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# Fabrication and Conductance Characterization of Single C<sub>60</sub> Molecular Junction in Solutions

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## Abstract

The conductance and stretching length of the single C<sub>60</sub> molecule bridging two Au electrodes (C<sub>60</sub> molecular junction) were studied in air, mesitylene and 0.1 M HClO<sub>4</sub> solution. In air, the C<sub>60</sub> molecular junction did not show any well-defined conductance value. In either mesitylene or HClO<sub>4</sub> solution, the systems showed a conductance value of 0.01 G<sub>0</sub>. The stretching length of the single C<sub>60</sub> molecular junction was determined to be 0.01 nm. The values of the conductance and stretching length in solution were smaller than those obtained in ultra high vacuum, indicating the weak C<sub>60</sub>-Au interaction in solution. Considering the particular shape of the C<sub>60</sub> molecule and the junction formation process in the present system, a sliding model was proposed to interpret the observation.

**Keywords:** Molecular junction; Molecular conductance; C<sub>60</sub>; Scanning probe microscopy

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## 1. Introduction

Recently, extensive interests have been focused on the single molecular junctions, because those studies provide a large number of candidates for molecular devices [1]. Various single molecular junctions have been fabricated with scanning tunneling microscope (STM) [2] and mechanically controllable break junctions (MCBJ) [3,4]. In most of previous studies, the molecules with two terminal anchor groups have been concerned in the junction, because they may form a linear connection between two metal tips. However, the study on the molecule without the terminal anchor group, especially those spherical molecules may much extend our understanding of the single molecular junction. Among the various spherical molecules,  $C_{60}$  is most attractive [5]. In addition to the spherical molecular shape, it also exhibits various interesting properties, such as Coulomb blockade behavior, tunable conductance by the mechanical deformation, and super lubrication [6-8]. In addition, it has narrow HOMO-LUMO gap (2.1~2.7 eV) [9], making it promising material for molecular electronic devices.

The conductance of a single  $C_{60}$  molecule bridging two Au electrodes ( $C_{60}$  molecular junction) has been examined experimentally. Morita *et al.* fabricated the single  $C_{60}$  molecular junction with the anchoring groups and determined the junction conductance of around  $1 \times 10^{-4} G_0$  ( $G_0 = 2e^2/h$ ) [10]. Böhler. *et al.* characterized the molecular junction of single  $C_{60}$  without the anchoring group in ultra high vacuum (UHV) [11]. They discussed that the interaction of  $C_{60}$  with gold electrodes was strong, because it showed the typical sigmoid  $I$ - $V$  curve and a larger conductance value of  $0.1 G_0$ . In the recent publication [12], by using an improved ultrahigh vacuum (UHV) setup we have refined the junction conductance to be  $0.2 \pm 0.1 G_0$ . Park *et al.* [6] used an alternative way. They fabricated the junction in an organic solution, and then transferred into UHV for the electric measurement. They proposed that the contact between  $C_{60}$  and Au is via a physical contact, showing a suppressed

conductance of  $\sim 2 \times 10^{-4} G_0$ . The various conductance values of the  $C_{60}$  molecular junction prompt us to consider the environment effect.

In this study, we investigated the conductance of the  $C_{60}$  junction in various environments, including organic and aqueous solutions, as well as in air. The Au- $C_{60}$  bond strength was estimated using the distance over which the molecular junction was stretched before the final disconnection. The conductance and bond strength of the junction were discussed by using the transformation model of the  $C_{60}$  molecular contact in solution.

## 2. Experimental

The electric measurement was performed using a modified Pico-STM system (Molecular Imaging). The tip was made of Au wire ( $\phi=0.25$  mm, 99.95%), and the Au (111) substrate was prepared by a flame annealing and quenching method.

Three environments of the electric characterization have been adapted in this work. (1) Measurement in air: The gold substrate was firstly immersed in benzene solution containing 1.0 mM  $C_{60}$  (Frontier carbon corporation), followed by rinsing with benzene and water and drying under  $N_2$  flow. (2) In mesitylene solution: The conductance measurements were performed in mesitylene solution containing 1.0 mM  $C_{60}$ . The molecular junction formation and electric characterization were achieved at the same time. (3) In  $HClO_4$  solution: The gold substrate was immersed in benzene solution containing 1.0 mM  $C_{60}$  firstly, and then rinsed with benzene and water. After this treatment, the conductance measurements were performed in 0.1 M  $HClO_4$  solution at a constant electrochemical potential by a potentiostat (Pico-Stat, Molecular Imaging). A Ag/AgCl was used as the reference electrode, a Pt wire ( $\phi=0.50$  mm) as the counter electrode. The electrochemical potential of the gold electrodes was maintained at 0.08 V vs. Ag/AgCl. The STM

tip was coated with wax to eliminate ionic conduction.

