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Amorphous Carbon-Coated TiO₂ Nanocrystals for Improved Lithium-Ion Battery and Photocatalytic Performance

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KEYWORDS TiO₂ nanocrystals, amorphous carbon coating, lithium ion battery, photocatalytic performance.

ABSTRACT: 10-time lithium rate improvement and 4-time photocatalytic performance enhancement have been achieved with TiO₂ nanocrystals when coated with a thin layer of amorphous carbon from a vacuum decomposition-deposition process. The enhanced performances can be attributed to lower lithium ion diffusion and electronic conduction resistance across the carbon layer into the TiO₂ electrode material and better surface adsorption of the dye molecules and ions. Thus, the current study may provide us an alternative approach in improving the performances of TiO₂ nanocrystals in both lithium ion battery and photocatalysis applications.

INTRODUCTION

Attracted tremendous research effort as a photocatalyst for photocatalytic water splitting and environmental pollutant removal,¹⁻⁷ TiO₂ has also been studied as a promising anode material for lithium ion batteries,⁷⁻¹⁵ based on the following reaction:

where x is the mole fraction of lithium in the titanium dioxide. It has a theoretical capacity up to 335 mAhg⁻¹, or 1.0 Li per TiO₂.⁷⁻¹⁵ However, for bulk anatase TiO₂, $x = 0.5$ is usually reported as the maximum,^{15,16} due to that the low diffusion coefficient and the low electronic conductivity in the solid phase limits only a thin surface layer of the host material available for Li intercalation at high charging-discharging rates for bulk materials.¹¹⁻¹³ On the other hand, successful realization electric vehicle with long-range single-charge capability requires high-power high-energy batteries with fast charge/discharge rates and high capacity.¹⁷⁻¹⁹ Decreasing the particle size into the nanometer-regime can shorten the lithium diffusion length requirements, alter the electrochemical reactions and reactivity to Li, and thus increase the accessible volume to near-full capacity.²⁰⁻²³ The size reduction along with unique morphologies may lead to increased capacity beyond 0.5 Li per unit formula based on the different Li-reaction and surface-confined charge storage mechanisms from those in the bulk materials.²⁰ Conductive carbons,⁸ carbon nanotubes,¹¹⁻¹³ graphene,¹⁴ and RuO₂ (with much more improved conductivities),²⁰ have been used to improve the electronic conduction paths in the host material.

However, poor rate performance still seems to be a bottleneck for batteries.

The effective diffusion length of the lithium ions and electrons can be estimated with the formula $L = (Dt)^{1/2}$, where D is the diffusion coefficient, and t is the time.⁸ Usually, the Li⁺ ion diffusion coefficient is much smaller than that of electrons. For example, the measured diffusion coefficient for Li⁺ ion and electrons is 10⁻¹¹ – 10⁻¹³ cm²s⁻¹ and $D = 3\text{--}8 \times 10^{-6}$ cm²s⁻¹, respectively, for TiO₂ material.¹¹⁻¹³ Thus, the main limiting factor in the charge diffusion in the electrode material is mainly from the sluggish transport of the lithium ion. The effective diffusion length for lithium ions is 24 – 240 nm under the charge/discharge rate of 1C and 3.2 – 32 nm under 60C. From this estimation, we can see that full capacity should be achieved if the particle diameter of the electrode is smaller than the above values. This belief has driven intense research in nanomaterials electrode materials research.^{8,9} However, many nanomaterials-based electrodes still display performance poorer than expected. This observation hints that other factors such as the lithium ion transfer across the interface may contribute to the limited battery performance. If this speculation is correct, we can expect better battery performance by lowering the interfacial transfer resistance.

Here we demonstrate that lower Li⁺ interfacial transfer resistance can be achieved by better adsorption on the electrode-electrolyte interface by coating the electrode with a thin layer of amorphous carbon. The lithium ion battery performance of crystalline TiO₂ nanocrystals can thus be dramatically enhanced. The amorphous carbon layer, mostly porous, possesses better adsorption capability of ions and molecules to facilitate Li⁺ transfer across

the electrolyte/TiO₂ interface, due to higher local concentration. Meanwhile, the better adsorption of molecules also benefits the photocatalytic performance as adsorption is normally the first step in the photocatalysis and the amorphous carbon layer can act as an efficient electron trapper to induce better charge separation capability of the carbon-TiO₂ composite, thus increasing the photocatalytic performance.

