

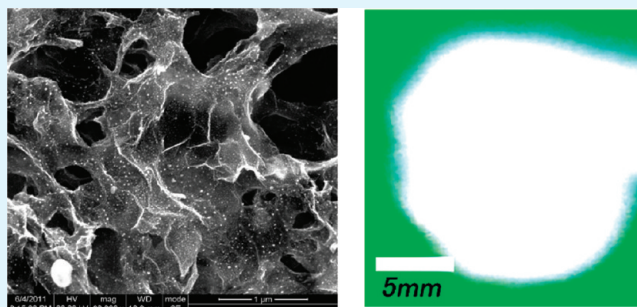
Enhanced Field Electron Emission of Graphene Sheets by CsI Coating after Electrophoretic Deposition

Jianlong Liu, Baoqing Zeng,* Zhe Wu, and Hao Sun

National Key Laboratory of Science and Technology on Vacuum Electronics, School of Physical Electronics, University of Electronic Science and Technology of China, Chengdu 610054, China

ABSTRACT: Because of the large quantities of edges, graphene can serve as an efficient edge emitter for field emission (FE). Cesium iodide (CsI) coating was promising to enhance the electron emission and utilized in FE applications. In this work, FE of graphene sheets after electrophoretic deposition (ED) was studied. Electron emission property of GS was obviously improved by coating with CsI. The turn-on field of GS decreased from 4.4 to 2.5 V/ μm ; and threshold field decreased from 9 to 5.8 V/ μm , respectively. This FE improvement must due to a higher effective density of emission site generated around the GS surface after coating. Scanning electron microscopy (SEM) and computation were taken to reveal the influence after coating. Investigations of CsI coated MWCNTs were also compared in order to better understand the origin of the low turn-on electric field obtained by GS.

KEYWORDS: graphene, electrophoretic deposition, cesium iodide, coating, field emission



INTRODUCTION

Graphene, a strict two-dimensional material, has a specific planar structure. Because of the high aspect ratio and excellent conductivity, graphene can serve as an efficient edge emitter for field emission (FE).¹ With a large number of edges, graphene might provide a high density of the effective emission site, and results in low electric field. Similar structure of carbon material grown by high temperature^{2–7} had disadvantages when it came to large-area and low-cost production. Relatively speaking, chemical oxidation was proved to be inexpensive and mass producible and showed the great expectation for application. Moreover, the GS prepared by chemical oxidation could be easily dispersed in solution and naturally fit for electrophoretic deposition (ED).⁸ Therefore, the investigation here focused on GS sample prepared by ED.

Previous studies reported that the FE properties of CNTs and other material would be greatly enhanced when coated by low work function materials, such as Cesium iodide (CsI).^{9–11} One of the most serious problems of the conventional emitter was the small effective emission density in FE. Moreover, field concentration under an extremely small area resulted in excessive emission and would destroy or changed the morphology of the emitter tips. Both factors made the GS had high electric field in FE. To overcome such drawbacks, we employed CsI to coat the GS and change the FE property. The intent of this work was that reducing the emission electric field of GS and enhancing the effective emission area. For comparison, the FE property and the mechanism of MWCNTs were also investigated and discussed.

EXPERIMENTAL SECTION

Materials and Methods. The GS used in this study was prepared by modified Hummers' method,¹² as we reported elsewhere.^{13,14}

1. Dispersion and Electrophoresis. *Dispersion.* As an initial step, 50 mg GS with same weight ratio of Mg (NO₃)₂·6H₂O^{8,15–17} were put in 100 mL of isopropyl alcohol and ultrasonicated for 2 h. The Mg²⁺ was then absorbed on GS. As a result, the electrostatic repulsion mechanism made GS separated and stable for electrophoresis.

2. Electrophoretic Deposition. The GS were deposited on the substrate by the electrophoresis. Figure 1 showed a schematic diagram of the electrophoresis process for the selective deposition of the GS. Titanium plates were used as substrate and electrodes at cathode. The distance of electrodes was separated by two piece of alumina ceramic and kept at 15 mm. A constant potential of 150 V dc was initially applied for 10 min. This resulted in deposition of the GS on the cathode electrode. Additionally, it is worth noting that the ion absorbed GS suspension colloid would be ineluctably delaminated during the electrophoresis. Therefore, we used planar parallel structure instead of perpendicular structure. To make sure the GS on the substrate were only deposited by electrophoresis rather than aggradation, the substrate was set on the top, as shown in Figure 1a. For comparison, MWCNTs bought from commerce were also deposited in the same condition.

