Preparation of RuO$_2$/CNTs by Atomic Layer Deposition and its application as binder free Cathode for polymer based Li-O$_2$ battery

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Polymer-based (Li-O$_2$) battery have paid much more devotions owing to their safety as compared to conventional liquid electrolyte batteries. However, the carbon-based cathode with polymer binder shows serious degradations in the electrochemical performance of Li-O$_2$ batteries due to parasitic decomposition reactions during operation of battery. Therefore, it is highly indispensable to develop a cathode that builds vigorous and outstanding performance in Li-O$_2$ batteries. Herein, a binder-free cathode of carbon nanotubes (CNTs) have been fabricated by surface modification using RuO$_2$ catalyst through ALD approach. A solid catalyst of RuO$_2$ has been deposited on CNTs defects sites which not only stops the decomposition of carbon but also endorse the reversible accumulation and breakdown of Li$_2$O$_2$ on cathode surface. The CNT/RuO$_2$ cathode with the distinctive structure illustrate excellent performance by showing a small potential gap of 0.6V at mid-point and better cycle stability without large capacity decay over 50 cycles. This study demonstrates that the surface engineering of carbon cathode could be a favorable approach to develop Li-O$_2$ batteries.

Keywords: Polymer based Li-O$_2$ battery; Binder-free cathode; RuO$_2$ catalyst; low potential gap.
1. INTRODUCTION

Lithium-oxygen batteries are currently attracting a lot of interest due to their higher energy density than Li-ion batteries. Although, the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) result in the formation and reversible breakdown of the discharge product $\text{Li}_2\text{O}_2$ into $\text{O}_2$ during Li-O$_2$ battery operation [1-5]. Since Li-O$_2$ battery introduction in 1996, the system has faced various scientific and technical challenges that must be addressed. Some of these challenges are the evaporation of organic electrolytes during discharge and charge process and the decomposition of discharge product from the cathode surface, that causes instability in Li-O$_2$ batteries [6-9]. Moreover, the excessive deposition of discharge product $\text{Li}_2\text{O}_2$ on cathode surface blocks the continuous diffusion of oxygen gas, which eventually effects the battery performance including specific capacity, charge potential and cycling stability [10-13]. Additionally, the continuous deposition of lithium carbonate ($\text{Li}_2\text{CO}_3$) and lithium carboxylates caused by the instability of $\text{Li}_2\text{O}_2$ with electrolyte and polymer binder trigger cathode passivation and eventually batteries death [14-16]. Although great progress has been made, the improvements do not yet outweigh the foregoing challenges, which prevent Li-O$_2$ batteries from becoming commercially viable. Another issue that needs to be addressed is the apparent increase in defect sites that occurs during repeated discharge and charge. It has been reported in the previous studies, that the carbon cathodes can be stabilized by passivating the surface defects through chemically stable materials [17-21]. As a result, it is critical to design and build a highly efficient cathode with a specific architecture that can significantly influence both ORR and OER in order to improve the performance of Li-oxygen batteries. The optimum cathode for Li-O$_2$ batteries should have high electronic conductivity, great porosity to accommodate abundant discharge product, smooth oxygen diffusion, and sufficient catalytic activity for the breakdown of discharge products [22-24]. Several efforts have been made to pursuit effective catalysts with sufficient catalytic activity including noble metals [25,26], metal oxides [27,28] metal nitrides [29,30] and carbides [31,32]. Among them, $\text{RuO}_2$ has been observed as one of the widely used catalysts for endorsing ORR and OER in Li-O$_2$ batteries [33,34]. Moreover, the surface engineering approaches of carbon cathode reported previously have demonstrated significant improvement in the cycle stability of Li-O$_2$ batteries [35-38]. Thus, implementing efficient catalysts in carbon-based cathodes that can decompose both $\text{Li}_2\text{O}_2$ and $\text{Li}_2\text{CO}_3$ at lower charge potentials should be a promising strategy for improving Li-O$_2$ battery electrochemical activity. However, the procedure is complicated and time-consuming since it involves two phases: metal oxides coating followed by noble metals. A "binder-free" carbon nanotube (CNT) cathode with $\text{RuO}_2$ nanoparticles coating has been claimed to improve rechargeability under low charge potential and shield the carbon surface during Li-O$_2$ battery operation [39-41]. Herein, the $\text{RuO}_2$ has been developed by Atomic Layer Deposition method as an electrocatalyst for Li-O$_2$ batteries. According to scanning electron microscopy SEM and electrochemical performance, the incorporation of $\text{RuO}_2$ catalyst in cathode formation not only protect the carbon nanotubes surface from decomposition but synergistically reduce the charge potential during charging of Li-O$_2$ battery. The overpotential is reduced from 1.40V to 0.6V, which is the obvious indication of $\text{RuO}_2$ catalysts for removal of discharge product at lower charge potential. Moreover, the distinctive porous structure of composite cathode leads to provide a continuous diffusion of oxygen, abundant space to accommodate large amount of discharge products and provide more active sites. The
Li-O₂ batteries based on RuO₂/CNT composite cathode has shown clearly reduced overpotential and improved cycling stability.