The measurements were carried out with the STM tip repeatedly moved into and out of contact with the substrate at a rate of 50 nm/s under all conditions. A bias of 20 mV was applied between the tip and substrate. All statistical data were obtained from a large number (1,200) of individual conductance traces. The experiments were performed for more than three independent samples.

### 3. Results and discussion

Figure 1 shows the typical conductance traces (Figure 1(a)) and corresponding conductance histograms (Figure 1(b)) of gold contacts in air (black line), mesitylene solution in the presence (red line) and absence (green line) of  $C_{60}$  molecules. In air, neither steps nor peaks were observed in the conductance trace or histogram. The conductance of the single  $C_{60}$  molecular junctions could not be determined in air. In the mesitylene solution in the presence of  $C_{60}$  molecules, the typical conductance trace decreased in a stepwise manner, with steps occurring at 0.01 and 0.02  $G_0$  (Figure 1(a)). Corresponding conductance histogram showed the peak features at 0.01  $G_0$  (Figure 1(b)). In comparison, no similar features were observed in this conductance region in the pure mesitylene solvent (green line). Based on these results, one can conclude that the steps at 0.01 and 0.02  $G_0$  in the traces are originated from the Au- $C_{60}$ -Au junction, with one and two  $C_{60}$  molecules bound, respectively [1]. The conductance of the single  $C_{60}$  molecular junctions was precisely determined to be 0.010 ( $\pm 0.003$ )  $G_0$  in mesitylene. The error of the conductance value was determined to be the standard deviation of the conductance values for five independent samples.

It has been well-recognized that the length of the last plateau of the conductance trace is directly correlated to the bond strength of the molecular junction [13]. In order to discuss the  $C_{60}$ -Au bond strength, the length of the last plateau was statistically analyzed as shown in Figure 2.

The length of the last plateau was the distance over which the single C<sub>60</sub> molecular junction could be stretched before the final disconnection. It was defined as the distance between the points at which the conductance dropped from 1.2 to 0.8  $G_0$  for the gold junction and from 0.013 to 0.007  $G_0$  for the C<sub>60</sub> junction. The length distribution was obtained by 1,200 individual traces. The average lengths of the last plateau were 0.01 and 0.07 nm for single C<sub>60</sub> molecular junction and gold mono atomic contact, respectively. The length for the C<sub>60</sub> molecular junction was smaller than that for the gold atomic contact. The result suggests that the interaction between Au and C<sub>60</sub> may exist to form the junction, but rather weaker than the Au-Au interaction. Here it should be noticed that the distribution of the stretching lengths did not show a peak. Recently, Kamenetska *et al.* reported the peak in the distribution of the stretching lengths of the last conductance plateau for single molecular junction with Au-NH<sub>2</sub>, Au-SMe<sub>2</sub> bonds [14]. The distribution of the stretching lengths showed a peak for the molecular junction with a strong metal-molecule bond. Since the Au-C<sub>60</sub> bond investigated in the present study are weaker than the Au-NH<sub>2</sub>, Au-SMe<sub>2</sub> bonds, the plateau length histogram did not show peaks in the present study.

The conductance measurements of the C<sub>60</sub> molecular junction were also performed in 0.1 M HClO<sub>4</sub> as shown in Figure 3. Similarly, the two steps at about 0.01 and 0.02  $G_0$  were observed in the conductance trace (Figure 3(a)), and 0.01 ( $\pm 0.003$ )  $G_0$  peak appeared in the histogram (Figure 3(b)). The conductance of the single C<sub>60</sub> molecular junctions in 0.1 M HClO<sub>4</sub> was determined to be 0.01  $G_0$ , which agreed with the conductance value obtained in mesitylene.