Coating Procedure. The as-synthesized samples were annealed at 500 °C for 2 h, by placing them in a quartz tube furnace under nitrogen environment. After that, both GS and MWCNTs were coated with CsI by drop coating. Essentially, the drop coating includes two key steps. First, the CsI must be dissolved in certain solution and easily

Received: September 25, 2011

Accepted: December 16, 2011

Published: December 16, 2011

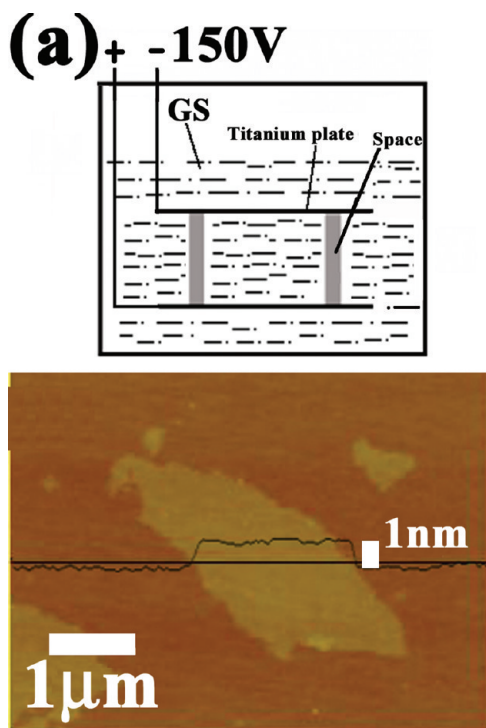


Figure 1. (a) Schematic diagram of ED, (b) AFM image of GS.

removed after coating. Second, the drop should not aggregate but rather uniformly distribute on the surface. Because the deposited GS and CNTs were hydrophobic in nature^{18,19} while easily soaking in methylene, we took the methanol for use. Twenty milligrams of CsI

was dissolved in 10 mL of methanol and ultrasonicated for 30 min. Fifteen microliters of CsI solution was then coated on $10 \times 10 \text{ mm}^2$ sample. Then the samples were quickly heated up to $650 \text{ }^\circ\text{C}$ and cool down, that process would make the CsI melt and make the good contact with the emitter.

Characterization. Scanning electron microscopy (SEM) was employed to examine both as-synthesized and coated samples. FE measurement was carried out in high vacuum chamber with parallel electrodes. The diameter of anode was 2 mm. Distance between the anode and cathode was remained $500 \text{ }\mu\text{m}$. The vacuum was kept about 6.0×10^{-7} Torr. For the analysis of the FE behavior, we define the turn-on electric field and threshold field as the field value corresponding to an emission current density of $10 \text{ }\mu\text{A}/\text{cm}^2$ and $1 \text{ mA}/\text{cm}^2$, respectively. In this experiment, we focused on the characteristic of FE behavior at $1 \text{ mA}/\text{cm}^2$.

RESULTS AND DISCUSSION

Atomic Force Microscopy. AFM measurements in Figure 1b indicated that the GS had a relatively smooth and planar structure. The thickness of GS was less than 1 nm, whereas the lateral size was at micrometer scale. Consequently, this structure would have a great enhancement when subjected to electric field.

Morphology. SEM images of the GS and MWCNTs films were shown in Figure 2. The samples in images a and b in Figure 2 are pristine GS, and images c and d in Figure 2 are GS coated with CsI. Figure 2a illustrated that the film has high density and relative uniform morphology. High-magnification in part b revealed that great deals of edges were protruded out. Images c and d in Figure 2 show the morphology changed after CsI coating. When methanol solution dropped on the GS, it

