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Preprint

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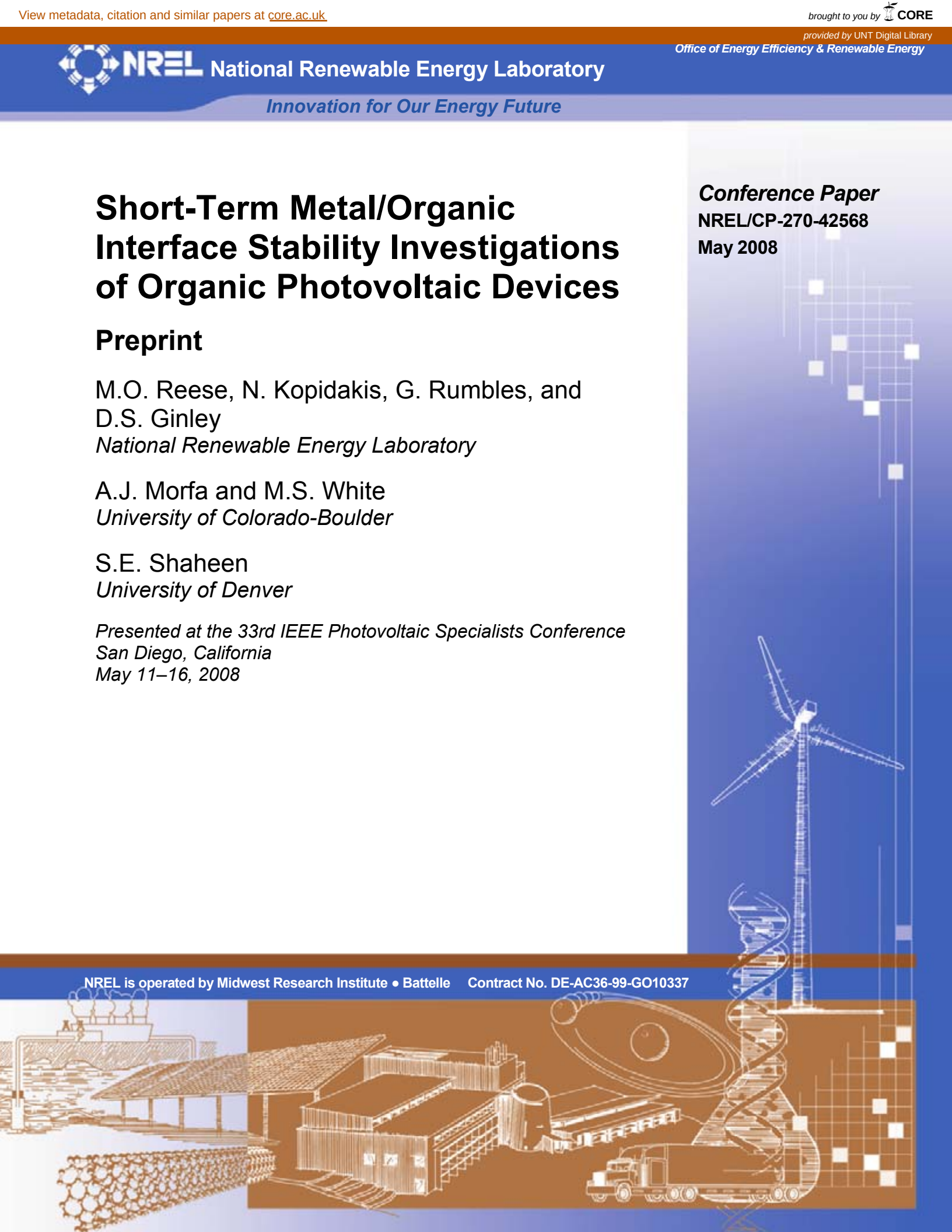

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Short-term Metal/Organic Interface Stability Investigations of Organic Photovoltaic Devices

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ABSTRACT

As organic photovoltaic (OPV) devices have begun to move toward initial applications, issues of their stability become increasingly of interest. The de facto standard OPV devices are made from a blend of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61-butyric acid methyl ester (PCBM); these serve as a test bed for lifetime testing. As delamination, oxidation, and chemical interactions at the metal electrode/organic interface have long been posited as a degradation pathway in organic electronic devices, two short-term experiments were employed to evaluate the stability of this interface in the light and dark. Devices and separate organic surfaces were stable in air over the course of 10's of minutes while in the dark. While devices were stable in air for 100 minutes under constant one sun illumination, the organic surface was not and good devices could not be made on it subsequently

