490 mAhg<sup>-1</sup> of charge capacity (lithium removal) at 0.05, 0.1, 0.2, 0.5, 1, and 2 C, respectively (Figure 2c). Si NT electrodes show degradation in capacity from 3360 to 1490 mAhg<sup>-1</sup> with increasing charge rate from 0.05 to 2 C. This degradation is likely due to low electron conductivity and lithium ion diffusivity, both of which are inherent properties of intrinsic silicon. These limitations can overcome by doping with boron or phosphorus or by using silicon with a porous microstructure.



FIGURE 3. Schematic illustration and electron microscopy images of Si NTs before reaction and after full lithiation and delithiation. (a) and (b), by using an ordered sacrificial template, uniform free spaces inside the Si NTs and regular intertube spacings are possible. These free surfaces offer mechanics that facilitates expansion, as manifested in an anisotropic response. The free spaces radially decrease in size during lithiation and fully recover during delithiation. Microscopy shows the morphological changes during the first cycling;  $dR_{out}^*$  is defined as the change in outer radius after cycling. (c) Top view SEM images. (d) TEM images. (e) Cross-sectional SEM images of Si NTs prepared by focused ion beam cross sectioning.

To explore further the physics and materials science of expansion/contraction, we performed high resolution electron microscopy analysis and theoretical mechanical modeling. Figure 3 presents schematic illustrations of the Si NTs at various stages of the process and image analysis of the pristine electrode, immediately after the first lithiation and after the first full cycle. Despite the large changes in volume, the Si NTs retain their overall shapes with only a modest increase (~50%; 120 to 180 nm) in diameter near the tip of the tube after full lithiation. Subsequently, this dimension decreases to 140 nm upon delithiation, corresponding to an increase of ~17% compared to that of the pristine Si NT (Figure 3c). Transmission microscopy images (TEM; Figure 3d) show that the

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#### NANOLETTERS

shell thickness increases from 30 to 100 nm upon lithium insertion and then decreases to 40 nm after delithiation, without the collapse of the tubular shape. The inner diameter shows similar reversible behavior. The inset of Figure 3d indicates that the Si transforms into an amorphous phase after one cycle, consistent with the previous reports.<sup>29,30</sup> Changes in lengths and diameters were also carefully monitored; Figure 3e shows cross sectional images of the same samples in Figure 3c, acquired using Ga<sup>+</sup> focused ion beam irradiation. We found that there is no delamination of the Si NTs from the stainless steel substrate with cycling (Figure 3e and Figure S5a), consistent with good cycle retention properties.

The first full lithiation leads to volumetric expansion of the Si NTs in which the lengths undergo small increases  $(\sim 5\%)$  while the diameter increases by nearly 150%. Additional lithiation cycles also exhibit anisotropic behavior, whereby the lengths change by  $\sim$ 35% and the diameters change by 120% (Figure S5b). The differences between the first and subsequent lithiation processes can be attributed to a change to the amorphous phase, as noted above, which has been previously reported to exhibit different expansion behavior compared to the crystalline phase.<sup>31</sup> After the first and second cycles, the Si NTs showed reversible behavior, with a small increase in the diameter. Reversible behavior of electrode is critically important for reliable and safe operation.32-34 Changes in inner diameter were evaluated in the delithiated state, as summarized in Table S1. Accurate measurements in the lithiated state were not possible.