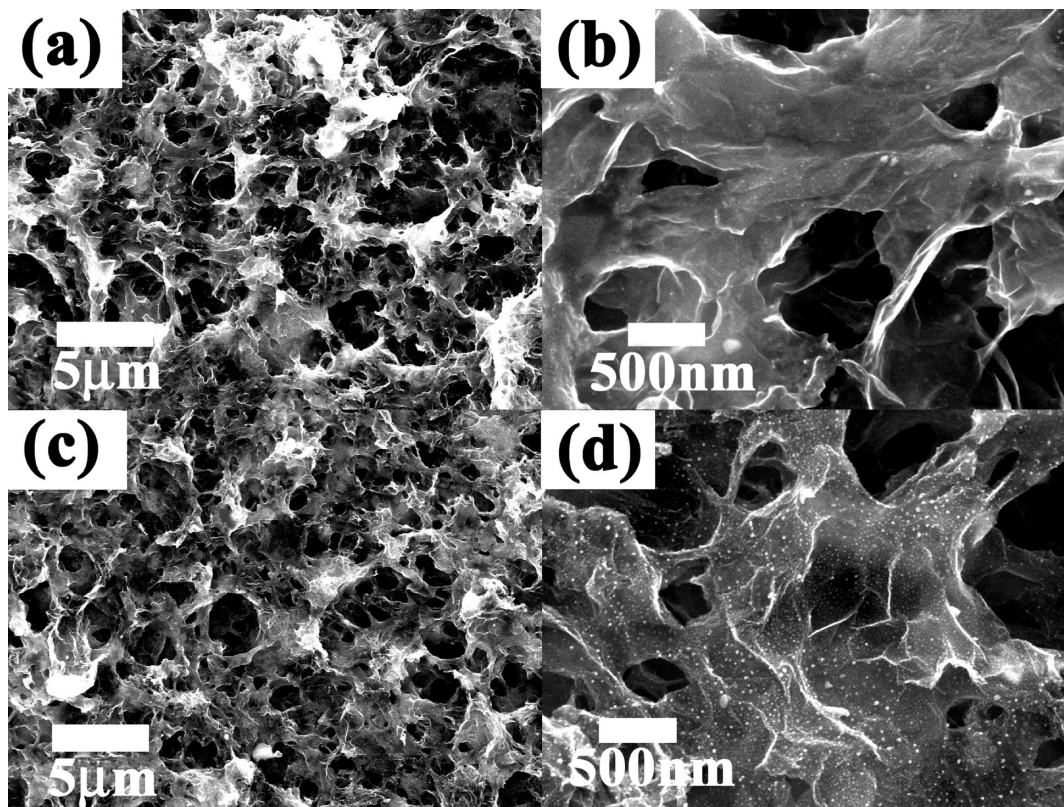


Figure 2. (a) Low-magnification image of pristine GS after ED, and (b) high-magnification image; (c) low-magnification image of GS after coating with CsI, and (d) high-magnification image.