EXPERIMENTAL SECTION

Nanocrystal synthesis. Crystalline and surface-disordered TiO₂ nanoparticles were prepared as follows. Briefly, crystalline TiO₂ nanoparticles were synthesized from a precursor solution consisting of titanium tetraisopropoxide, ethanol, hydrochloric acid, deionized water, and a polymer template, Pluronic F127. The solution was maintained at 40 °C for 24 hours and then dried at 110 °C. The dried powders were divided into two parts. One part was calcinated in air at 500 °C for 6 hours to remove the polymer template and to enhance the crystallization of TiO₂ nanoparticles. The calcinated TiO₂ nanocrystals and the other uncalcinated part were put into two separate beakers in one oven and heated under vacuum at 600 °C for 4 hours. The decomposition of the uncalcinated TiO₂ precursor deposited a thin-layer of amorphous carbon on the surface of the crystalline TiO₂ nanocrystals to obtain the carbon-coated (C-coated) TiO₂ nanocrystals.

Nanocrystal characterization. The TEM study was performed on a FEI Tecnai F20 TEM. The electron accelerating voltage was at 200 kV. Small amount of sample was first dispersed in water and then dropped onto TEM grids. The grids were then dried at 60 °C overnight before TEM examination. The PXRD was performed using a Rigaku Miniflex PXRD machine with Cu K α as the X-ray sources (wavelength = 1.5418 Å) and the 2-theta range was from 15° to 80° with a step width of 0.08 and count time of 3 sec/step. The Raman spectra were collected on an EZ-Raman-N benchtop Raman spectrometer (Enwave Optronics, Inc.). The Raman spectrometer is equipped with a 300 mW diode laser and the excitation wavelength is 785 nm. The spectrum range was from 100 cm⁻¹ to 3100 cm⁻¹. The spectrum collection time was 4 seconds and was averaged over three measurements to improve the signal-to-noise ratio. The TGA experiments were performed on an SDT-Q600 analyzer (TA Instruments Inc.) instrument in flowed air environment, the temperature range was from room temperature to 1000°C at a ramp rate of 5°C/min. The FTIR spectra were obtained on a Nicolet 6700 FT-IR Spectrometer with an attenuated total reflection (ATR) unit.

Electrode preparation. Half cells were fabricated as follows.^{24,25} The materials used in the fabrication of these half cells included acetylene black (AB), polyvinylidene fluoride (PVDF) and N-methylpyrrolidone (NMP). The preparation of the TiO₂ electrodes was conducted in an argon-filled glove box. The electrode mixture (82 wt% TiO₂, 8 wt% AB and 10 wt% PVDF) was steadily dispersed in NMP using a Polytron PT10-35 homogenizer at 2700 rpm for 30 minutes. The slurry was cast on a battery-grade copper sheet using a doctor blade. After being dried

overnight, the electrodes were punched to 1/2" diam. discs and dried in *vacuo* at 110°C overnight before being assembled into coin cells. The electrode loading was controlled at around 1.15 mg TiO₂/cm².

Coin cell fabrication and testing. Coin cell assembly was prepared in standard 2325 hardware under dry argon atmosphere. The separator was from Celgard (product 2400). 1M lithium hexafluorophosphate (LiPF₆) in ethylene carbonate (EC): diethyl carbonate (DEC) (1:2 weight ratio) was used as the electrolyte solution, and lithium as the counter electrode. Cells were discharged to 0.95 V and charged to 3.05 V after 15 min resting for the first cycle at C/25 (calculated from a specific capacity value of 336mAh/g) using a Maccor battery cycler at 30°C. For the 2nd cycle, cells were discharged to 1.0 V and charge to 3.0 V at C/5. Then the cells were cycled at 1C from 1.0 V to 3.0 V. One data point was recorded every 10 mV of voltage change. For the first 18 cycles of the rate performance test, the charge and discharge rates were changed simultaneously; and for the following cycles only the charging rates changed while the discharge rate was kept at 1C.

Electrochemical impedance spectroscopy (EIS) measurement. The EIS measurements were performed on a Biologic potentiostat/EIS instrument. The frequency range was between 1 MHz and 10 mHz. The voltage modulation applied was 100 mV. All cells were cycled for two cycles at 1C and 50% discharged before EIS measurements.

Photocatalytic decomposition of methylene blue (MB) and rhodamine B (RB). The photocatalytic activities of the samples were determined by measuring the photocatalytic decomposition process of MB and RB under simulated solar light irradiation. The solar simulator (81094, Newport) has a 150 watt Xe lamp with an AM 1.5 air mass filter. 1.0 mg of catalyst was added into 3.0 ml MB or RB solution (optical density of 1.0). The UV-vis absorption spectrum of MB or RB was monitored over time after the photocatalytic reaction started. The UV-vis spectrum was measured with an Agilent Cary 60 UV-Vis spectrometer with a spectrum range of from 400 nm to 800 nm.