Here, we briefly comment on the formation of the C<sub>60</sub> dimer in the solution. It is well known that C<sub>60</sub> dimer is formed by photo radiation or high temperature treatment [15]. Under the present experimental condition, the concentration of C<sub>60</sub> is close to the solubility limit of C<sub>60</sub> in mesitylene [16]. So, C<sub>60</sub> dimer might exist in the solution. However, the peak in the conductance histogram

would originate from not  $C_{60}$  dimer but  $C_{60}$ . If  $C_{60}$  dimer bridged the two Au electrodes, there would be various configurations, i.e., various conductance values of the molecular junction [17]. This is against our observation of the conductance peak in the histogram. Therefore, the peak in the conductance histogram would originate from the single  $C_{60}$  molecular junction.

It is instructive to compare the conductance values and the lengths of the last plateau in the different environments. In UHV, the conductance was 0.1 [11] or 0.2  $G_0$  [12]. The average stretching length of the last plateau was 0.07 nm which was close to that for the clean gold atomic contact. In organic and aqueous solutions, the conductance was reduced to 0.01  $G_0$ . The average stretching length was reduced to 0.01 nm. The experimental results of conductance and the stretching length of the last plateau indicated that the interaction between gold and  $C_{60}$  was drastically reduced in the both solutions. In air, the conductance could not be determined.

To gain insight into the environment effect on the junction conductance measurement, the experimental observations were compared as follows. First, the observation in air was compared with that in both solutions and in UHV. Unlike in UHV and solutions, any conductance feature could not be observed in the conductance region from 0.01 to 0.2  $G_0$  in air. This is because that various contaminants, such as  $O_2$  and alkane molecules, can adsorb onto the surface of the metal electrode and the molecular junction. When a molecule adsorb onto the surface of the metal electrode or the molecular junction, it can change the conductance of the molecular junction. The effect of the molecular adsorption on the conductance of the molecular junction varies with the chemical species and coverage of the molecule [17]. Therefore, the conductance of the  $C_{60}$  molecular junction can not be determined in air. In addition, the adsorbed molecules would disturb the formation of the  $C_{60}$  molecular junction.

Second, it is important to compare the UHV and solution for the junction conductance

measurement. It is well-recognized that UHV is a good environment for the molecular conductance measurement. UHV condition ensures that exposed gold atoms during stretching remain as an active state. Therefore, a rather strong chemical bond can form between  $C_{60}$  molecule and Au surface, leading to higher conductance ( $0.2 G_0$ ) for the single  $C_{60}$  molecular junction [12]. The average stretching length of the single  $C_{60}$  molecular junction was 0.07nm in UHV, which was comparable to that of the clean gold mono atomic contact. The present study demonstrated that the solution might be also a proper environment for this purpose. In solution, the metallic wire is always covered uniformly by a layer of adsorbed and/or weakly oriented solvent molecules. This layer protects the junction from the contamination and ensures the reliable electric measurement. In addition, the fabrication and measurement of single molecular junctions in solution looks more convenient as compared with in UHV.

However, the formation of the  $C_{60}$  junction in solution proceeds via following different mechanism. This can be identified from the conductance value and length of the last conductance plateau. Since the gold wire stretching was performed in solution, it was always covered by a layer of solvent molecules. The  $C_{60}$  molecule was minority in solution, and was therefore, likely to be supported on the solvent layer (see Figure 4a). The thickness of the solvent layer is expected to be in the order of mono layer [18,19]. The  $C_{60}$  molecule would adsorb on the molecule which strongly adsorb on the metal electrode. During the wire stretching,  $C_{60}$  molecule would diffuse on the surface and then bridge between Au electrodes on this surface (see Figure 4b). Therefore, the junction is actually composed by solvent layers and  $C_{60}$  molecule, and then we may observe the reduced conductance. In addition, the interaction between  $C_{60}$  and gold would be mediated by the solvent layer, leading to the decrease in the stretching length of the  $C_{60}$  molecular junction compared to that in UHV.