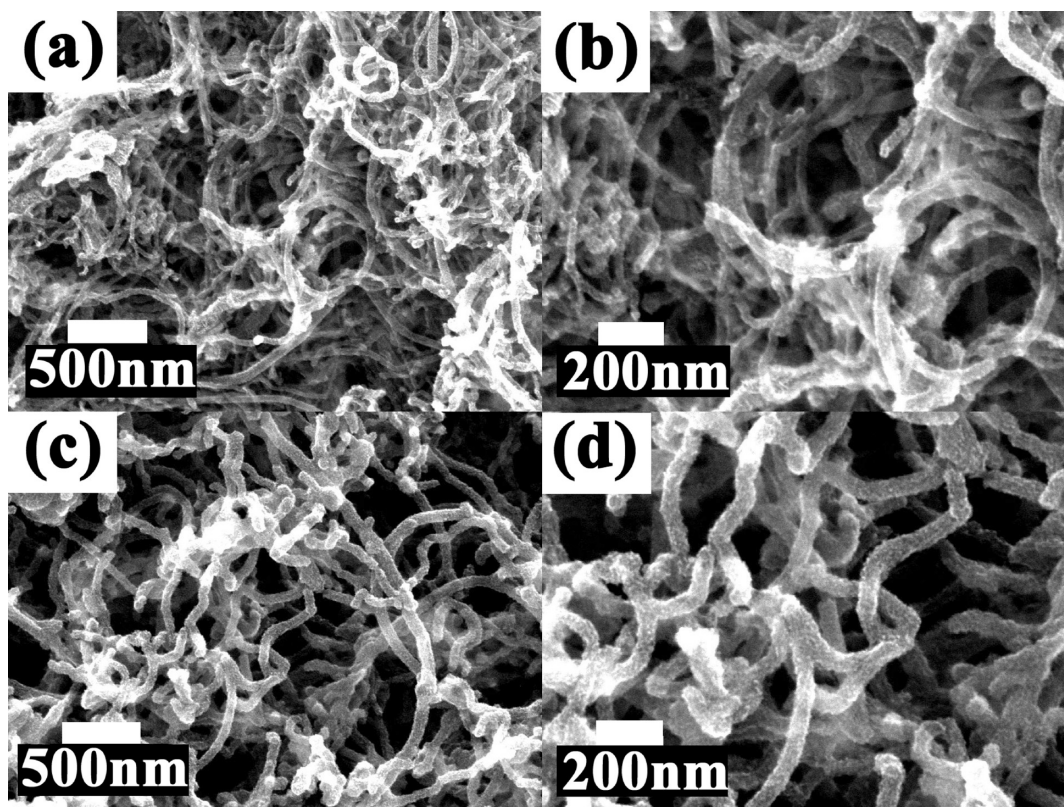


Figure 3. (a) Low-magnification image of pristine MWCNTs after ED, and (b) high-magnification image; (c) low-magnification image of MWCNTs after coating with CsI, and (d) high-magnification image.

quickly dispersed on the surface because of soakage. Then the CsI dissolved in methanol spontaneously dispersed well on the surface of GS. As shown in Figure 2d, many uniform CsI particles were appeared on the GS. Those low-affinity electron particles would make the electrons emission more easily; consequently, many edges and even some of the crinkly area would serve as active emitters. As a result, the effective emission sites would be greatly enhanced.

For comparison, MWCNTs was also deposited on Ti substrate in the same condition. In contrast with GS, the morphology of MWCNTs after deposition was agglomerative, as shown in Figure 3a. High-magnification image in (b) revealed that the diameter of MWCNTs were about 60 nm; and the small particles on them was MgO, which was decomposed from $\text{Mg}(\text{NO}_3)_2$ after annealing. The CsI coated MWCNTs was also prepared, as shown in images c and d in Figure 3.

Electron Emission. The experiment result shows that the FE characteristic was significantly enhanced after the CsI coated, as shown in Figure 4. FE of the pristine GS indicated that the turn-on field was $4.4 \text{ V}/\mu\text{m}$, and the threshold was $9 \text{ V}/\mu\text{m}$, whereas after coating, the turn-on field was decreased $2.5 \text{ V}/\mu\text{m}$, and the threshold field was reduced to $5.8 \text{ V}/\mu\text{m}$. For MWCNTs, the turn-on field was reduced from 3.9 to $3.2 \text{ V}/\mu\text{m}$ after coating. And the threshold field for MWCNTs after coating was received at $6.8 \text{ V}/\mu\text{m}$. Both turn-on field and threshold field of coated GS were substantially lower than those of the MWCNTs. We suggested that this was attributed to the great deals of edges, which were rendered by low-affinity electron material of CsI and served as effective emission tips.

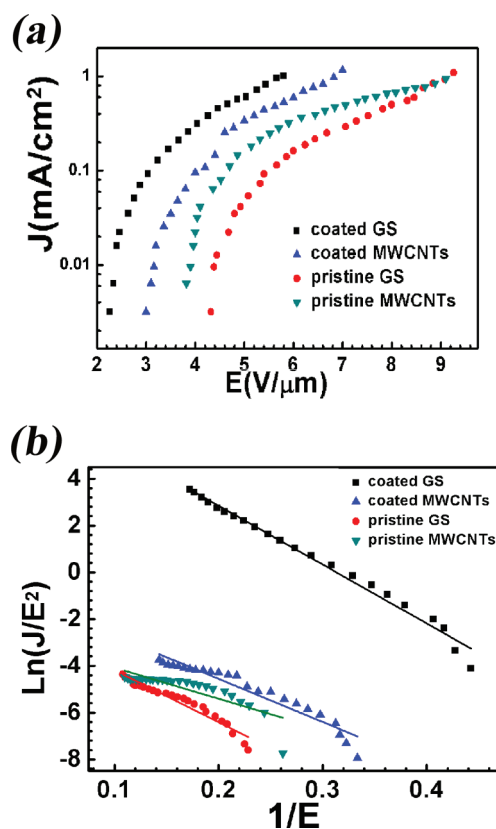


Figure 4. Field-emission curves of GS and MWCNTs. (a) Field emission–current density of pristine sample and the coated sample; (b) corresponding F–N curves.

