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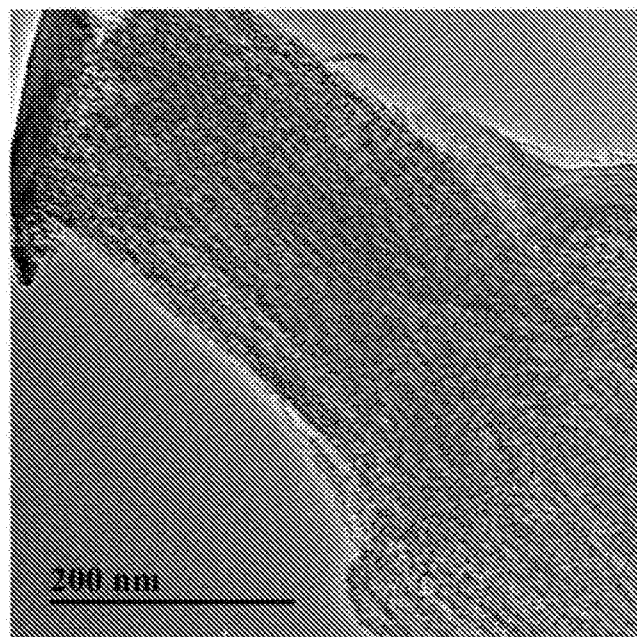
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Preparation method of ordered mesoporous Co/CMK composite nano anode material.

(57)

A method for preparing an ordered mesoporous Co/CMK composite nano negative electrode material, which belongs to the technical field of nano materials and chemical power sources. The method includes first using the copolymer P123 as a template and tetraethylorthosilicate as a silicon source to synthesize SBA-15 by hydrothermal method, and then use this as a hard template and sucrose as a carbon source to synthesize ordered mesoporous carbon material CMK-3; then, the ordered mesoporous Co/CMK-3 composite nanomaterial was obtained in the $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ solution through reduced pressure ultrasound, and finally the ordered mesoporous Co/CMK composite nanomaterial was reduced by hydrothermal method with hydrazine hydrate. The ordered mesoporous Co/CMK composite nano material prepared by this method can relieve the volume expansion/shrinkage during charging and discharging, and at the same time, the cobalt metal component increases the conductivity of the material. The cycle performance and coulombic efficiency of the battery are improved.



DESCRIPTION

Preparation method of ordered mesoporous Co/CMK composite nano anode material

TECHNICAL FIELD

The invention belongs to the technical field of nano materials and chemical power sources, and relates to a method for preparing an ordered mesoporous Co/CMK composite nano negative electrode material, and in particular to a hydrothermal method for preparing CMK-3 and an ultrasonic method for preparing a cobalt-loaded CMK-3 mixture.

BACKGROUND

With the development of the world economy, while people's living standards are improving, energy crisis and environmental pollution have increasingly become unavoidable problems in today's society. With the gradual depletion of resources, the acquisition and storage of renewable energy has gained extensive attention and research in the world. Lithium-ion batteries have many advantages, such as high energy density, long service life, environmental friendliness, and no memory effect. In recent years, lithium-ion batteries have been widely used in portable electronic equipment, transportation and other fields, and have also been greatly promoted and applied in aerospace and military fields. With the rapid development of transportation industry and electronic communication, the service life and energy density of lithium ion batteries are required to be higher. As the main body of lithium storage, the cathode materials of lithium batteries play a decisive role in the performance of lithium batteries. However, most of the cathode materials of commercial lithium batteries are carbon materials with low specific capacity, which can no longer meet people's demand for high energy density.

Ordered mesoporous carbon materials have high specific surface area and high porosity. The aperture size can be adjusted within a certain range; mesopores have various shapes and adjustable pore wall composition, structure and properties. High thermal stability and hydrothermal stability can be obtained by optimizing synthesis conditions. The synthesis is simple, easy to operate, and has no physiological toxicity. The interconnected carbon walls give it excellent electrical conductivity. However, when mesoporous carbon materials are directly applied to lithium battery cathode materials, the first coulombic efficiency can only reach about 34%, which makes it impossible to be used in commercial batteries. Through the

combination of mesoporous carbon with metal and its oxide, the specific surface area of mesoporous carbon is reduced, and the activation point is reduced, thus reducing the irreversible capacity. Meanwhile, the three-dimensional network structure of mesoporous carbon provides a good channel for lithium ion transmission, which is beneficial to the mutual reaction between electrolyte, lithium ion and electrode materials, thus facilitating the charge-discharge contact between lithium ion and active substances, improving its coulombic efficiency and improving its cycle performance. LU500737