RESULTS AND DISCUSSION

Nanocrystal properties. To confirm the formation of an amorphous layer on the surface of the crystalline TiO₂ nanocrystals, we performed transmission electron microscopy (TEM) studies on both samples (Figure 1). The low resolution TEM images showed that the bare TiO₂ nanocrystals had a primary particle size in the range of 8 – 15 nm in diameter (Figure 1A). The selected area electron diffraction pattern (SAED) of the bare TiO₂ nanocrystals showed clear anatase diffraction rings made of clean diffraction dots, suggesting the highly crystalline nature of the nanocrystals (Inset in Figure 1A). The high-resolution TEM (HRTEM) image (Figure 1B) suggested the bare TiO₂ nanocrystals were highly crystalline throughout the whole particle. The low resolution TEM images showed that the C-coated TiO₂ nanocrystals had a similar particle size in the range of 8 – 15 nm in diameter (Figure 1C), and the milky diffraction background besides

the anatase diffraction rings observed in the SAED suggested the existence of the amorphous carbon layer.^{26,27} The HRTEM image in Figure 1D apparently suggested that in the C-coated TiO₂ nanocrystals, the TiO₂ nanocrystals were coated with a layer of amorphous carbon or embedded within the amorphous carbon matrix. This displayed the successful coating of the TiO₂ nanocrystals with an amorphous carbon layer.

Figure 1. TEM images with SAED patterns, and HRTEM images of bare (A, B) and C-coated (C, D) TiO₂ nanocrystals, respectively.

We also performed the structural characterization of the samples with X-ray diffraction (XRD). The spectra were normalized to the (101) peak with 2θ around 25.3° . The strong diffraction peaks of the XRD suggest that both TiO₂ nanocrystals had highly crystalline anatase phases (Figure 2A). We estimated the particle size with the Scherrer equation: $\tau = (K\lambda)/(\beta\cos\theta)$, where τ is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size, K is the shape factor with a typical value of 0.9, λ is the X-ray wavelength, β is the line broadening full width at half maximum (FWHM) peak height in radians, and θ is the Bragg angle.^{28,29} The size of both nanocrystals was similar, around 11 nm when calculated from the (100) peak. We further conducted comparative Raman measurements on both samples. A very weak peak at around 148.7 cm^{-1} (E_g) with a large featureless background was observed for the carbon-coated TiO₂ nanocrystals, compared to the strong characteristic vibrational modes of anatase for the bare TiO₂ nanocrystals at 144.6 cm^{-1} (E_g), 199.1 cm^{-1} (E_g), 397.8 cm^{-1} (B_{1g}), 519.2 cm^{-1} ($A_{1g} + B_{1g}$), and 641.6 cm^{-1} (E_g) (Figure 2B).^{5,30-32} The large background in the Raman spectroscopy suggested a thin layer of amorphous carbon possibly existed on the surface of the C-coated TiO₂ nanocrystals, as Raman is

more sensitive to the surface, and XRD tells more about the bulk.^{5,30-32]}

To find out how much carbon was coated on the TiO₂ nanocrystals, we did thermal gravimetric analysis (TGA) measurements on both samples. The TGA were conducted under air atmosphere from room temperature to 1000°C (Figure 2C). The 1.2 wt% weight loss below 220°C was attributed mainly to the water physically or chemically adsorbed on the surface or trapped inside the porous amorphous carbon layer. The 4.9 wt% weight loss between 220°C and 412°C was attributed to the decomposition of the porous amorphous carbon layer (4.6 wt%) and loss of OH groups (0.3 wt%) on the TiO₂ nanocrystals. The slight weight change above 412°C was mainly due to the phase transition of the TiO₂ nanocrystals. Thus, the total amount of carbon deposited on the TiO₂ nanocrystals was about 4.6 wt%.

Figure 2. (A) XRD and (B) Raman spectra of bare (curves a) and C-coated TiO₂ nanocrystals (curves b), (C) TGA and (D) FTIR spectra of bare and C-coated TiO₂ nanocrystals.

In order to check if there are any organic residues left in the amorphous carbon layer formed by decomposing the organic template and the TiO₂ precursor at high temperature in vacuum, we measured the Fourier-transform infrared spectrum of the C-coated TiO₂ nanocrystals in comparison with bare TiO₂ nanocrystals. Both samples displayed similar Fourier transform infrared spectroscopy (FTIR) spectra (Figure 2D): a broad adsorption band center at 3400 cm^{-1} from the O-H stretch modes of the surface hydroxyl groups with hydrogen bonds and chemisorbed water and the peak centered at 1630 cm^{-1} from O-H bending of physisorbed water.³³⁻³⁵ The slightly large OH bands in the C-coated TiO₂ nanocrystals suggest that its OH content was slightly higher than the bare TiO₂ nanocrystals.