2. EXPERIMENTAL SECTION

2.1. Materials

The modified silyl-terminated polyether (MSTP) monomer, Tetra ethylene glycol dimethyl ether (TEGDME, 99.9%), lithium bis (trifluoromethane sulfonamide) (LiTFSI, 99.95%), Tin catalyst (Tin), N-methyl-2-pyrrolidinone (NMP) Carbon nanotubes (CNTs) and Ruthenium dioxide (RuO₂), Nitric acid (HNO₃) and deionized water (DI) were bought from Aladdin, and placed in the glove box.

2.2. Preparation of polymer electrolytes

The polymer electrolyte has been prepared by simple solution casting method in which 1.75g LiTFSI salt was dissolved in 2.5 mL TEGDME solution. Afterward, 0.75g methyl silyl terminated polyether (MSTP) was mixed with the as-prepared solution and stirred for 40 minutes to obtain a homogenous solution. In order to speed up the polymerization rate, 20 µL tin catalyst was added to synthesize precursor solution and stirred it for further 10 minutes. The precursor solution was poured into the Whatman filter paper which give mechanical strength to polymer film. The pores of the Whatman paper were filled with the polymer precursor. The solution was then shifted to vacuum oven for drying at 60°C for 3 hours. The polymer electrolyte was transferred to another oven for further drying at 80°C for more 2 hours. After all these steps, the MSTP based polymer electrolyte was obtained used for characterizations and electrochemical tests in Li-O₂ battery.

2.3. Fabrication of CNT/RuO₂ cathode

The composite cathode of CNT/RuO₂ was synthesized by atomic layer deposition method. The carbon nanotubes were washed by ultrasonication method with 40% dilute solution of HNO₃. The ultrasonicated CNTs were centrifuged and washed three times with deionized water to remove remedies. The collected CNTs were dried at 80°C for 12 hours. After that, the CNTs solution was prepared in NMP solvent, and binder free cathode was prepared by simple filtration method. The CNTs coated carbon papers were then shifted to deposit RuO₂ for 200, 400 and 800 ALD cycles. The composite cathode of CNTs coated with 400 ALD cycles were used as an active material in testing the electrochemical performance of the Li-O₂ batteries. The Carbon paper (Toray Company) was utilized as the current collector with mass loading of CNT/RuO₂ from 3.0 ~ 5.0 mg cm⁻².

2.4 Li-O₂ Cell Assembly and Characterizations.

The Li-O₂ cells were assembled an Ar filled glove box having water and oxygen concentration less than 0.1ppm. A polymer electrolyte film of MSTP is employed between cathode and anode. The cell was oxygenated for 20 minutes through the gas inlet and outlet in the home made glass bottle to
provide pure oxygen environment. The bottle was carefully sealed to enclose the oxygen for battery operation. For conducting discharge-charge tests, Land battery system was used. Moreover, the fluctuation in specific capacity can be calculated on basis of CNTs weight on carbon paper.