INTRODUCTION

As organic photovoltaics (OPV) have become more efficient, with certified efficiencies as high as 5.4%[1], issues of their stability become increasingly of interest. Until recently,[2] there has been only scattered data quantifying degradation and exploring the mechanisms in OPV, leaving this area still in its nascent stages. There is not even a clear understanding if the mechanisms are predominately extrinsic or intrinsic. While there are several degradation mechanisms that have already been identified including molecular (thermal and photo-induced) instability, photolytic instability, and interfacial instability (e.g. ITO/PEDOT:PSS), not enough is currently known to determine their relative importance.[3]

This paper addresses one source of degradation in OPV devices: the metal/organic interface. It builds on previously published work from our group, that investigated degradation over the course of days as opposed to minutes.[4] In this previous work, we observed two dominant timescales in the degradation process similar to earlier reports.[5,6] During the rapid initial degradation (over the course of the first hour), devices lost 10% to more than 30% of their initial efficiency values.[4] Depending on the conditions the devices were exposed to, after the initial degradation, as little a few percent of the initial efficiency value could be lost over the course of the next ten days. Furthermore, there were indications that the metal/organic interface of the devices studied might have contributed to a significant amount of the overall degradation.

Due to the fact that the short-term degradation was so catastrophic, we decided to revisit this time regime with two simple sets of experiments that would help indicate the role of the metal/organic interface and its stability in air and light. The basic approach was to study the completed device stability vs. the stability of the organic film itself as shown in subsequent devices fabricated from the films.

EXPERIMENTAL APPROACH

Devices made from a blend of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61-butyric acid methyl ester (PCBM) were prepared in the same manner as the previous study.[4] Each sample prepared had room for six typical (0.11 cm^2) devices. Three Ca/Al electrodes were deposited on each sample, completing three devices per sample. These original devices were measured and used for baseline measurements to normalize later results. Samples were exposed to different conditions, retested, then three more electrodes were deposited and all six devices were retested. All efficiency measurements as well as sample preparations of the active layer and electrode deposition were conducted in a nitrogen glovebox atmosphere. Tungsten halogen lamps (ELH) were used to generate "one sun" conditions (100 mW/cm^2), both inside and outside of the glovebox. Samples were kept below 40C for the experiments with fan cooling.

One set of samples was used for dark measurements, the other for constant one sun illumination. For the dark set, one sample was left in the glovebox, the remaining samples were exposed to air (21±1C, 26±1% relative humidity) for one min., ten min., or 100 min. For the light set, one sample was left in the glovebox under constant one sun exposure for 155 min., the remaining samples were exposed to air (≤37C, 17±1% relative humidity) for five min., 25 min., or 100 min.

	Variable	Time exposed (min.)			
Dark (21±1C, 26±1% R.H.)	**air**	**0**	**1**	**10**	**100**
Light (≤37C, 17±1% R.H.)	**air**	**0**	**5**	**25**	**100**
	light	**150**	**5**	**25**	**100**

Table 1: Experimental matrix for samples. All samples were made with 3 original devices, which were measured before any air exposure. This later served as the baseline for normalization. Dark samples were exposed only to air, whereas light samples were exposed to both air and light to varying degrees. After exposure, the original devices were remeasured, then 3 more devices were completed on each sample by depositing more electrodes and all 6 devices on each sample were tested.