Owing to the spherical shape of  $C_{60}$  molecule and liquid environment, we observed the reduced junction conductance and bond strength. In the previous studies, most junctions were composed of a small linear molecule with two terminal anchor groups [1-3]. All chemical bonds in the molecule and the chemical interaction between the molecule and gold are stronger than the sliding barrier of the gold atoms along the [111] facet. Therefore, the last conductance plateau is mainly contributed by the atomic sliding of the gold tip [20]. This feature can be clearly observed from the high-resolution transmission tunneling microscope image [21]. When the large spherical  $C_{60}$  is used instead, the interaction between electrode and molecule is weaker than the interatomic interaction of the gold electrode. Therefore, the sliding takes place more likely along the spherical molecular surface than the common sliding between gold-gold interfaces does. Here, we proposed an alternative model for the spherical molecular junction. Figure 4 shows the full pictures of the proposed model. In solution, the gold contact is covered by a layer of solvent molecules, on which a few big  $C_{60}$  molecules are adsorbed. During stretching till breakdown,  $C_{60}$  molecule may diffuse on the surface and then bridge between gold electrodes whose surface would be covered with molecule as seen in Figure 4b. During the stretching the junction,  $C_{60}$  molecule diffuse on the surface of the electrode, keeping the  $C_{60}$ -electrode contact. The contact area would not change a lot during the stretching the junction, leading to a fixed conductance value. Here, it should be noticed that the distance in which  $C_{60}$  can diffuse on the electrode should be smaller than the diameter of the  $C_{60}$  under the sliding model. The distribution of the stretching length (Fig. 2) showed that the maximum stretching length was 0.03 nm, which agreed with the above discussion, supporting the validity of the sliding model.

#### 4. Conclusion

In this paper, we carried out the electric characterization of  $C_{60}$  molecular junctions in air, mesitylene and 0.1 M  $HClO_4$  solutions using modified STM system. In air, the junction did not show any fixed conductance value. The conductance of the single molecular junction was  $0.01 G_0$ , both in mesitylene and 0.1 M  $HClO_4$  solution. Comparing the conductance results in solution with those in UHV and air, the solvent effect was found to be important in the determination of conductance. The effect was discussed using our proposed sliding model. This model can explain the junction formation as well as the conductance characteristics.

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## Figure Captions

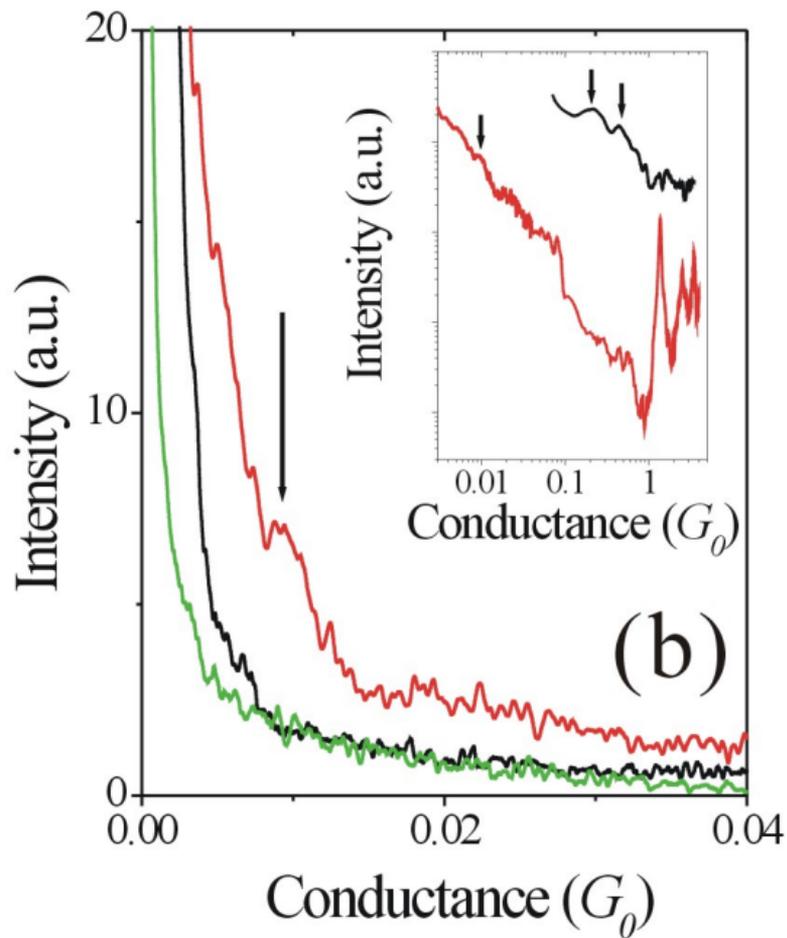
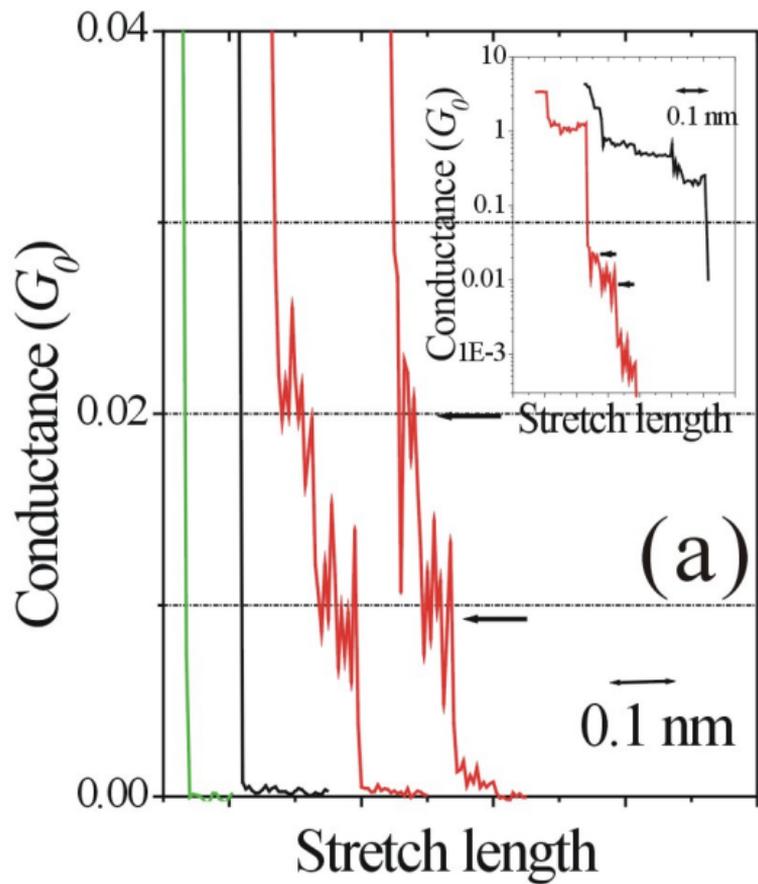
**Figure 1.** (a) The conductance trace and (b) conductance histogram of gold nano-contacts in the mesitylene solution in the presence (red line) and absence (green line) of  $C_{60}$  molecules. The black line is the results measured in air. Conductance histogram was obtained from 1,200 individual conductance traces. The inset of the figure shows the experimental result in the log-scale. The red line is the result of gold nano-contacts in the mesitylene solution in the presence of  $C_{60}$  molecules. The black line is the result of gold nano-contacts after the introduction of  $C_{60}$  in UHV.