The ionic conductivity of polymer electrolyte film was deliberated by Electrochemical Impedance Spectroscopy (EIS) via Versa STAT 3 system at room temperatures. To record the spectra in the frequency, range from 0.1 to 105 Hz using 10 mV AC amplitude, the polymer film was sandwiched between two stainless steel plates. The bulk resistance ($R_b$) of the polymer film was calculated by using the impedance spectrum. Using the equation ($\sigma = d/R_b S$), the ionic conductivity was calculated, where $R_b$ denotes the bulk resistance, $d$ is the thickness of the film and $S$ is area of the polymer film, respectively. Ex-Situ SEM was used to study the morphology of discharge product formed on the cathode surface after disassembling of the fully discharge Li-O$_2$ battery in an Ar filled glove box. For X-ray analysis, Cu Ka radiation ($\lambda=1.5406$) was used for X-ray diffraction with a Bruker D8 Focus Power X-ray diffract meter. To stop the air reaction with discharge product, the samples were put onto a glass substrate and afterward wrapped with a Kapton polyimide sheet. Ex-situ SEM, XRD, Raman and XPS have been used to investigate each composite cathodes of pristine, discharged, and recharged phases, respectively. For SEM, XRD Raman and XPS characterization, the discharged and recharged composite cathodes were transferred for testing without exposing to air for a long period of time.

3. RESULTS AND DISCUSSION

The polymer electrolyte film was blended by simple solution casting approach, which has been explained in the previous reports [42-44]. An appropriate ionic conductivity is one of the major aspect for the enhancement of electrochemical performance in polymer based Li-O$_2$ batteries. The ions transformation ability of as-prepared polymer film is determined from the intercept on the real axis at room temperature using bulk resistance ($R_b$) as shown in Fig.1a. The estimated ionic conductivity for polymer electrolyte is $1.3 \times 10^{-4}$ S cm$^{-1}$, which is comparable to liquid electrolyte and beneficial for boosting the electrochemical performance of Li-O$_2$ batteries. Therefore, it demonstrates, that the as-prepared polymer film has satisfactory ionic conductivity to be utilized in Li-O$_2$ batteries. The ionic conductivity of polymer film was calculated by using the formula $\sigma = d/ R_b S$ where $d$ is the thickness of polymer film, $S$ is the surface area (diameter $\Phi = 16$ mm) and $R_b$ is the bulk resistance [45]. Another important property of the polymer electrolyte is its thermal durability. The thermo-gravimetric TG and differential scanning calorimetry (DSC) curves in Fig.1b demonstrate that the polymer electrolyte with whatman paper framework can retain its stability below 150 $^\circ$C, which is critical for improving safety as compared to a liquid electrolyte at elevated temperatures. The polymer starts electrolyte begins melting at 200$^\circ$C, as evidenced by the prominent DSC peak. Moreover, the polymer film with application of whatman paper filter provides high mechanical strength and smooth surface as shown in Fig.1c. The inset of Fig.1c shows the flexibility of polymer film, which is suitable for application in foldable devices and easy to handle in assembling Li-O$_2$ batteries. Furthermore, the smooth surface and high flexibility of polymer electrolyte is beneficial for enhancing the electrochemical performance and better interfacial contacts with electrodes in Li-O$_2$ batteries.
Figure 1. (a) Electrochemical impedance spectroscopy of Stainless steel/Polymer electrolyte/S Stainless steel at room temperature (b) Thermo-gravimetric (TG) and Differential Scanning Calorimetry (DSC) curves of Polymer electrolyte film (c) Photograph of polymer electrolyte and the in-situ shows the flexibility of polymer film.

Figure 2. The SEM images of the (a) pristine CNTs and (b) composite cathode with deposition of RuO$_2$ catalyst (c) show EDX mapping for carbon element (d) Ruthenium element. (e) Shows the X-ray photoelectron spectroscopic analysis of CNT/RuO$_2$ (f) spin-orbit of Ru (g) Ru 3p (h) O 1s and (i) C 1s spectra of CNT in CNT/RuO$_2$ cathode.
The surface morphology of both CNT and composite cathode of CNT/RuO\textsubscript{2} was investigated using SEM. According to Fig. 2a, the CNT cathode has a porous framework with a large surface area, which is required for a higher specific capacity in Li-O\textsubscript{2} batteries. The carbon cathode has enough gas diffusion paths and has adequate active sites for the accommodation of discharge products. After fabricating the composite cathode by atomic layer deposition method, RuO\textsubscript{2} catalyst is deposited on the active sites of CNTs uniformly as shown in Fig. 2b. The elemental distributions of C, O and Ru in CNT/RuO\textsubscript{2} composite cathode are explored by Energy Dispersive X-ray spectroscopy (EDS) as demonstrated in Fig. 2(c & d). The EDS results depict that the RuO\textsubscript{2} nanoparticles have uniformly distributed on CNTs surface. Thus, it is concluded that RuO\textsubscript{2} nanoparticles deposited on the surface of CNTs not only circumvent it from passivation but also contribute widely for the breakdown of Li\textsubscript{2}O\textsubscript{2} during charge process.