Cobalt is a simple metal. As the cathode material of lithium battery, although it can not react directly with lithium ions, it can catalyze the electrochemical reaction in the battery. Combining the advantages of cobalt and mesoporous carbon, we made cobalt nanoparticles nano-sized, and the cobalt nanoparticles were uniformly diffused in the internal pore channels of mesoporous carbon by ultrasound, which was conducive to the direct contact between active materials and electrolyte, which not only improved the lithium storage performance of negative electrode materials, but also improved the discharge capacity and cycle stability of batteries.

In the prior art, there is an urgent need for a method for preparing an ordered mesoporous Co/CMK composite nano-electrode material.

SUMMARY

The purpose of the present invention is to overcome the defects of the above technology, and provide a preparation method of ordered mesoporous Co/CMK composite nano negative electrode material, which is required to improve cycle performance and initial capacity. At the same time, the method has low processing cost, simple production method, energy saving and environmental protection, and is convenient for large-scale investment and production.

According to the technical scheme of the invention, copolymer P123 is used as a template agent, tetraethyl orthosilicate (TEOS) is used as a silicon source, mesoporous molecular sieve SBA-15 is hydrothermally synthesized, and then ordered mesoporous carbon material CMK-3 is synthesized by using SBA-15 as a template and sucrose as a carbon source. Then, the Co/CMK nano-composite cathode material was prepared by combining the precursor of cobalt with ultrasonic under reduced pressure, and finally reducing it with hydrazine hydrate through hydrothermal reaction.

In order to achieve the above technical purpose, the technical scheme of the invention is as follows:

the method for preparing the ordered mesoporous Co/CMK composite nano cathode material comprises the following steps:

(1) weighing a certain amount of template P123, dissolving it in 2mol/L hydrochloric acid solution at 35°C, adding a certain amount of tetraethylorthosilicate TEOS and distilled water, and continuously stirring for 5-12h; transferring the solution to a reaction kettle, hydrothermal aging at 120°C for 24h, washing with water, filtering, drying, carbonizing under the protection of N₂, heating from room temperature to 550°C, keeping the temperature for 5h, and naturally cooling to room temperature after calcination to obtain SBA-15;

(2) weighing a certain amount of SBA-15 prepared in step (1) and add it into a solution containing a certain amount of sucrose, concentrated sulfuric acid and distilled water, and heat it at 100°C and 160°C for 6h respectively. After cooling, add a certain amount of sucrose, concentrated sulfuric acid and distilled water, continue heating at 100°C and 160°C for 6h respectively, and then carbonize it at 877°C under N₂ protection. After the carbonization is finished, the template is removed with 5% HF solution, washed with distilled water, and dried at 120°C. Finally, add the dried sample to a 1mol/L concentrated sulfuric acid solution and reflux, place it at 80°C for 3 hours, and then wash and dry it to obtain ordered mesoporous carbon CMK-3;

(3) weighing a certain amount of CMK-3 prepared in step (2), a certain amount of CoCl₂·6H₂O and cetyltrimethylammonium bromide CTAB into distilled water, ultrasonic under circulating water, adding a certain amount of hydrazine hydrate after ultrasonic, continuously stirring for 1-2h, transferring the solution to a reaction kettle, performing hydrothermal reaction, washing with water, and drying in vacuum for 1-2h to obtain the Co/CMK composite nano negative electrode material.

Further, in the step (3), the ultrasonic time is 1-2h, and the ultrasonic power is 60-100w.

Furthermore, the temperature of the hydrothermal reaction in step (3) is 180°C, the hydrothermal reaction time is 5 h, and the heating rate in the hydrothermal reaction process is 2°C/min.

Compared with the prior art, the invention has the following beneficial effects:

(1) the ordered mesoporous Co/CMK composite nano cathode material of the present invention combines the excellent catalytic performance of metallic cobalt with the advantages of high conductivity and high specific surface area of mesoporous carbon to form complementary advantages, make up for the defects of single mesoporous carbon material, improve the cycle stability and initial capacity of lithium batteries, and open up new ideas for the application of mesoporous materials.