Lithium-Ion Battery Performance. In order to test the concept of the stabilization of the lithium insertion and extraction with the C-coated TiO₂ nanocrystals, we fabricated half cells and tested their performances. In the half cell configuration, lithium metal was used as the an-

ode, and TiO_2 nanocrystals were used as the cathode materials. The discharge and charge corresponded to the lithium insertion and extraction, respectively. The theoretical specific capacity value of 336 mAh/g was used for C-rate calculation. The half cells were initially discharged to 1.0 V and charged to 3.0 V after 15 min resting for the first cycle at C/25. For the 2nd cycle, the cells were discharged and charge at C/5. Finally the cells were cycled at 1C. The initial discharge capacity of the C-coated TiO_2 nanocrystals was 278 mAh/g at C/25 rate, 211 mAh/g at C/5 rate, 178 mAh/g at 1C rate for the first, second, and third cycle, respectively, 17%, 30% and 29% higher than that of the bare TiO_2 nanocrystals (237 mAh/g, 162 mAh/g and 138 mAh/g) (Figure 3A). After 100 cycles, the discharge capacity of the C-coated TiO_2 nanocrystals was 166 mAh/g at 1C rate, 47% higher than that of the crystalline TiO_2 nanocrystals (113 mAh/g). The C-coated TiO_2 nanocrystals displayed 93% capacity retention rate after 100 cycles at 1C rate, compared to the 82% retention rate of the bare TiO_2 nanocrystals. The discharge capacity of the C-coated TiO_2 nanocrystals after 100 cycles at 1C rate was even higher than that of the initial capacity of the bare TiO_2 nanocrystals at C/5 rate: a 5 times rate performance increase.

Figure 3. (A) Variation of discharge capacity versus cycle number for the first 100 cycles and (B) Variation of Coulombic efficiency along with the charge/discharge versus cycle number for the first 20 cycles, for bare and C-coated TiO_2 nanocrystals. Galvanostatic charge/discharge profiles at first cycle at C/25 rate, 35th cycle at 1C rate, and 100th cycle at 1C rate for the electrode made of bare (C) and C-coated TiO_2 nanocrystals (D).

Better Coulombic efficiency was observed for the C-coated TiO_2 nanocrystals over the bare TiO_2 nanocrystals. The Coulombic efficiency here was defined as the ratio of charge (lithium extraction) capacity/discharge (lithium insertion) capacity. A closer look at the first 20 cycles revealed that the discharge efficiency increased with large fluctuation for the bare TiO_2 nanocrystals in the first four cycles followed by slight decrease in the next 16 cycles, while the discharge efficiency of and the C-coated TiO_2

nanocrystals increased steadily to the maximum within the first 5 cycles and followed with steady maximum efficiency in the next 15 cycles (Figure 3B). The bare TiO_2 nanocrystals showed a quick drop of the discharge efficiency in the initial stage followed by a climb-up to the efficiency of around 99.5% after the first 30 cycles which is steady afterward for the remaining 70 cycles; the C-coated TiO_2 nanocrystals show a rapid climb in the initial 5 cycles to the efficiency of around 99.7% which is steady afterward for the remaining 95 cycles (Figure S1). The large fluctuation in the discharge efficiency of the bare TiO_2 nanocrystals could be due to structural struggling to form a stable solid-electrolyte interface (SEI) layer at the initial cycles in the charge/discharge process, while the quick and steady ramp up of the discharge efficiency of the C-coated TiO_2 nanocrystals suggested a better formation of SEI layer and a smaller charge transfer resistance across the interface.

Besides the larger charge/discharge capacity at various cycles, the C-coated TiO_2 nanocrystals showed longer charge/discharge plateaus and smaller potential difference between the charge and discharge cycle. The potential difference between the first charge and discharge cycle of the C-coated TiO_2 nanocrystals was about 0.10 V, 47% smaller than that of the bare TiO_2 nanocrystals of about 0.19 V (Figures 3C and 3D). This smaller potential difference indicated decreased charge transport resistance across the interface and even in the TiO_2 nanocrystalline lattice. The longer charge/discharge plateaus suggested that more host matrix materials were efficiently involved with the charge insertion/distraction in the charge/discharge processes. Overall, the charge transfer was smoother for the C-coated TiO_2 nanocrystals than for the bare TiO_2 nanocrystals.