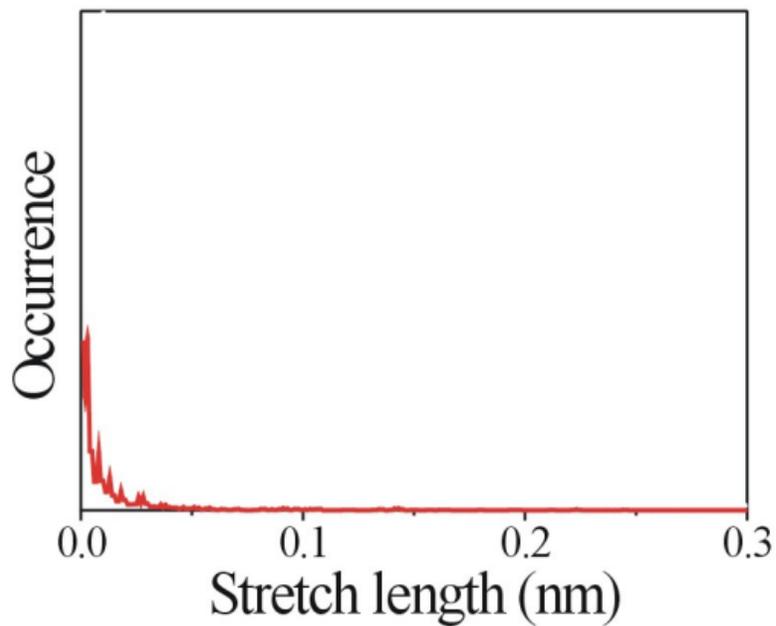
**Figure 2** The distribution of the stretching lengths of the last conductance plateau for  $C_{60}$  molecular junction (red line) and Au junction (black line) in the mesitylene solution.