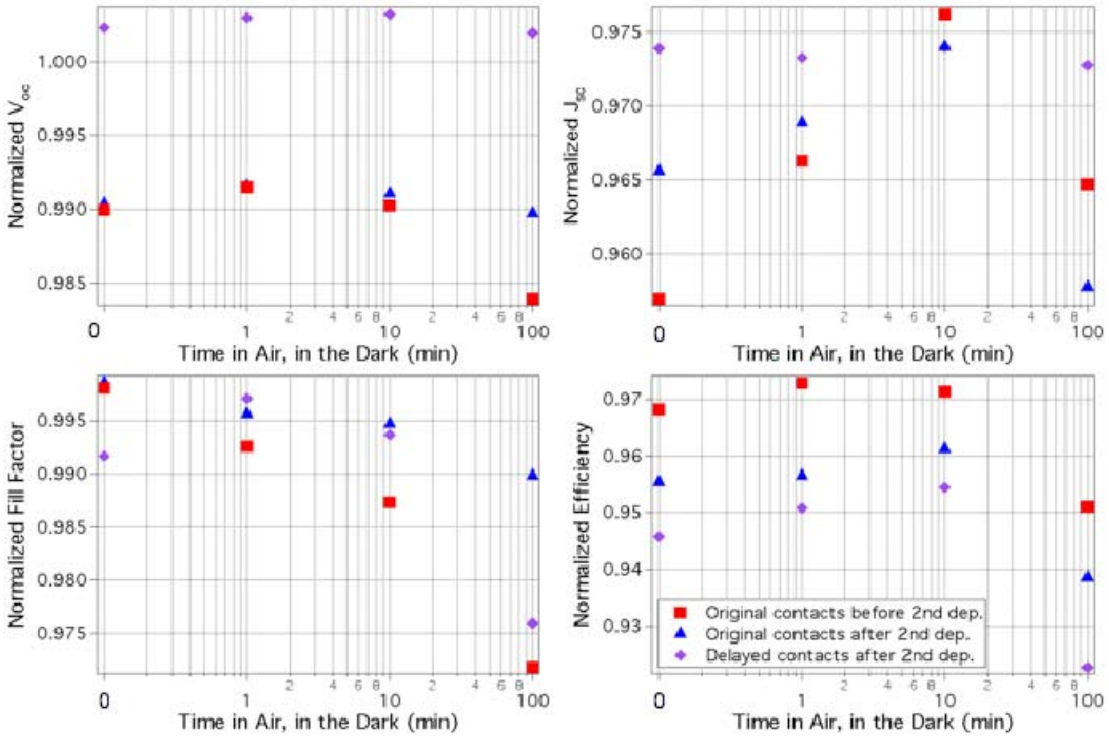

Fig. 1: Samples exposed to air (in the dark) for up to 100 min. The devices, as well as the organic surface are remarkably stable over this timescale. The starting efficiencies for all devices, to which all data is normalized, were roughly 4%.

RESULTS AND DISCUSSION

Dark, Delayed Contact Experiment

A summary of device performance for the dark set of experiments is presented in Figure 1. As can be seen, there is no substantial difference between the original or delayed set of devices on each sample exposed to air from zero to ten minutes. For 100 minutes of air exposure, however, there appears to be a little degradation. Measurements were made after exposure to air both before and after the second deposition, to see if the extra vacuum step associated with evaporation might reverse some portion of any observed damage. It is not clear that there was any real effect, from this on the original set of devices.

Here, the greatest reduction in efficiency comes in the short circuit current density (J_{sc}). Larger J_{sc} variations were noted in this study, than previously for devices kept in a glovebox under partial illumination for ten days.[4] Across all of the samples, the open circuit voltage (V_{oc}) is the most robust of the critical parameters remaining relatively constant even for devices with delayed contacts. In the previous study, while there was no completely analogous measurement, a V_{oc} reduction of ~4% was observed for devices illuminated at one sun for 10% of the time (over a ten day period), and ~2% reduction for their siblings with delayed contacts.[4]

One Sun Illumination, Delayed Contact Experiments

A summary of device performance for the constant one sun illumination set of experiments is presented in Figure 2. As can be seen, 150 min. of constant exposure to light (and somewhat elevated temperature) in an inert environment caused more degradation than 100 min. in air, in the dark. In fact, 150 min of light exposure in a glovebox, caused more degradation than either 5 or 25 min. constant illumination in air to the original set of devices. The original devices from the glovebox sample performed very similarly to the original devices from the sample with 100 min. of air and light exposure.

While illumination in or out of a glovebox causes some degradation, the glovebox apparently protects the organic surface from significant degradation when illuminated as seen in the relative performance of the delayed contact devices for the 25 and 100 min. samples.

In this set of experiments, the extra vacuum step again had no significant effect on the devices' overall performance. The greatest reduction in overall performance again comes from changes in J_{sc}, this time with 28% and 65% drops relative to the original baseline devices for 25 min. and 100 min. exposures to air and light.

In the previous study, an almost 10% reduction in V_{oc} was observed after ten days of constant illumination in a glovebox for the original set of devices and about a 4% reduction for delayed contacts.[4] Here, there is at most a few percent permanent degradation in V_{oc}, with the extra vacuum step's reviving the devices' V_{oc}.