(2) The ordered mesoporous Co/CMK composite nano cathode material has simple preparation process, low cost and environmental friendliness.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a transmission electron microscope image of an ordered mesoporous Co/CMK nanocomposite;

Figure 2 is a graph of the cycle performance of ordered mesoporous Co/CMK nanocomposites.

DESCRIPTION OF THE INVENTION

In order to make the technical means, creative features, objectives and effects of the present invention easy to understand, the present invention will be further described in conjunction with the accompanying drawings and specific embodiments below.

Embodiment 1

(1) Weighing 2g of template agent P123, dissolve it in 60mL of 2mol/L hydrochloric acid solution at 35°C, then add 4.4mL of tetraethylorthosilicate (TEOS) and 15mL of distilled water, and continue to stir for 5-12h, transferring the solution to a reaction kettle, hydrothermal aging at 120°C for 24h, washing with water, filtering, drying, carbonizing under the protection of N₂, heating from room temperature to 550°C, keeping the temperature for 5h, and naturally cooling to room temperature after calcination to obtain SBA-15.

(2) Adding 1g SBA-15 into the solution containing 1.25g sucrose, 0.14g concentrated sulfuric acid and 5mL distilled water, heat it at 100°C and 160°C for 6h respectively, add 0.8g sucrose, 0.09g concentrated sulfuric acid and 5g distilled water after cooling, continue heating at 100°C and 160°C for 6h respectively, and then carbonize it at 877°C for 6h under N₂ protection. After carbonization and grinding, the template was removed with 5% HF solution, washed repeatedly with distilled water and dried at 120°C. And finally, adding the dried

sample into 1mol/L concentrated sulfuric acid solution for refluxing, standing at 80°C for 3h, and then washing and drying to obtain the ordered mesoporous carbon CMK-3.

(3) Weighing 0.1g of CMK-3, 0.476g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 0.360g into 40mL of distilled water, sonicate under circulating water for 2h, the ultrasonic power is 60W, adding 45ml of hydrazine hydrate after sonication, and continue to stir for 2h. Then the solution was transferred to the reaction kettle, hydrothermally reacted at 180°C for 6 hours, washed with water, and dried under vacuum at 50°C for 12 hours to obtain an ordered mesoporous Co/CMK composite nano-electrode material.

Embodiment 2

(1) Weighing 2g of template agent P123, dissolve it in 60mL of 2mol/L hydrochloric acid solution at 35°C, then add 4.4mL of tetraethylorthosilicate (TEOS) and 15mL of distilled water, and continue to stir for 5-12h, transferring the solution to a reaction kettle, hydrothermal aging at 120°C for 24h, washing with water, filtering, drying, carbonizing under the protection of N_2 , heating from room temperature to 550°C, keeping the temperature for 5h, and naturally cooling to room temperature after calcination to obtain SBA-15.

(2) Adding 1g SBA-15 into the solution containing 1.25g sucrose, 0.14g concentrated sulfuric acid and 5mL distilled water, heat it at 100°C and 160°C for 6h respectively, add 0.8g sucrose, 0.09g concentrated sulfuric acid and 5g distilled water after cooling, continue heating at 100°C and 160°C for 6h respectively, and then carbonize it at 877°C for 6h under N_2 protection. After carbonization and grinding, the template was removed with 5% HF solution, washed repeatedly with distilled water and dried at 120°C. And finally, adding the dried sample into 1mol/L concentrated sulfuric acid solution for refluxing, standing at 80°C for 3h, and then washing and drying to obtain the ordered mesoporous carbon CMK-3.

(3) Weighing 0.1g of CMK-3, 0.532g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 0.391g into 40mL of distilled water, sonicate under circulating water for 2h, the ultrasonic power is 70W, adding 50ml of hydrazine hydrate after sonication, and continue to stir for 2h. Then the solution was transferred to the reaction kettle, hydrothermally reacted at 180°C for 6 hours, washed with water, and dried under vacuum at 60°C for 12 hours to obtain an ordered mesoporous Co/CMK composite nano-electrode material.