Theoretical modeling of the mechanics of the process provides a route to explore these counterintuitive anisotropic changes in the dimensions of the Si NTs and to gain insights into underlying design rules for electrode geometry. For analysis, we assume that the insertion of Li into bulk Si, in general, leads to isotropic volumetric expansion. This expansion becomes anisotropic near free surfaces because the surface normal direction is unconstrained, thereby enabling larger expansion compared to other directions on the surface or in the bulk. To quantify these considerations, we model the volume changes during lithiation based on two contributions: (1) isotropic expansion associated with uptake of Li (this process is stress-free, similar to thermal expansion) and (2) expansion caused by stresses (i.e., misfit stresses) due to insertion of Li atoms into vacancies between Si atoms.<sup>35</sup> We assume linear elastic behavior, to enable an analytical treatment suitable for gaining insights into the process, even though the magnitudes of the strains induced in the silicon during full lithiation vastly exceed the fracture strains of the material, leading to plastic deformation. For this reason, and because of other assumptions, we do not expect, then, the theoretical treatment to yield quantitative comparison the experiment. Certain qualitative aspects are, however, valuable.

The misfit stresses, written  $\sigma_{rr}^*$ ,  $\sigma_{\theta\theta}^*$ , and  $\sigma_{zz}^*$  in a cylindrical coordinate frame, can be determined analytically in terms of the difference between the Li atomic radius and the typical Si vacancy size. These quantities are isotropic, i.e.,  $\sigma_{rr}^* = \sigma_{\theta\theta}^*$  $= \sigma_{zz}^* = \sigma^*$ , far away from free surfaces but they become anisotropic, i.e.,  $\sigma_{rr}^* = 0$  and  $\sigma_{\theta\theta}^* = \sigma_{zz}^* = 3\sigma^*/2$ , near free surfaces, where  $\sigma^*$  can be obtained in terms of Li and Si properties, the volume fraction of Li in the alloy, the Li atom radius and Si vacancy size (Supporting Information). The general distribution of misfit stresses throughout the wall of the Si NT is  $\sigma_{rr}^* = \lambda(r)\sigma_{zz}^* = \lambda(r)\sigma_{\theta\theta}^*$ , where  $\lambda = 0$  at both inner and outer surfaces,  $\lambda = 1$  far away from free surfaces, and in general  $0 \le \lambda \le 1$  We define the inner and outer radii as  $R_{\rm in}$  and  $R_{\rm out}$ , respectively, and the length as *h*. The changes in these quantities are  $dR_{in}$ ,  $dR_{out}$ , and dh. The radial and axial expansions of a Si NT (i.e.,  $dR_{out}/R_{out}$  and dh/h) due to lithiation can be obtained analytically (Supporting Information); their difference is given as

$$\frac{dR_{out}}{R_{out}} - \frac{dh}{h} = \frac{3(1+\nu)\sigma^*}{E(R_{out}^2 - R_{in}^2)} \int_{R_{in}}^{R_{out}} \left[ \frac{1-\lambda(r)}{2+\lambda(r)} \left( 1 - \frac{R_{in}^2}{r^2} \right) \right] r \, dr$$
(1)

where E and v are the Young's modulus and Poisson's ratio of the alloy. This quantity is positive, consistent with experiment. The anisotropy is due to free surfaces (inner and outer) that can more easily accommodate radial expansion than expansion in the plane of the surface (i.e., axial direction). To determine the level of anisotropy, we take a representative misfit stress distribution  $\lambda(r) = 1 - [e^{(r-R_{out})/\delta} + e^{(R_{in}-r)/\delta}]/\delta$  $[1 + e^{-(R_{out} - R_{in})/\delta}]$ , with  $\delta = 10$ ,<sup>36</sup> that satisfies the boundary conditions. For  $R_{out} = 70$  nm,  $R_{in} = 30$  nm, and full lithiation, we find that the anisotropy is 12%, which is considerably lower than that observed experimentally due at least in part to deviations from a perfectly tubular shape and to many simplifying assumptions concerning the size of Si vacancies, the presence of defects in the Si and its alloy with Li, and boundary effects ranging from surface roughness to conditions at the bases and tips of the structures. For example, changing the vacancy size from 0.8 to 0.5 nm increases the level of anisotropy from 12% to 25%. In spite of uncertainties in the magnitudes, we believe that the models capture important aspects of the essential physics, as embodied by the anisotropy in the expansion. The distribution of stresses, normalized by  $\sigma^*$ , are shown in Figure 4a. The maximum stress is  $\sigma_{\theta\theta}$  at the outer surface (Supporting Information), with a state of tension near both inner and outer surfaces. The stress decreases quickly away from the surfaces and becomes compressive inside the body.