In the previous study, after ten days the delayed contact devices exposed to constant illumination and air were dead, while the (unencapsulated) original set had degraded less than 50% of its original value.[4] Here, we can see that the kinetics for total organic surface degradation in air are on the timescale of maybe a few hours when exposed to one sun (and somewhat elevated temperature).

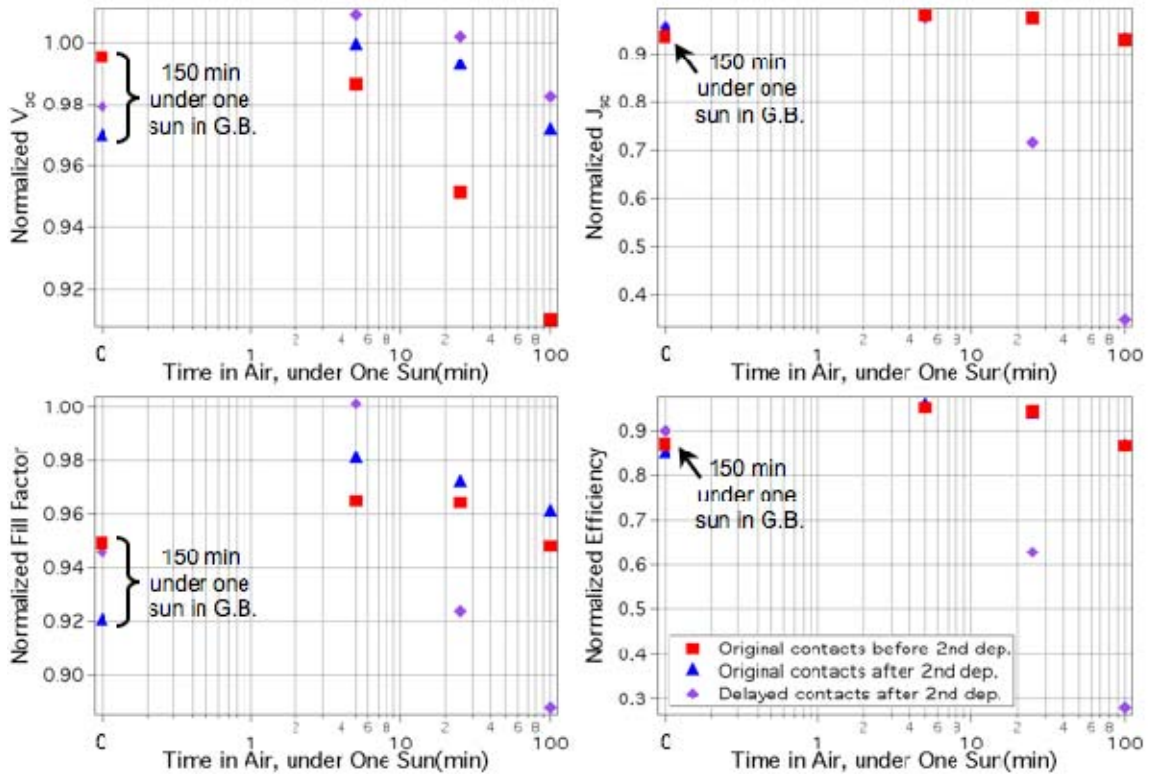

Fig. 2: Samples exposed to air (under one sun constant illumination) for up to 100 minutes. The original devices are more influenced by their exposure to light (and the somewhat elevated temperature) than air. The organic surface, however, degrades quite quickly, with significant degradation apparent after only 25 minutes. The starting efficiencies for all devices, to which all data is normalized, were roughly 4%.

CONCLUSIONS

This study follows on a previous study, that investigated the stability of metal/organic over the timescale of ten days.[4] The previous study showed that completed devices could continue to operate after days of light and air exposure while the surrounding organic film surface degraded to the point where devices could no longer be made from the films.

Here, devices were not only observed to retain most of their overall efficiency when exposed to short durations of air in the dark, but the surrounding organic film was still capable of being made into devices of similar efficiency. The length of time a completed device is exposed to one sun illumination (at somewhat elevated temperatures), appears to be more important for stability than whether or not a device is exposed to air. The surface of incomplete devices with one sun exposure in air, however, does appear to degrade quite rapidly, with significant degradation setting in after tens of minutes. This may not be surprising as oxidation on the surface may make subsequent device fabrication very difficult. The dry box experiments indicate there may be some intrinsic decomposition in the device.

ACKNOWLEDGEMENTS

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