Figure 4. (A) Rate performances of the bare and C-coated TiO_2 nanocrystals. Galvanostatic charge/discharge profiles at various charge (lithium extraction) rates for the electrode made of the bare (B) and C-coated TiO_2 nanocrystals (C). (D) Comparison of the charge/discharge profiles for bare and C-coated TiO_2 nanocrystals at charge rates of 50C.

We tested the rate performance of the bare TiO₂ nanocrystals and the C-coated TiO₂ nanocrystals under varied charge rates (Figure 4A). The discharge (lithium insertion) rate was kept at 1C and only the charge (lithium extraction) rate changed. The C-coated TiO₂ nanocrystals showed much better performance over the crystalline TiO₂ under the same testing condition. The capacity of C-coated TiO₂ was 186 mAh/g at 1C, 156 mAh/g at 10C, and 103 mAh/g at 50C, 118%, 149% and 294% as that of bare TiO₂ at the same conditions (157 mAh/g at 1C, 105 mAh/g at 10C, and 35.0 mAh/g at 50C), respectively. At higher charge rates, the improvement was more apparent for the C-coated TiO₂ over the crystalline TiO₂. The C-coated TiO₂ nanocrystals sustained much higher charge rate than crystalline TiO₂ nanocrystals. It would take around 1 hour (1C) to charge with bare TiO₂ nanocrystals to 150 mAh/g capacity, but only 6 min (~10C) for C-coated TiO₂ nanocrystals. Thus, the charge rate of the C-coated TiO₂ is 10 times as that of bare TiO₂. Testing under simultaneously changed discharge/charge rate displayed similar rate performance (Figure S2). The higher rate performance of the C-coated TiO₂ nanocrystals was possibly due to the lower energy barrier of the lithium ion transport across interface.

The galvanostatic charge/discharge profiles at various charging rates for the electrode made of bare and C-coated TiO₂ nanocrystals were shown in Figures 4B and 4C, respectively. The C-coated TiO₂ nanocrystals showed higher capacity and larger charge/discharge plateaus over the bare TiO₂ at each charging rate. The larger charge/discharge plateaus indicated that smoother charge transport between the host matrix and the transferred charges. The discharge curve for the nanoporous anatase electrode can be divided into three different voltage regions (Figure 4D).^{20,36-38} A monotonic voltage drop to ≈ 1.75 V occurs in region A, which is attributed to a homogeneous Li insertion into the bulk, up to a solid-solution limit of Li in TiO₂.^{20,36-38} A typical biphasic plateau (region B) is observed at a potential of ≈ 1.75 V, where Li-rich phases are expected to coexist with the Li-poor TiO₂ phase. Further reversible storage of Li is able to occur at particle interfaces in this voltage region, representing region C.²⁰ At voltages over 1.75 V, the phases no longer reversibly dissolve Li, although more Li can be accommodated by further two-phase bulk intercalation ($x > 0.5$). As reported previously, Reducing the particle size is indeed effective in improving both the bulk intercalation and the interfacial storage capacities, leading to an increase of region B (due to the shorter diffusion length) and C (due to the larger interfacial area), with a slight increase in the proportion of region C.²⁰ Thus, the high surface area of the nanometer-sized TiO₂ provided many available extra sites for lithium accommodation at interfaces (interfacial storage), beyond the fraction of octahedral sites available for the lithium-intercalation reaction in the bulk.²⁰

In order to analyze why the charge transfer/transport across the crystalline matrix was facilitated through a thin layer of amorphous carbon coating, electrochemical im-

pedance spectra (EIS) were measured on both samples under the same condition (Figure 5A). Both cells were cycled for two cycles and 50% discharged before EIS measurements. The equivalent circuit modeling³⁹ and fitting results (Figure 5B) suggested that the charge transfer and transport resistance was largely reduced for C-coated TiO₂ nanocrystals compared to bare TiO₂ nanocrystals. First, the ohmic resistance was slightly reduced for the C-coated TiO₂ nanocrystals, suggesting better electrical contacts between the electrode materials and the copper foil. The double layer charge capacitances in both carbon/electrode (C_i) and TiO₂ electrode/carbon (CPE-T) interfaces were similar. The electron transfer resistance across the interfaces (R_i) was reduced in the C-coated TiO₂ to 4.1 Ω from 5.6 Ω of bare TiO₂. The Li⁺ transfer resistance across TiO₂ electrode/electrolyte interface (R_{CPE}) was largely reduced from 104.7 of bare TiO₂ to 48.2 Ω of C-coated TiO₂. The lowered Li⁺ transfer resistance could be due to the slightly higher Li⁺ concentration near the TiO₂ electrode as seen from the slightly higher double layer capacitance (CPE-T). The charge transport/diffusion resistance (W_o-R) in the C-coated TiO₂ electrode was smaller (41.6 Ω) than that in bare TiO₂ electrode (56.5 Ω). The smaller charge diffusion resistance could be attributed to the possibly oxygen vacancy created during the vacuum carbon deposition process by the reduction of TiO₂ with carbon at high temperature,⁴⁰ as oxygen vacancy has been shown to lower the charge transfer resistance due to improved electrical conductivity.^{20,41}