This type of theoretical mechanical analysis suggests that free surfaces can minimize stresses associated with lithiation. For example, eq 1 can be used to describe the



### NANO LETTERS



FIGURE 4. Theoretical analysis of the mechanics of Si NT and NW electrodes. (a) Computed distributions of stress in a fully lithiated NW (red) and NT (blue) with similar outer radii. The inner space in the case of the Si NTs reduces the peak stress, due to the comparatively larger total free surface area afforded by the empty core and the traction free boundary conditions at these regions. This mechanics leads to an enhanced anisotropic expansion, and explains, at least in part, the improved performance of Si NTs over Si NWs. (b) The optimized Si NT inner and outer radii ( $R_{in}$  and  $R_{out}$ , respectively), as well as the normalized maximum stress, versus area fraction. The inset shows a square array of Si NTs, corresponding to the modeled system.

behavior of a Si NW, as shown also in Figure 4a, by taking a vanishing inner radius (Supporting Information):

$$\frac{\mathrm{d}R'_{\mathrm{out}}}{R_{\mathrm{out}}} - \frac{\mathrm{d}h'}{h} = \frac{3(1+\nu)\sigma^*}{ER_{\mathrm{out}}^2} \int_0^{R_{\mathrm{out}}} \frac{1-\lambda(r)}{2+\lambda(r)} r \,\mathrm{d}r \quad (2)$$

which is positive, as with the case of Si NTs. For  $R_{out} = 70$  nm and a misfit stress distribution analogous to the one used for the Si NTs,  $\lambda(r) = 1 - \exp[(r - R_{out})/\delta]$  with  $\delta = 10$  nm, the expansion anisotropy is 9% (Supporting Information), which is less than that of Si NTs. The distributions of stresses  $\sigma_{\theta\theta}$  and  $\sigma_{rr}$  appear in Figure 4a. The maximum stress in the Si NW is also  $\sigma_{\theta\theta}$  at outer surface, but most of the material experiences mild compression. As shown in Figure 4a, the maximum stress in the Si NWs is larger than in the Si NTs, which explains, at least in part, the improved performance of the Si NT system over the Si NW. The results for Si NWs with the

same volume as the Si NTs (NWs with outer radii of  $R_{out}$  = 63 nm) show only slight differences from Si NWs with  $R_{out}$  = 70 nm. The advantage of tubes over wires, then, derives directly from the additional free expansion on the inner surfaces to accommodate more easily the volume expansion during the lithiation process.

The mechanics model can also be used to determine geometries of Si NTs and their arrangement into arrays in a fashion that minimizes the elastic stresses induced by lithiation, subject to the assumptions in the analysis. For a square array of Si NTs, the optimal spacing (*d*) is such that the outer surfaces of Si NTs just come into contact in the fully expanded, lithiated state. If this expansion corresponds to an outer radius of  $\alpha R_{out}$ , then  $d = 2\alpha R_{out}$ , where a represents the fractional increase in the value of  $R_{out}$  due to full lithiation. The area fraction (*f*) of Si NTs is given by  $\pi (R_{out}^2 - R_{in}^2)/d^2$ . This equation, then provides a relation between  $R_{in}$  and  $R_{out}$ 

$$R_{\rm in} = R_{\rm out} \sqrt{1 - \frac{4f\alpha^2}{\pi}}$$
(3)

Using this expression, it is possible to compute the maximum stress, ( $\sigma_{max}$ ) as a function of  $R_{out}$  for different values of f. The optimal  $R_{out}$  minimizes  $\sigma_{max}$ ; eq 3 then determines  $R_{in}$  corresponding to this optimal condition. (For details, see the Supporting Information.) The optimized dimensions, as well as the normalized maximum stress, versus area fraction appear in Figure 4b. A triangular array of Si NTs can further improve the performance (Supporting Information, Figure S8). The geometries of the electrodes presented previously are reasonably close to the optimum configuration suggested by this theoretical treatment.