Furthermore, the CNT framework can provide abundant pathways for smooth transport of electrons. The porous cathode of CNT/RuO\textsubscript{2} in polymer-based Li-O\textsubscript{2} batteries, as shown in Fig. 2b, has sufficient reaction sites, an interconnected framework of CNTs for electron transport, and smooth gas flow. Considering the advantages listed above, the electrochemical processes on the CNT/RuO\textsubscript{2} cathode surface are far more easy. Furthermore, the porous nature of the composite cathode can accommodate a considerable amount of discharge products, allowing for a high specific capacity.

The elemental composition and valence state of the composite cathode were determined using X-ray photoelectron spectroscopy (XPS) analysis. In Fig. 2e, the typical XPS spectrum for RuO\textsubscript{2}/CNTs shows numerous peaks that confirm the presence of C, O, and Ru components. Ru 3d has 3/2 and 5/2 spin-orbit regions of 284.5 and 281.3 eV, respectively, as shown in Fig. 2f, whereas Ru 3p has a significant peak at 463.5 eV, as seen in Fig. g. The Ru 3d\textsubscript{5/2} binding energy is 281.3 eV, which overlaps somewhat with the C 1s peak and corresponds to the Ru\textsuperscript{4+} oxidation state in metallic Ru (280 eV). Furthermore, two new segments have arisen at 286.0 and 284.8 eV, which are typically assigned to Ru (III) and RuO\textsubscript{2} respectively. Furthermore, the O 1s XPS spectrum (Fig. 2h) reveals a peak at 529.8 eV, which corresponds to Ru-O-Ru bond. The C 1s spectra of CNTs in CNTs/ RuO\textsubscript{2} is shown in Fig. 2i, with two prominent peaks at 284.9 eV and 285.9 eV corresponding to C=C graphite carbon, C–C, bonds in produced materials. The presence of the C–C peak suggests the presence of defects in the structure of CNTs.

The cathode has been designed and developed to promote the kinetics for OER reaction during the charge process in Li-O\textsubscript{2} batteries using a carbon-based cathode with/without RuO\textsubscript{2} catalyst. During the rate performance of the polymer-based Li-O\textsubscript{2} battery with CNT cathode shown in Fig. 3a, a substantial charge potential of nearly 4.45V was achieved. Furthermore, the rate performance seems unsatisfactory at elevated current density (1000 mA g\textsuperscript{-1}) because of unsatisfactory ionic conductivity of polymer electrolyte, low electronic conductivity of Li\textsubscript{2}O\textsubscript{2} and poor kinetics for decomposition of Li\textsubscript{2}O\textsubscript{2} during charge process. In contrast, a CNT/RuO\textsubscript{2} composite cathode has been designed to test the improvement in OER activity and lowering the charge potential. A significant reduction in the potential from 4.45 V to 3.87V has been achieved in the Li-O\textsubscript{2} battery based on the composite cathode of CNT/RuO\textsubscript{2}. The outstanding rate performance with low charge potential at high current density has confirmed the contribution of RuO\textsubscript{2} for OER reaction during charge process of Li-O\textsubscript{2} battery. Therefore,
the pure CNT cathode was substituted by composite cathode with highly efficient catalyst to enhance the rate capability.

Figure 3. (a) Discharge-charge curves for polymer electrolyte based Li-O₂ batteries with CNT cathode and (b) CNT/RuO₂ based cathode at different current rate ranging from 100 to 1000 mA g⁻¹ at limited capacity of 1000 mAh g⁻¹.