Figure 5. (A) EIS spectra of bare and C-coated TiO₂ nanocrystals. (o) and (□) are the raw data, the lines are the fitted curves. (B) The equivalent circuit used to fit the EIS spectra and the fitted values for the corresponding components in the circuit. **R_s**: ohmic resistance, including the bulk resistance of the electrolyte, separator, and electrode; **R_i**: electron transfer resistance at the TiO₂/carbon/electrolyte interface; **C_i**: double layer charge capacitance in the carbon/electrode interface. **CPE-T**: time constant component of the constant phase element (CPE), approximate to the double layer charge capacitance in the TiO₂/electrolyte interface; **CPE-P**: the exponential part of the constant phase element; **R_{CPE}**: Li⁺ transfer resistance cross the TiO₂/electrolyte interface; **W_o-R**: Warburg charge diffusion resistance in the TiO₂ electrode; **W_o-T**: Warburg diffusion time = L^2/D in the electrode, L is the length of the diffusion layer in the electrode, and D is the diffusion coefficient in the electrode; **W_o-P**: Warburg exponent.

Photocatalytic performance. To reveal their photocatalytic and surface adsorption activity, we conducted pho-

photocatalytic decomposition of methylene blue (MB) and rhodamine B (RB) solution with both samples under simulated solar light irradiation. The UV-vis absorption spectra of MB and RB were monitored over time after the photocatalytic reaction started. The MB solution quickly lost its color in the short course of 10 minutes irradiation with the C-coated TiO₂ nanocrystals as catalyst (Figures 6A and S3), indicating most of the MB was decomposed. It took about 40 minutes for the pristine TiO₂ nanocrystals to decompose the same amount of MB molecules under the same condition. This suggested that C-coated TiO₂ nanocrystals had an about four-fold better photocatalytic activity than pristine TiO₂ nanocrystals in decomposing MB. It took around 40 minutes for the C-coated TiO₂ nanocrystals to decolor the RB solution, while a large amount of RB still remained after 60 minutes' irradiation with pristine TiO₂ nanocrystals (Figures 6B and S4). Apparently, C-coated TiO₂ nanocrystals displayed much higher activity in decomposing RB as well.

Figure 6. (A) The maximum optical absorbance change of methylene blue and (B) rhodamine B solution as a function of solar irradiation time with pristine and C-coated TiO₂ nanocrystals. (C) $\ln(C_0/C)$ of methylene blue and (D) rhodamine B as a function of solar irradiation time with pristine and C-coated TiO₂ nanocrystals.

When the initial concentration of dye is very small, the degradation of dyes can be described by an apparent first-order equation with a simplified Langmuir-Hinshelwood model:

$$\ln(C_0/C) = k_a t \quad (2)$$

where C_0 is the initial concentration of dye, k_a is the apparent first-order rate constant, C is the concentration of the dye and t is the illumination time.^{42,43} The slope of the $\ln(C_0/C) \sim t$ tells the rate constant of the reaction, and the intercept on the y axis tells the amount of adsorption. The $\ln(C_0/C) \sim t$ plots in Figures 6C and 6D showed that the rate constant of the C-coated TiO₂ nanocrystals (16.4/h) was almost 4 times of the bare TiO₂ nanocrystals (4.14/h) in decomposing MB, and 5.5 times (4.9/h vs. 0.89/h) in decomposing RB. The intercept on the y axis suggested that the surface adsorption was much obvious for C-coated

TiO₂ nanocrystals than for the bare TiO₂ nanocrystals. The improvement of the photocatalytic activity of the C-coated TiO₂ nanocrystals was likely due to the better dye adsorption on the surface and faster decomposition possibly from the better charge separation efficiency from the C-TiO₂ interfacial heterojunction. The better dye adsorption capability of the C-coated TiO₂ also suggested its better Li⁺ adsorption as the color centers of the both dyes are cationic. This could increase the local Li⁺ near and the Li⁺ transfer across the TiO₂/electrolyte interface.