The field electron emission relied on the Fowler–Nordheim (FN) equation,²⁰

$$J = \frac{AE^2}{\phi t^2(y)} \exp\left(-\frac{B\phi^{3/2}v(y)}{E}\right)$$

where J was emission current density, A and B are constants, ϕ was the work function, E was the electric field equated to, here $E = \beta V/d$, V was the applied voltage, d was the space between the cathode and anode, and β was the FE enhancement factor. The FN plots of pristine GS, MWCNTs, and CsI-coated GS and MWCNTs were shown in Figure 4b. During the calculation, we used the approximate value of $t(y)$ and $v(y)$ as to 1. And the FE enhancement factor relied on $\beta = -(B\phi^{3/2})/(k_E)$, where k_E was the slope of F–N curve.

The β values of the pristine and coated samples, both GS and MWCNTs, were calculated by comparing FN slopes of the emitters before and after the CsI coating. By assuming that the work function of GS and MWCNTs were 5 eV, the β values for GS and MWCNTs were calculated at 3650 and 8251, respectively. Previous report indicated that the enhancement factor would dramatically increase²¹ or stay the same after coating.^{17,18} On the contrary, it was very interesting that the β values of our samples after coating were decreased. The β values for GS and MWCNTs after coating were reduced to 3000 and 5820, respectively.

Mechanism Discussion. The mechanism of field electron emission from materials was that electrons tunneling escape from Fermi level when the potential energy barrier (PEB) was reduced to proper level by electric field. Here the local electric field E was the combination of applied electric field and the local enhancement. The mechanism could be illustrated in the schematic diagram in Figure 5. As the initial voltage U added,

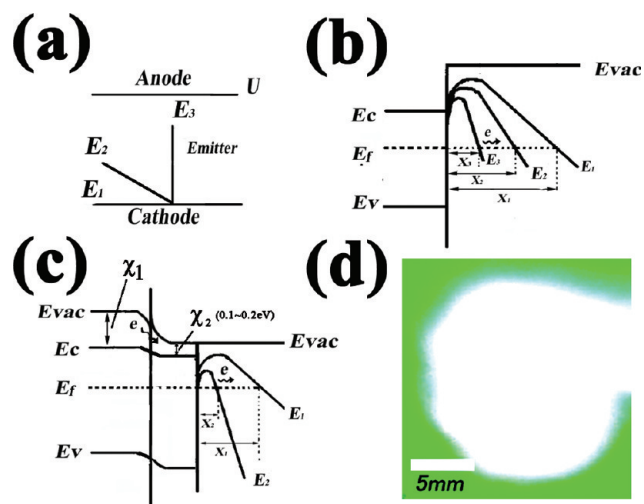


Figure 5. Schematic diagram of field emission. (a) Applied voltage U , and the local field enhancement of emitter at different level $E_1 < E_2 < E_3$, (b) the band of pristine GS (MWCNTs). (c) Band bended after coating. (d) Field-emission pattern of coated GS.

the band of vacuum bended because of the corresponding electric field E_1 and the width of barrier (WB) was reduced to X_1 . In this case, the emitter did not have chance to emit electrons because of the PEB. To obtain better enhancement and reduce the barrier, the emitter was pulled up to enhance the electric field, such as E_2 . In pristine GS (MWCNTs), the

electron emission still could not happen because of the big PEB and the WB X_2 , shown in Figure 5b. And the emitter was continuously pulled up until the local enhance field reached at proper level E_3 , which the PEB decreased to small enough for electron emission, as WB X_3 in Figure 5b. And the morphology change of cathode result in high β values. When the GS (MWCNTs) was coated, the potential barrier is low at the interface of the GS or MWCNTs and the CsI, the electron could easily transport to CsI, as shown in Figure 5c. Subsequently, electrons can escape from the CsI surface to vacuum more easily because the electron affinity of CsI χ_2 is lower than that of GS χ_1 .^{22,23} Thus far, the GS and MWCNTs could emit electrons when local field was at E_2 (The WB X_2 in Figure 5c was reduced to the same level with the WB X_3 in Figure 5b). As a result, the emitters would not be greatly pulled up as before by the electric field. And the β values after coating would be lower of its own accord.