Figure 4. Comparisons of galvanostatic discharge-charge profiles of cycling stability for polymer based Li-Oxygen batteries with (a) Pure CNT cathode (b) CNT/RuO₂ cathode at current density of 200 mAh g⁻¹ with cut off capacity of 1000 mAh g⁻¹ (c) Comparison of discharge and charge terminal potential of CNT and CNT/RuO₂ based cathode at the same current density.
As described above, the CNT/RuO₂ cathode illustrate remarkable catalytic performance for the OER reaction, which can dramatically reduce the charge potential. As a result, the addition of RuO₂ in the cathode fabrication greatly increased the rate performance with synergistic catalytic activity with remarkable reduction in the charge potential at high current density of 1000 mAg⁻¹ as shown in Fig. 3b.

Furthermore, the galvanostatic discharging and charging profile for cycling stability of Li-O₂ batteries were investigated at current density of 200 mAg⁻¹ with curtailing capacity of 1000 mAhg⁻¹. The charge potential for the Li-O₂ battery with pure CNT cathode is higher than 4.45V after 50 cycles, as shown in Fig. 4a.

**Table 1.** Comparison of terminal charge stability using RuO₂ catalyst in cathode

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Methods of preparation</th>
<th>Terminal charge potential of 1st and last cycle</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuO₂/CNT</td>
<td>Atomic Layer Deposition</td>
<td>3.94-3.95V</td>
<td>This work</td>
</tr>
<tr>
<td>TiO₂@RuO₂/KB</td>
<td>Sol-gel method</td>
<td>3.9-4.5V</td>
<td>49</td>
</tr>
<tr>
<td>RuO₂/NiNCs</td>
<td>Hydrothermal method</td>
<td>3.6-4.5V</td>
<td>50</td>
</tr>
<tr>
<td>RuO₂@MnO₂/CNT</td>
<td>Vacuum filtration method</td>
<td>4.2-4.5V</td>
<td>51</td>
</tr>
<tr>
<td>RuO₂@LSCF-NFs</td>
<td>Co-precipitation method</td>
<td>4.2-4.3V</td>
<td>52</td>
</tr>
<tr>
<td>RuO₂@GNRs</td>
<td>Co-precipitation method</td>
<td>3.5-4.5V</td>
<td>53</td>
</tr>
<tr>
<td>RuO₂+TTF/CNT</td>
<td>Hydrothermal method</td>
<td>3.6-4.05V</td>
<td>54</td>
</tr>
<tr>
<td>RuO₂@MnO₂-TIT</td>
<td>Electrospinning</td>
<td>4.50-4.55V</td>
<td>55</td>
</tr>
<tr>
<td>α-MnO₂@RuO₂/XC-72</td>
<td>Hydrothermal method</td>
<td>4.1-4.0V</td>
<td>56</td>
</tr>
<tr>
<td>RuO₂@MnO₂/Ni/G</td>
<td>Solution impregnation method</td>
<td>3.5-4.5V</td>
<td>57</td>
</tr>
</tbody>
</table>

It's worth mentioning that polymer-based Li-O₂ without RuO₂ catalyst has poor cycling stability, which could be attributed to the inadequate breakdown of discharge product Li₂O₂ and by products generated during the discharge and charge process, particularly at high overpotential. On the other hand, the incorporation of RuO₂ in CNTs cathode can immensely reduce charge overpotential to the terminal
value lower than 3.95 V as shown in Fig. 4b. The reduction of over potential from 1.40V to 0.6V for the CNT/RuO₂ cathode and extended cycling stability for 50 cycles is attributed to the fast kinetics of RuO₂ for OER during charge process. In addition, Fig. 4c compares the charge and discharge terminal potential of polymer-based Li-O₂ batteries with and without RuO₂ catalyst. An obvious decrease in the overpotential is observed for cathode of CNT/RuO₂ based Li-O₂ battery. The reduction in overpotential illustrates the critical role of RuO₂ catalysts in facilitating reversible decomposition of discharge product. The substantial improvement in electrochemical performance is due to the synergistic effect of CNTs/RuO₂ catalyst on the effective disintegration of Li₂O₂ at the interfacial contact between air cathode and polymer electrolyte. This reduces overpotential and improves cycle stability.