CONCLUSIONS

We have demonstrated successfully that a thin layer of amorphous carbon can be created on crystalline TiO₂ nanocrystals with a vacuum decomposition-deposition process. We evaluated the C-coated TiO₂ nanocrystal as an electrode material for lithium ion batteries and found it exhibited greatly improved lithium insertion/extraction performance compared with crystalline TiO₂, and showed an excellent rate capability improvement (103 mAh/g vs. 35 mAh/g at 50C, and 10C vs. 1C at around 156 mAh/g). We also studied their photocatalytic performance and found the C-coated TiO₂ nanocrystal displayed over 4 times improvements in decomposing organic dye molecules (MB and RB), besides the better adsorption capability, over bare TiO₂ nanocrystal. We attributed the greatly enhanced lithium storage properties of the C-coated TiO₂ nanocrystals to the lower lithium ion diffusion and electronic conduction resistance and better surface adsorption in the amorphous carbon layer. Thus adding a thin layer of amorphous carbon on crystalline materials may be applied as an alternative approach for improving the battery and photocatalytic performance of other materials as well.

ASSOCIATED CONTENT

Supporting Information. Variation of Coulombic efficiency along with the charge/discharge versus cycle number for bare and C-coated TiO₂ nanocrystals; Rate performances of the bare and C-coated TiO₂ nanocrystals. The charge and discharge rate were the same for each cycle; Optical absorbance spectrum change of methylene blue and rhodamine B solution under solar irradiation time using bare and C-coated TiO₂ nanocrystals.