Embodiment 3

(1) Weighing 2g of template agent P123, dissolve it in 60mL of 2mol/L hydrochloric acid solution at 35°C, then add 4.4mL of tetraethylorthosilicate (TEOS) and 15mL of distilled water, and continue to stir for 5-12h, transferring the solution to a reaction kettle, hydrothermal aging at 120°C for 24h, washing with water, filtering, drying, carbonizing under the protection of N₂, heating from room temperature to 550°C, keeping the temperature for 5h, and naturally cooling to room temperature after calcination to obtain SBA-15.

(2) Adding 1g SBA-15 into the solution containing 1.25g sucrose, 0.14g concentrated sulfuric acid and 5mL distilled water, heat it at 100°C and 160°C for 6h respectively, add 0.8g sucrose, 0.09g concentrated sulfuric acid and 5g distilled water after cooling, continue heating at 100°C and 160°C for 6h respectively, and then carbonize it at 877°C for 6h under N₂ protection. After carbonization and grinding, the template was removed with 5% HF solution, washed repeatedly with distilled water and dried at 120°C. And finally, adding the dried sample into 1mol/L concentrated sulfuric acid solution for refluxing, standing at 80°C for 3h, and then washing and drying to obtain the ordered mesoporous carbon CMK-3.

(3) Weighing 0.1g of CMK-3, 0.621g of CoCl₂·6H₂O, 0.450g into 60mL of distilled water, sonicate under circulating water for 2h, the ultrasonic power is 80W, adding 55ml of hydrazine hydrate after sonication, and continue to stir for 2h. Then the solution was transferred to the reaction kettle, hydrothermally reacted at 180°C for 5 hours, washed with water, and dried under vacuum at 70°C for 12 hours to obtain an ordered mesoporous Co/CMK composite nano-electrode material.

Embodiment 4

(1) Weighing 2g of template agent P123, dissolve it in 60mL of 2mol/L hydrochloric acid solution at 35°C, then add 4.4mL of tetraethylorthosilicate (TEOS) and 15mL of distilled water, and continue to stir for 5-12h, transferring the solution to a reaction kettle, hydrothermal aging at 120°C for 24h, washing with water, filtering, drying, carbonizing under the protection of N₂, heating from room temperature to 550°C, keeping the temperature for 5h, and naturally cooling to room temperature after calcination to obtain SBA-15.

(2) Adding 1g SBA-15 into the solution containing 1.25g sucrose, 0.14g concentrated sulfuric acid and 5mL distilled water, heat it at 100°C and 160°C for 6h respectively, add 0.8g sucrose, 0.09g concentrated sulfuric acid and 5g distilled water after cooling, continue heating

at 100°C and 160°C for 6h respectively, and then carbonize it at 877°C for 6h under N₂ protection. After carbonization and grinding, the template was removed with 5% HF solution, washed repeatedly with distilled water and dried at 120°C. And finally, adding the dried sample into 1mol/L concentrated sulfuric acid solution for refluxing, standing at 80°C for 3h, and then washing and drying to obtain the ordered mesoporous carbon CMK-3.

(3) Weighing 0.1g of CMK-3, 0.476g of CoCl₂·6H₂O, 0.360g into 40mL of distilled water, sonicate under circulating water for 2h, the ultrasonic power is 60W, adding 45ml of hydrazine hydrate after sonication, and continue to stir for 2h. Then the solution was transferred to the reaction kettle, hydrothermally reacted at 180°C for 6 hours, washed with water, and dried under vacuum at 50°C for 12 hours to obtain an ordered mesoporous Co/CMK composite nano-electrode material.

Embodiment 5

(1) Weighing 2g of template agent P123, dissolve it in 60mL of 2mol/L hydrochloric acid solution at 35°C, then add 4.4mL of tetraethylorthosilicate (TEOS) and 15mL of distilled water, and continue to stir for 5-12h, transferring the solution to a reaction kettle, hydrothermal aging at 120°C for 24h, washing with water, filtering, drying, carbonizing under the protection of N₂, heating from room temperature to 550°C, keeping the temperature for 5h, and naturally cooling to room temperature after calcination to obtain SBA-15.