**Figure 3.** (a) The conductance trace and (b) conductance histogram of gold nano-contacts in 0.1 M  $HClO_4$  in the presence (red line) and absence (black line) of  $C_{60}$  molecules. Conductance histogram was obtained from 1,200 individual conductance traces. The inset of the figure shows the experimental result in the log-scale.

**Figure 4.** The proposed sliding model for the junction of the big spherical molecule. Step 1: The metallic wire is fully covered by a layer of solvent molecules during stretching and a few big  $C_{60}$  molecules are adsorbed. Step 2: The  $C_{60}$  molecule diffuses into the junction and bridges the two electrodes just after the disconnection of the metallic wire; Step 3: Further stretching leads to the sliding along the spherical molecular surface that forms the conductance plateau; Step 4 The final disconnection happens with further stretching. The right panel shows the corresponding conductance state of the contact during stretching the contact. The dotted line in figure at the bottom right indicates the offset current in our

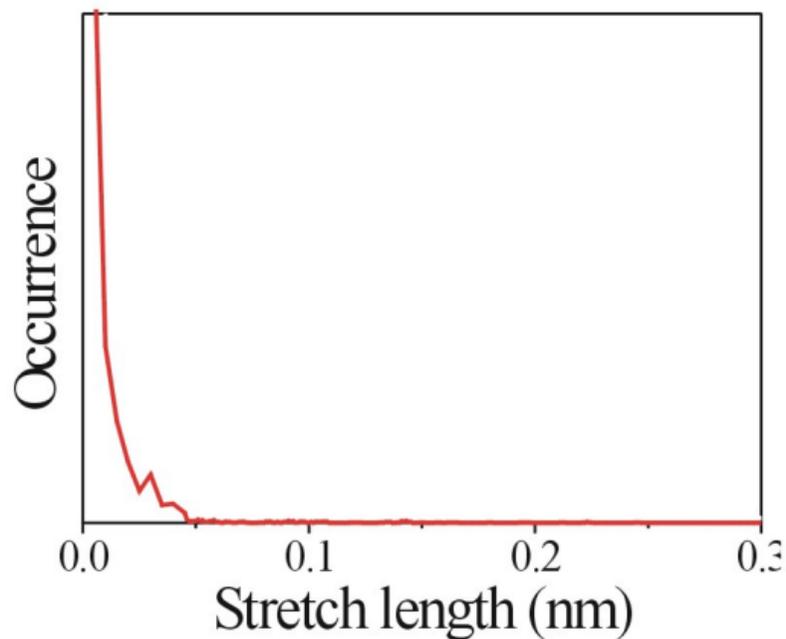
experimental setup.



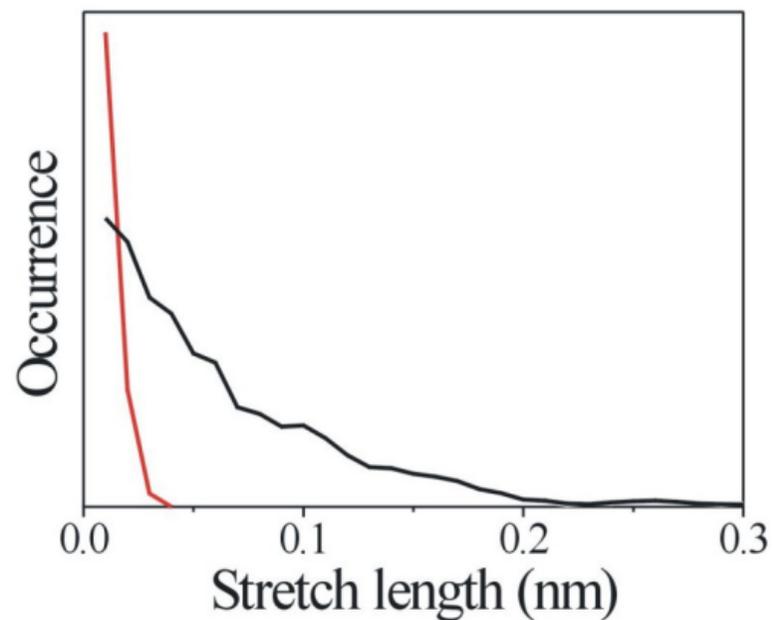


bin: 0.001nm

original fig.2



bin: 0.005nm



bin: 0.01nm

revised fig.2