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REFERENCES

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- (1) Fujishima, A.; Honda, K. *Nature* **1972**, 238, 37 – 38.
- (2) Choi, W.; Termin, A.; Hoffmann, M. R. *J. Phys. Chem.* **1994**, 98, 13669 – 13679.
- (3) Asahi, R.; Morikawa, T.; Ohwaki, T.; Aoki, K.; Taga, Y. *Science* **2001**, 293, 269 – 271.
- (4) Chen, X.; Mao, S. S. *Chem. Rev.* **2007**, 107, 2891 – 2959.
- (5) Chen, X.; Liu, L.; Yu, P. Y.; Mao, S. S. *Science* **2011**, 331, 746 – 750.
- (6) Chen, X.; Burda, C. J. *Am. Chem. Soc.* **2008**, 130, 5018 – 5019.
- (7) Chen, X.; Li, C.; Gratzel, M.; Kostecki, R.; Mao, S. S. *Chem. Soc. Rev.* **2012**, 41, 7909 – 7937.
- (8) Bruce, P. G.; Scrosati, B.; Tarascon, J.-M. *Angew. Chem. Int. Ed.* **2008**, 47, 2930 – 2946.
- (9) Xia, T.; Zhang, W.; Li, W.; Oyler, N. A.; Liu, G.; Chen, X. *Nano Energy*, **2013**, 2, 826 – 835.
- (10) Wagemaker, M.; Kentgens, A. P. M.; Mulder, F. M. *Nature* **2002**, 418, 397 – 399.
- (11) Moriguchi, I.; Hidaka, R.; Yamada, H.; Kudo, T.; Murakami, H.; Nakashima, N. *Adv. Mater.* **2006**, 18, 69 – 73.
- (12) Solbrand, A.; Henningsson, A.; Sodergren, S.; Lindstrom, H.; Hagfeldt, A.; Lindquist, S.-E. *J. Phys. Chem. B* **1999**, 103, 1078 – 1083.
- (13) Abayev1, I.; Zaban, A.; Fabregat-Santiago, F.; Bisquert, J. *Phys. Stat. Sol. (a)* **2003**, 196, R4 – R6.
- (14) Li, N.; Liu, G.; Zhen, C.; Li, F.; Zhang, L.; Cheng, H.-M. *Adv. Funct. Mater.* **2011**, 21, 1717 – 1722.
- (15) Lindström, H.; Södergren, S.; Solbrand, A.; Rensmo, H.; Hjelm, J.; Hagfeldt, A.; Lindquist, S.-E. *J. Phys. Chem. B* **1997**, 101, 7717 – 7722.
- (16) van de Krol, R.; Goossens, A.; Meulenkamp, E. A. *J. Electrochem. Soc.* **1999**, 146, 3150 – 3154.
- (17) Armand, M.; Tarascon, J. M. *Nature* **2008**, 451, 652 – 657.
- (18) Tollefson, J.; Scully, T.; Witze, A.; Morton, O. *Nature* **2008**, 454, 818 – 822.
- (19) Cao, Y. L.; Xiao, L. F.; Wang, W.; Choi, D.; Nie, Z. M.; Yu, J. G.; Saraf, L. V.; Yang, Z. G.; Liu, J. *Adv. Mater.* **2011**, 23, 3155 – 3160.
- (20) Shin, J.-Y.; Samuelis, D.; Maier, J. *Adv. Funct. Mater.* **2011**, 21, 3464 – 3472.
- (21) Wagemaker, M.; Borghols, W. J. H.; Mulder, F. M. *J. Am. Chem. Soc.* **2007**, 129, 4323 – 4327.
- (22) Kavan, L.; Kalbac, M.; Zukalova, M.; Exnar, I.; Lorenzen, V.; Nesper, R.; Grätzel, M. *Chem. Mater.* **2004**, 16, 477 – 485.
- (23) Kim, J.; Cho, J. *J. Electrochem. Soc.* **2007**, 154, A542 – A546.
- (24) Xun, S.; Song, X.; Grass, M. E.; Roseguo, D. K.; Liu, Z.; Battaglia, V. S.; Liu, G. *Electrochem. Solid-State Lett.* **2011**, 14, A61 – A63.
- (25) Liu, G.; Xun, S.; Vukmirovic, N.; Song, X.; Olalde-Velasco, P.; Zheng, H.; Battaglia, V. S.; Wang, L.; Yang, W. *Adv. Mater.* **2011**, 23, 4679 – 4683.
- (26) Fultz, B.; Howe, J. *Transmission Electron Microscopy and Diffractometry of Materials*, Springer, New York, **2009**.
- (27) Champness, P. E. *Electron Diffraction in the Transmission Electron Microscope*, Taylor & Francis, **2001**.
- (28) Jenkins, R.; Snyder, R. L. *Introduction to X-ray Powder Diffractometry*, John Wiley & Sons Inc., New York, **1996**.
- (29) Xia, T.; Otto, J. W.; Dutta, T.; Murowchick, J.; Caruso, A. N.; Peng, Z.; Chen, X. *J. Mater. Res.* **2013**, 28, 326 – 332.
- (30) Kelly, S.; Pollak, F. H.; Tomkiewicz, M. *J. Phys. Chem. B* **1997**, 101, 2730 – 2734.
- (31) Tian, F.; Zhang, Y.; Zhang, J.; Pan, C. *J. Phys. Chem. C* **2012**, 116, 7515 – 7519.
- (32) Zhang, J.; Li, M.; Feng, Z.; Chen, J.; Li, C. *J. Phys. Chem. B* **2006**, 110, 927 – 935.
- (33) Zou, J.; Gao, J.; Xie, F. *J. Alloys Compd.* **2010**, 497, 420 – 427.
- (34) Li, G.; Li, L.; Boerio-Goates, J.; Woodfield, B. F. *J. Am. Chem. Soc.* **2005**, 127, 8659 – 8666.
- (35) Kuvarega, A. T.; Krause, R. W. M.; Mamba, B. B. *J. Phys. Chem. C* **2011**, 115, 22110 – 22120.
- (36) Guo, Y.-G.; Hu, Y.-S.; Maier, J. *Chem. Commun.* **2006**, 2783 – 2785.
- (37) Guo, Y.-G.; Hu, Y.-S.; Sigle, W.; Maier, J. *Adv. Mater.* **2007**, 19, 2087 – 2091.
- (38) Hu, Y.-S.; Kienle, L.; Guo, Y.-G.; Maier, J. *Adv. Mater.* **2006**, 18, 1421 – 1426.
- (39) Orazem, M. E.; Tribollet, B. *Electrochemical impedance spectroscopy*, John Wiley & Sons, NJ, USA, **2011**.
- (40) Li, Y.; Li, X.; Li, J.; Yin, J. *Mater. Lett.* **2005**, 59, 2659 – 2663.
- (41) Xia, T.; Zhang, W.; Murowchick, J.; Liu, G.; Chen, X. *Adv. Energy Mater.* **2013**, DOI: 10.1002/aenm.201300294.
- (42) Mizukoshi, Y.; Ohtsu, N.; Semboshi, S.; Masahashi, N. *Appl. Catal. B* **2009**, 91, 152 – 156.
- (43) Chen, X.; Halasz, S.; Giles, E. C.; Mankus, J. V.; Johnson, J. C.; Burda, C. *J. Chem. Educ.* **2006**, 83, 265 – 267.

SYNOPSIS TOC. 10-time lithium rate improvement and 4-time photocatalytic performance enhancements have been achieved on carbon-coated TiO_2 nanocrystals due to lower interfacial lithium ion diffusion and electronic conduction resistance and better surface adsorption of ions and dye molecules.