(2) Adding 1g SBA-15 into the solution containing 1.25g sucrose, 0.14g concentrated sulfuric acid and 5mL distilled water, heat it at 100°C and 160°C for 6h respectively, add 0.8g sucrose, 0.09g concentrated sulfuric acid and 5g distilled water after cooling, continue heating at 100°C and 160°C for 6h respectively, and then carbonize it at 877°C for 6h under N₂ protection. After carbonization and grinding, the template was removed with 5% HF solution, washed repeatedly with distilled water and dried at 120°C. And finally, adding the dried sample into 1mol/L concentrated sulfuric acid solution for refluxing, standing at 80°C for 3h, and then washing and drying to obtain the ordered mesoporous carbon CMK-3.

(3) Weighing 0.1g of CMK-3, 0.476g of CoCl₂·6H₂O, 0.360g into 40mL of distilled water, sonicate under circulating water for 2h, the ultrasonic power is 60W, adding 45ml of hydrazine hydrate after sonication, and continue to stir for 2h. Then the solution was transferred to the reaction kettle, hydrothermally reacted at 180°C for 6 hours, washed with

water, and dried under vacuum at 50°C for 12 hours to obtain an ordered mesoporous Co/CMK composite nano-electrode material. LU500737

The above is only the best mode of the present invention, and any simple change or equivalent replacement of the technical scheme that can be obviously obtained by any person familiar with the technical field within the technical scope disclosed by the present invention falls within the protection scope of the present invention.

CLAIMS

1. A preparation method of ordered mesoporous Co/CMK composite nano-electrode material, characterized in that it comprises the following steps:

(1) weighing a certain amount of template agent P123 and dissolving it in a 2mol/L hydrochloric acid solution at 35°C, then adding a certain amount of tetraethylorthosilicate TEOS and distilled water, and continuing to stir for 5-12 hours, transferring the solution to a reaction kettle, hydrothermal aging at 120°C for 24h, washing with water, filtering, drying, carbonizing under the protection of N₂, heating from room temperature to 550°C, keeping the temperature for 5h, and naturally cooling to room temperature after calcination to obtain SBA-15;

(2) weighing a certain amount of SBA-15 prepared in step (1) and adding it to a solution containing a certain amount of sucrose, concentrated sulfuric acid, and distilled water, and heating it at 100°C and 160°C for 6 hours, respectively, after cooling, adding a certain amount of sucrose, concentrated sulfuric acid and distilled water, continue to heat at 100°C and 160°C for 6 hours respectively, and then carbonize at 877°C under the protection of N₂; after carbonization and grinding, the template was removed with 5% HF solution, washed with distilled water and dried at 120°C, finally, adding the dried sample to a 1mol/L concentrated sulfuric acid solution and reflux, placing it at 80°C for 3 hours, and then washing and drying it to obtain ordered mesoporous carbon CMK-3;

(3) weighing a certain amount of CMK-3 prepared in step (2), a certain amount of CoCl₂·6H₂O and cetyltrimethylammonium bromide CTAB into distilled water, after circulating underwater ultrasound, a certain amount of hydrazine hydrate is added, stirring is continued for 1-2h, the solution is transferred to a reaction kettle for hydrothermal reaction, after washing with water and drying for 12 hours in a vacuum environment, a Co/CMK composite nano-electrode material is obtained.

2. A method for preparing an ordered mesoporous Co/CMK composite nano-electrode material according to claim 1, wherein the ultrasound in step (3) has a duration of 1 to 2 hours and an ultrasound power of 60 to 100W.

3. A method for preparing an ordered mesoporous Co/CMK composite nano-electrode material according to claim 1, the temperature of the hydrothermal reaction in step (3) is

180°C, the hydrothermal reaction time is 5 hours, and the temperature rise rate during the hydrothermal reaction is 2°C/min. LU500737

PATENTANSPRÜCHE

1. Ein Verfahren zur Herstellung eines geordneten mesoporösen Co/CMK-Komposit-Nano-Kathode-Materials ist dadurch gekennzeichnet, dass es die folgenden Schritte umfasst:

(1) Abwiegen einer bestimmten Menge des Schablonenmittels P123 und Auflösen in einer 2 mol/L Salzsäurelösung bei 35°C, dann Zugabe einer bestimmten Menge Tetraethylorthosilikat TEOS und destilliertes Wasser und weiteres Rühren für 5-12 Stunden, Einfüllen der Lösung in einen Reaktionskessel, hydrothermale Alterung bei 120°C für 24 Stunden, dann Waschen mit Wasser, Filtrieren, Trocknen, Karbonisieren unter dem Schutz von N₂, Erhitzen der Temperatur von Raumtemperatur auf 550°C, Halten der Temperatur für 5 h und natürlich Abkühlen auf Raumtemperatur nach der Kalzinierung, um SBA-15 zu erhalten;