Based on the findings, it is concluded that combining CNT and RuO₂ would significantly improve OER activity in polymer-based Li-O₂ batteries. As a result, we distinguish the cathode structure with adequate catalyst deposition using appropriate method as key characteristics impacting cycling stability in polymer Li-O₂ batteries. In addition, some previous reports using RuO₂ catalyst coated on carbon surface through various approaches have been compared to our work in the table 1. It is concluded, that Li-O₂ battery using CNT/RuO₂ via Atomic Layer Deposition method have shown better consistency between 1ˢᵗ and last charge potentials. The stable charge potential for 50 cycles has been endorsed to the effective contribution of RuO₂ catalyst for improving OER reaction during charging of Li-O₂ battery.

Furthermore, SEM, XRD, and Raman characterization were performed for discharged and recharged cathodes to explore the structure of discharge yields and the reversibility of creating and breaking down Li₂O₂ under pure oxygen atmosphere. A thin film-like morphology of discharge product Li₂O₂ appears on the CNTs surface [45,46] has been observed in the SEM images collected after discharging (Fig. 5a), while after successive recharge of cathode, most of the discharge product Li₂O₂ are removed (Fig. 5b) [47]. These findings clearly reveal the contribution of RuO₂ for the reversible decay of discharge product Li₂O₂. Further investigations were obtained conducting XRD test to study the creation and breakdown of Li₂O₂ during discharge and charge process as demonstrated in Fig. 5c. A clear peak of Li₂O₂ can be observed in the discharge cathode, which indicates that the leading product was Li₂O₂ during the discharge process of Li-O₂ battery with CNT/RuO₂ cathode and polymer electrolyte [48]. Moreover, in recharge process the diffraction peak for Li₂O₂ disappear, which clearly shows that discharge and charge is associated with reversible accumulation and disintegration of Li₂O₂.

For further confirmation, Raman technique has been used to gain additional information about the deposition of RuO₂ on carbon nanotubes as shown in the Fig. 5(d). Moreover, the fully discharge and charge cathodes were also compared with the pristine cathode to confirm the reversible formation and decomposition of discharge product Li₂O₂. In pure CNTs and CNT/RuO₂ cathodes, the characteristic bands at around 1329 and 1574 cm⁻¹ were appeared which can be allocated to D band and G band of CNTs. The band intensities for the D and G band in CNT/RuO₂ cathodes were much smaller than pristine cathode, which clearly indicate the large deposition of RuO₂ on CNT surface. In the Raman spectrum, three additional peaks were found at 509, 627, and 685 cm⁻¹ in the CNT/RuO₂ cathode. Which correspond to the three Raman modes for RuO₂: E₉g, A₁₈g, and B₂₉g modes, respectively. Additionally, the reversibility of Li₂O₂ accumulation and disintegration on the cathode surface is also established by ex-
situ Raman spectra. After fully discharge, the typical peak for Li$_2$O$_2$ can be seen, while on the recharge cathode, it completely disappears clearly shows the reversibility of Li-O$_2$ battery.

Figure 5. SEM images of (a) fully discharged and (b) recharged cathode of CNT/RuO$_2$ (c) XRD and (d) Raman spectrum of pristine, discharged, and recharged cathode of CNT/RuO$_2$ in polymer based Li-O$_2$ batteries.

4. CONCLUSION

In summary, a binder-free composite cathode of CNT/RuO$_2$ has been developed using a simple vacuum filtration method, in which carbon nanotubes (CNTs) defect sites were coated with RuO$_2$ catalyst for 400 cycles by Atomic Layer Deposition method. The surface engineering of CNTs (highly reactive for Li$_2$O$_2$) with RuO$_2$ catalyst avoid it from parasitic reactions. Consequently, the improved electrochemical performance in polymer-based Li-O$_2$ battery is attributed to the incorporation of RuO$_2$ catalyst in binder-free cathode. The lower potential gap of $\sim$0.9 V has revealed the efficient role of RuO$_2$ catalyst for better electrochemical activities. Furthermore, the efficient electrochemical performance of Li-O$_2$ battery could be ascribed to the film-like morphology of discharge product. As a result, these
findings could pave the way for surface modification of binder-free cathodes as a viable strategy for improving Li-O₂ battery electrochemical performance.

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References
24. Q-C. Liu, L. Li, J-J. Xu, Z-W. Chang, D. Xu, Y-B. Yin, X-Y. Yang, T. Liu, Y-S. Jiang, J-M. Yan, X-

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