Additional experimental results show qualitative trends consistent with the theoretical results. Figure 5 provides SEM images and data on the behavior of Si NT array electrodes with  $R_{out}$  of 80 and 110 nm during the first cycling, both with  $R_{\rm in}$  = 30 nm and spacings comparable to those of the systems described previously. Table 1 summarizes some observations. Although the samples all exhibit morphological reversibility, the degree of anisotropic volume expansion diminishes with increasing  $R_{out}$  and the cycle retention degrades with R<sub>out</sub>, as shown in Figure 5e. Both trends are consistent with mechanics modeling, where free surfaces are the origins of anisotropy in expansion and improved performance. This type of design rule can be extended to more intricate nanostructured electrode designs, for possible further benefit to battery performance. Taken together with consideration of the effects of undesired side reactions related with the electrolyte decomposition and  $SiO_x$ , one can postulate that closed form structures, like tubes, would be most beneficial.

In conclusion, we demonstrated that despite tremendous stresses and volume changes involved in charge–discharge

#### NANO LETTERS



FIGURE 5. Morphological changes and electrochemical properties of Si NTs with  $R_{out}$  of 80 and 110 nm. (a and c) Top view SEM images for  $R_{out} = 80$  and 110 nm during the first cycling, respectively. (b and d) Cross sectional SEM images for  $R_{out} = 80$  and 110 nm during the first cycling, respectively. The left, center and right panels are SEM images corresponding to the cases before the reaction, after full lithiation and after the first cycle (delithiation), respectively. (e) Cycle retention at 0.2C for Si NTs array electrodes with various  $R_{out}$  values and  $R_{in}$  fixed at 30 nm (square:  $R_{out} = 60$  nm, circle:  $R_{out} = 80$  nm, triangle:  $R_{out} = 110$  nm, open symbols: Coulombic efficiency, closed symbols: capacity).

cycles, robust performance in silicon based lithium ion batteries is possible by structuring the silicon into arrays of nanotubes. Theoretical analysis of the mechanics suggests that the additional free surfaces provided by the empty interior spaces of these tubes improve the ability of these structures to accommodate volume expansion associated with lithiation. Besides the specific promise of nanotube architectures for this type of application, the results and associated analysis provide more general design guide-

TABLE 1.	Summary of morphological changes of Si NTs with	
different g	eometries and similar spacings during the first cyclin	ıg

Rin	R <sub>out</sub>	Lithiation		Delithiation	
		Diameter (%) <sup>a</sup>	Length (%) <sup>b</sup>	Diameter (%) <sup>a</sup>	Length (%) <sup>b</sup>
30 nm	60 nm	150	105	117	100
	80 nm	not available <sup>c</sup>	185	115	100
	110 nm	not available <sup>c</sup>	200	110	100

<sup>*a*</sup> Normalized values compared to the original diameter and length during the first cycle, respectively. <sup>*b*</sup> Normalized values compared to the original diameter and length during the first cycle, respectively. <sup>*c*</sup> Not possible to measure an exact diameter of a single Si NT due to the formation of merged structures at the fully lithiated state.

lines for more advanced shapes, with the promise of further improvement in performance. Exploring these possibilities together with application to alloy-type anode materials that combine silicon with other species, such as Ge, Sn, Al, and Sb, or other lithium inactive metals, such as Cu, Ni, and Co, represent important directions for future work.

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**Supporting Information Available.** Details of experiments and additional supplementary figures about the charge dissipations. This material is available free of charge via the Internet at http://pubs.acs.org.

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