(2) Wiegen einer bestimmten Menge der in Schritt (1) hergestellten SBA-15 und Zugabe der zu einer Lösung von einer bestimmten Menge Saccharose, konzentrierte Schwefelsäure und destilliertes Wasser, Erhitzen bei 100°C bzw. 160°C für 6 Stunden, Zugabe einer bestimmten Menge Saccharose, konzentrierter Schwefelsäure und destilliertem Wasser nach dem Abkühlen, weiteres Erhitzen bei 100°C bzw. 160°C für 6 Stunden, und dann Karbonisieren bei 877°C unter dem Schutz von N₂; nach der Karbonisierung und dem Mahlen, Entfernen der Schablone mit 5% HF-Lösung und Waschen mit destilliertem Wasser und dann Trocknen bei 120°C; schließlich wird die getrocknete Probe in eine 1 mol/L konzentrierte Schwefelsäurelösung zum Rückfluss gegeben, bei 80°C für 3 Stunden zurückgelegt, dann gewaschen und getrocknet, um geordneten mesoporösen Kohlenstoff CMK-3 zu erhalten;

(3) Wiegen einer bestimmten Menge von in Schritt (2) hergestelltem CMK-3, einer bestimmten Menge von CoCl₂·6H₂O und Cetyltrimethylammoniumbromid CTAB, dann Zugabe der in destilliertes Wasser, Zirkulieren des Unterwasser-Ultraschalls; Zugabe einer bestimmten Menge Hydrazinhydrat, weiteres Rühren für 1-2 Stunden, Einfüllen der Lösung in einen Reaktionskessel für die hydrothermale Reaktion, Waschen mit Wasser, Trocknen im Vakuum für 12 h, dann Erhalten des Co/CMK-Komposit-Nano-Kathode-Materials.

2. Das Verfahren zur Herstellung eines geordneten mesoporösen Co/CMK-Komposit-Nano-Kathode-Materials nach Anspruch 1 ist dadurch gekennzeichnet, dass der Ultraschall in Schritt (3) 1-2 Stunden dauert; die Ultraschalleistung 60-100 W beträgt.

3. Das Verfahren zur Herstellung eines geordneten mesoporösen Co/CMK-Komposit-Nano-Kathode-Materials nach Anspruch 1 ist dadurch gekennzeichnet, dass die Temperatur der hydrothermalen Reaktion in Schritt (3) 180°C beträgt, die hydrothermale Reaktionszeit 5 h dauert und die Temperaturanstiegsrate während der hydrothermalen Reaktion 2°C/min beträgt.