Computation. For further study, computation was carried out according to the according to Fowler–Nordheim equation. And β was the field-emission enhancement factor adopted from the experiment curve. Each β value was calculated from experiment result, which was the average value of effective emitter during the electron emission. In spite of effective emission area, the computed emission current of pristine GS would be greater than coated GS because of the higher β value, as shown in Figure 6a. Because of the effective emission area in experiment, the emission current of coated GS was greater than pristine GS. FE was a statistic result and each emission site had an individual β value. Because each β value could be considered as an effective emitter, the contributing ratio of each emitter in total emission current could be defined in Figure 6b. In contrast with pristine GS, the emission of coated GS distributed more uniform. The β values of the emitters were statistical data. And these statistical data could be dealt with normal distribution to define the probability of each β value, as shown in Figure 6c. So that the transverse axis was the emitter and the longitudinal axis was the probability of the emitter. According to normal distribution, the integral area of the curve was 1. Then the shadow between the curve and transverse axis meant the effective emission area. Figure 6d showed that the 80% emission current was dominated by small area in pristine GS, whereas the coated GS shared well with larger area. That meant the effective emission area enhanced greatly after coating with CsI. So that the stability of GS after CsI coating turned to more stable, as shown in Figure 7.

Notably, the field-emission improvement of GS was greater than that of MWCNTs. That may due to the high aspect ratio surface morphology of protruding MWCNTs emitters, which inevitably involved in great field concentration (high β values), and these emitters took on the major emission whereas in the GS sample, especially after coating, the homogeneous surface morphology and the low β value made them have lower field concentration. Consequently, not only the edges on the GS tip but also the corrugation may serve as emitters. According to the calculation of effective emission area,¹⁷ the pristine GS was 3×10^{-13} cm², whereas coated GS was almost increased three orders and reached 1.5×10^{-10} cm². And the emission pattern of coated GS in Figure 5d was homogeneous. Unlike the GS, MWCNTs emitted electrons on their tips. Even the low-affinity electron CsI coating would make the electron emission more easily, the effective emission area would not dramatically increase. As a result, the coating of CsI on MWCNTs would not enhance the emission property as GS did.