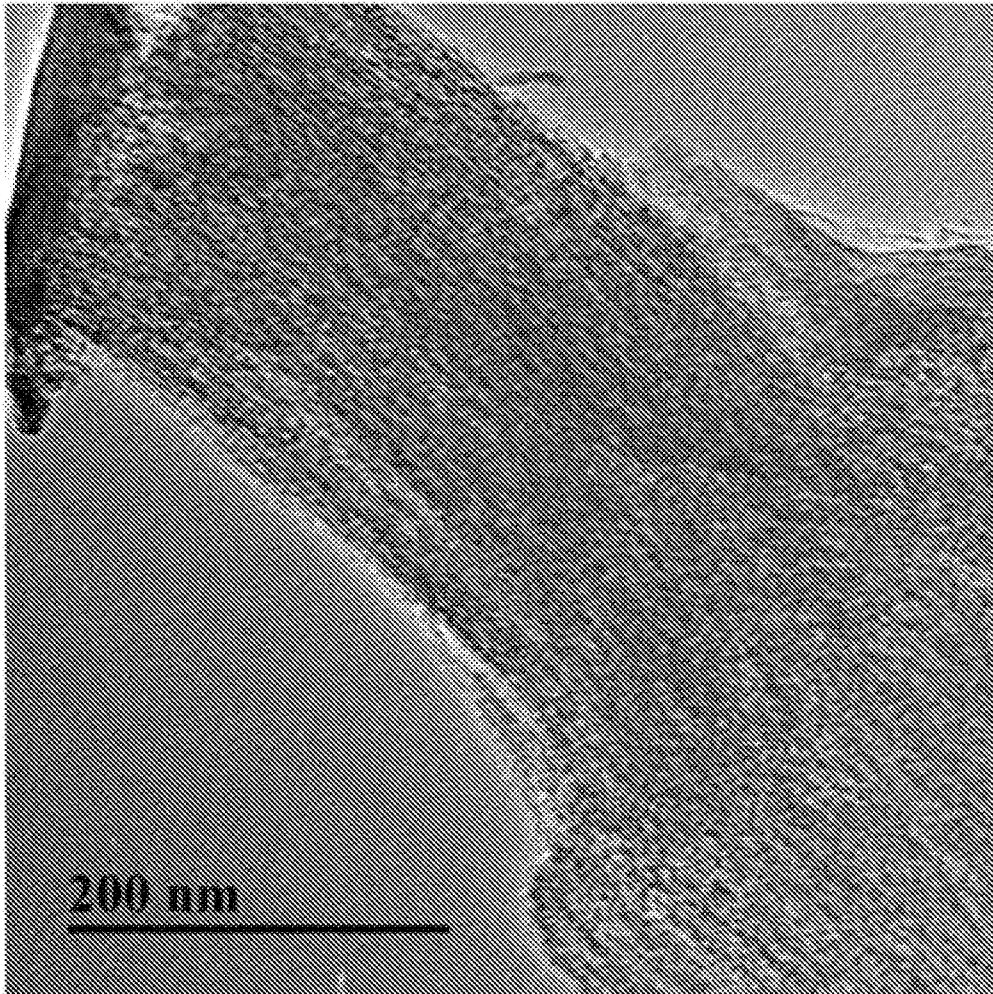


Figure 1

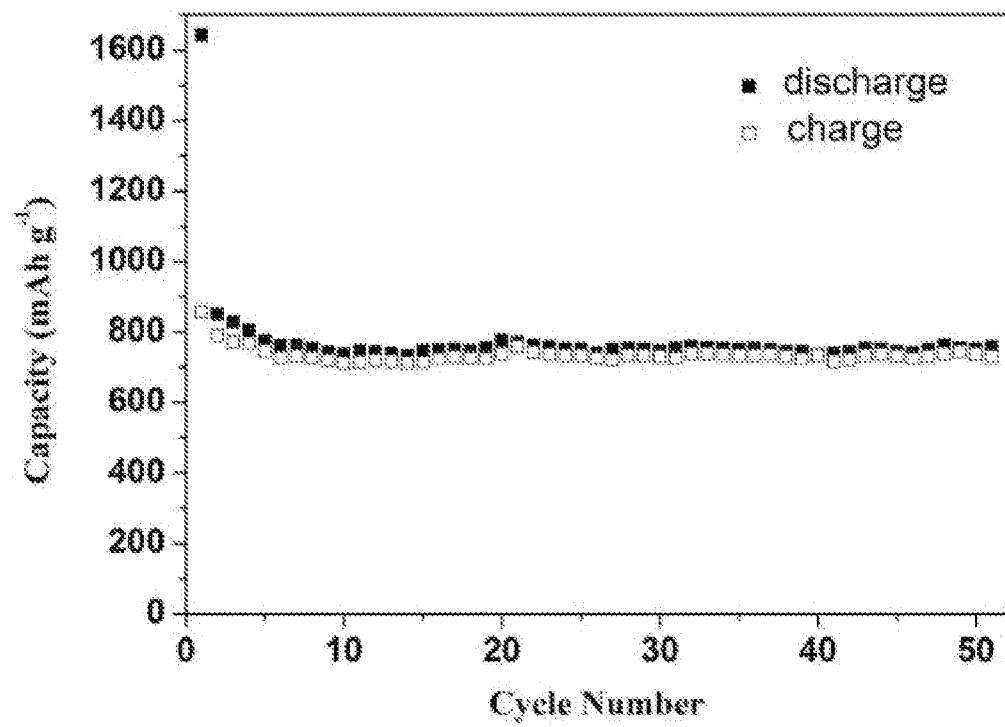


Figure 2