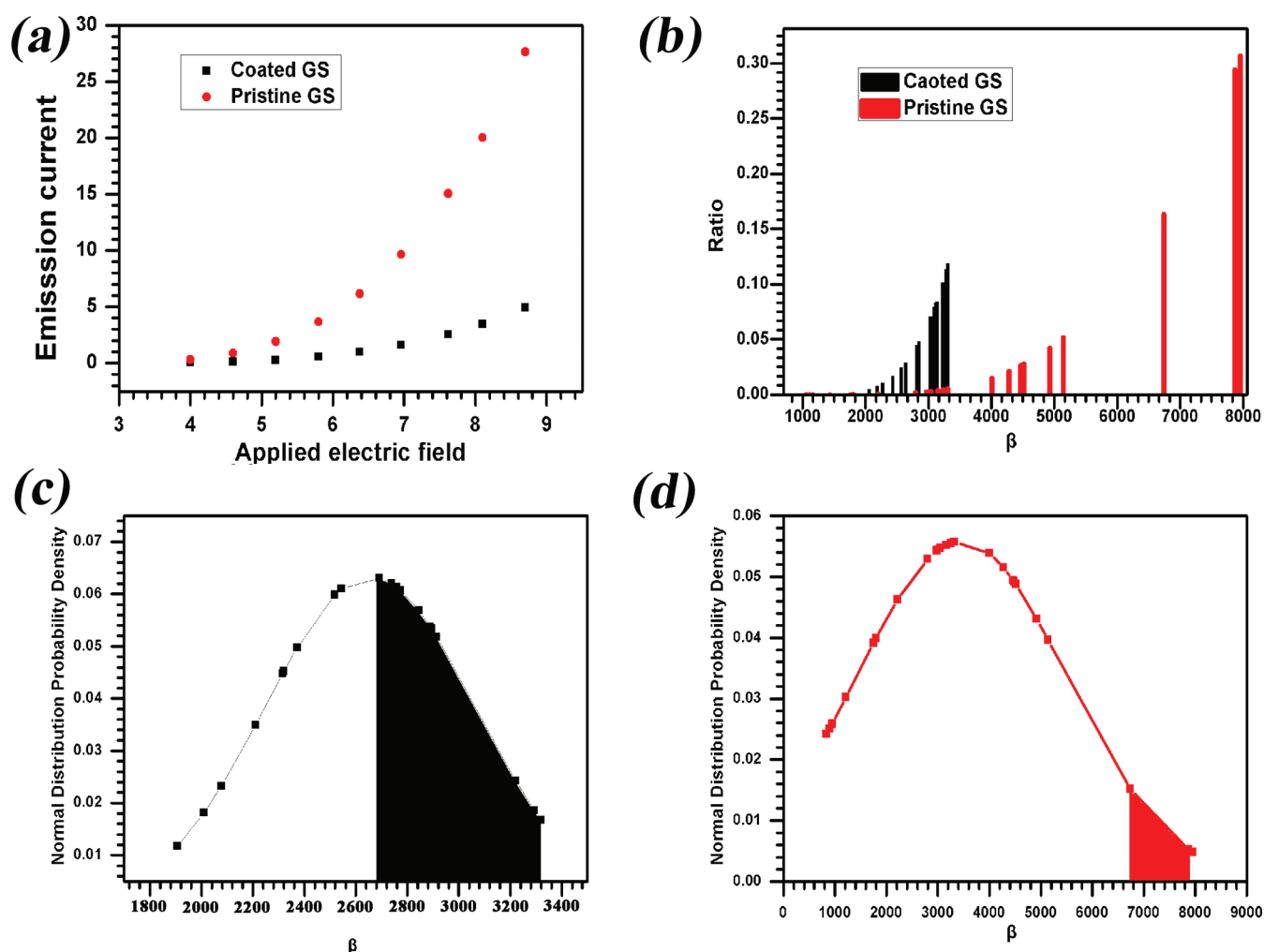


Figure 6. Simulation diagram of GS. (a) Computation of emission current of coated GS and pristine GS, (b) emission contribution ratio of each emission sites in total current, (c) normal distribution of β value from coated GS, (d) normal distribution of β value from pristine GS; and the shadow was equivalent to effective emission area.

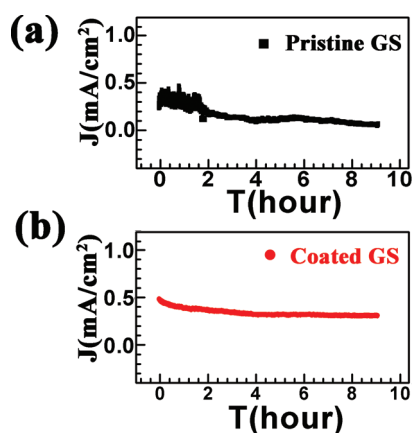


Figure 7. Stability test of GS. (a) Stability of pristine GS, (b) stability of CsI-coated GS.

CONCLUSION

In summary, we improve the field emission property of GS by coating of CsI. The FE properties of coated GS revealed that the turn-on field was reduced from 4.4 to 2.5 V/ μm . And the threshold field was remarkably reduced from 9 to 5.8 V/ μm . The low electron affinity of CsI not only made the GS emitted

the electron more easily, but also enhanced the emission area and the emission stability. Because of the great deals of edges and shared with the emission, the enhancement after CsI coating of GS was greater than that of MWCNTs. Finally, the FE test and the luminous images suggested that the optimized GS can serve as a potential field emitter.

AUTHOR INFORMATION

Corresponding Author

*E-mail: bqzeng@uestc.edu.cn. Tel.: +86-28-83200158. Fax: +86-28-83203371.

ACKNOWLEDGMENTS

The work is partially supported by NSFC (Grant 60071043), the Doctor Station Foundation of the Ministry of Education of China (Grant 200806140007), Prestudy Foundation of Electronic Science Academic, and National Key Laboratory of Science and Technology on Vacuum Electronics.

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