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# Effect of additives: Organic-metal oxide nanocomposites for $\gamma$ -ray sensors

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## ABSTRACT

The transition metal oxide embodied organic composites have great promise for high energy radiation detection. The interaction of high energy radiation such as  $\gamma$ -rays with the organic composite can generate photoelectric responses, Compton scattering and electron hole pairs, which can provide favorable properties to enhance the radiation detectivity of the composite. These effects along with changes of oxidation state of metal oxides, provide significant change in the electrical characteristics of composites due to radiation exposure. We have developed nickel oxide (NiO<sub>2</sub>) nanoparticles embodied urea composite (urea-NiO<sub>2</sub>), and determined effect of  $\gamma$ -radiation on the current – voltage characteristics in the frequency range of 100 Hz to 100,000Hz. In this paper, we describe the results of effect of additional oxidizing agent MnO<sub>2</sub> (urea-NiO<sub>2</sub>-MnO<sub>2</sub>) on the morphology, processing and current voltage characteristics due to exposure of Cs-137  $\gamma$ -radiation. It was observed that addition of MnO<sub>2</sub> in urea-NiO<sub>2</sub> composite decreases the sensitivity of detection. However, urea-NiO<sub>2</sub>-MnO<sub>2</sub> composite recovers to original properties after irradiation much faster than urea-NiO<sub>2</sub> composite.

**Keywords:**  $\gamma$ -ray, nanocomposite, urea, oxides, detectors, sensors, radiation, exposure

## 1. BACKGROUND

There is a strong need for an innovative approach for developing fast and low cost  $\gamma$ -ray and neutron sensors due to very high cost involved in single crystal and helium based radiation detectors. Semiconductor crystals of semiconductor materials such as cadmium zinc telluride (CZT), thallium arsenic selenide (TAS), thallium gallium selenide and (TGSe), binary and ternary halides and chalcogenides of mercury and lead, have been studied [1-3] in details for  $\gamma$ -ray detectors. These crystals have shown great promise. However, growth and fabrication development is very time consuming. In addition, halides such as hygroscopic materials LaBr<sub>3</sub> have shown promise, but stability and fabrication is big road block for their applications in sensors. Another approach involving nickel oxide film has been used by Arshak and coworkers [4-6]. These films of nickel oxide sputtered on silicon wafers have shown promise for detecting  $\gamma$ -radiations. We have developed ionizing organic based ethylene carbonate-NiO<sub>2</sub> and urea-NiO<sub>2</sub> composites [7], which have demonstrated great promise for increasing the sensitivity for detection of  $\gamma$ -rays. Since the interaction of  $\gamma$ -radiations with organic composites involves three interaction processes; photoelectric effect, Compton scattering, and pair production, composites have better chance for enhancing detectivity. The probability of the photoelectric effect, where a  $\gamma$ -ray interacts with an atom resulting in the ejection of an electron from the atom is proportional to the atomic number of the absorbing element, and inversely related to the energy of the  $\gamma$ -radiation. For the composite containing metal oxide, upon exposure of high energy radiation, the resistivity of the oxide composite will increase due to decrease in holes' concentration. In this paper, we describe the effect of manganese dioxide impurity in the urea-NiO<sub>2</sub> composite. Effect of addition on the morphology and detectivity for  $\gamma$ -radiation is described in in this paper.

## 2. EXPERIMENTAL METHODS

The passage of  $\gamma$ -rays or other charged particles such as  $\beta$  and  $\alpha$  particles through a material causes ionization. Even fast neutrons which produce fast protons can lead to ionization as the result of collision. Since ionization is the

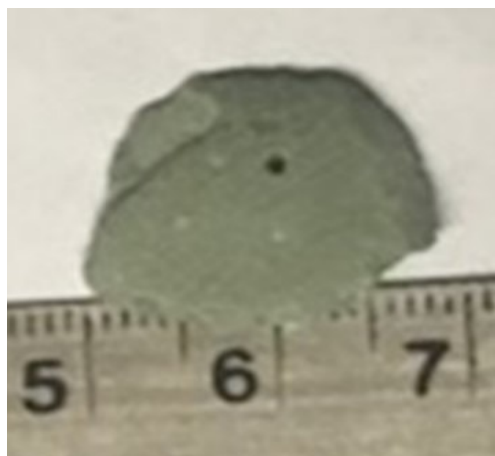
major mechanism in organic compounds, we chose urea as the matrix to hold active nickel oxide nanoparticles in this study.

**2.1 Preparation of composite:** Urea (99.9% purity) was provided by Sigma Aldrich and used without further purification. It was characterized for its thermal and solidification properties. It melts at 133.5°C and has a large undercooling ( $T_m - T_s > 15K$ ); where  $T_m$  denotes the melting temperature and  $T_s$  is the solidification temperature. Taking advantage of this large undercooling, urea-NiO<sub>2</sub> and urea-NiO<sub>2</sub>-MnO<sub>2</sub> composites were prepared using metal oxide nanoparticles. Both the nickel oxide (99.9%) and manganese oxides (99.9%) were purchased from Sigma Aldrich. These metal oxides were placed in a wig-L-bug and ground to produce uniform size metal nanoparticles (50 -100nm). Urea was melted in a beaker on a hot plate and maintained at a temperature of 150-160°C, while nickel oxide was added to the molten urea in a 10:1 ratio (urea to nickel oxide) and stirred continuously for 15 minutes to ensure uniform mixing. The resulting molten material was then poured in a shaped container and placed in an ice water bath to rapidly freeze the sample. MnO<sub>2</sub> was added in a 5:1 ratio (NiO<sub>2</sub> to MnO<sub>2</sub>) in the composite. Molten material was mixed with nickel oxide and manganese oxide and then poured in a shaped container placed in ice cold water to freeze. As casted sample is shown in **Fig.1**. Morphology of the composite is shown in **Fig. 2**.

**2.2 Evaluation of  $\gamma$ -ray response of the composite:** A commercially supplied Cs-137 g-radiation source was used to evaluate  $\gamma$ -ray response. The  $\gamma$ -radiation source Cs-137 was listed for 0.25  $\mu$ Ci, 30.2year half-life,  $\beta$  and  $\gamma$ -radiation. Both urea-NiO<sub>2</sub> and urea-NiO<sub>2</sub> - MnO<sub>2</sub> composites were placed 5 mm distance from the radiation source. The current-voltage response profile of both composites was measured and compared to results from the same material prior to irradiation. The current voltage responses of composites were measured at different voltages, ranging from 50 mV to 1000 mV and frequencies ranging from 100 Hz – 100 kHz using an Agilent/HP 4284A LCR meter. **Figs. 3** and **4** show the current - voltage (I-V) characteristics of non-irradiated and irradiated composites.

### 3. RESULTS AND DISCUSSION

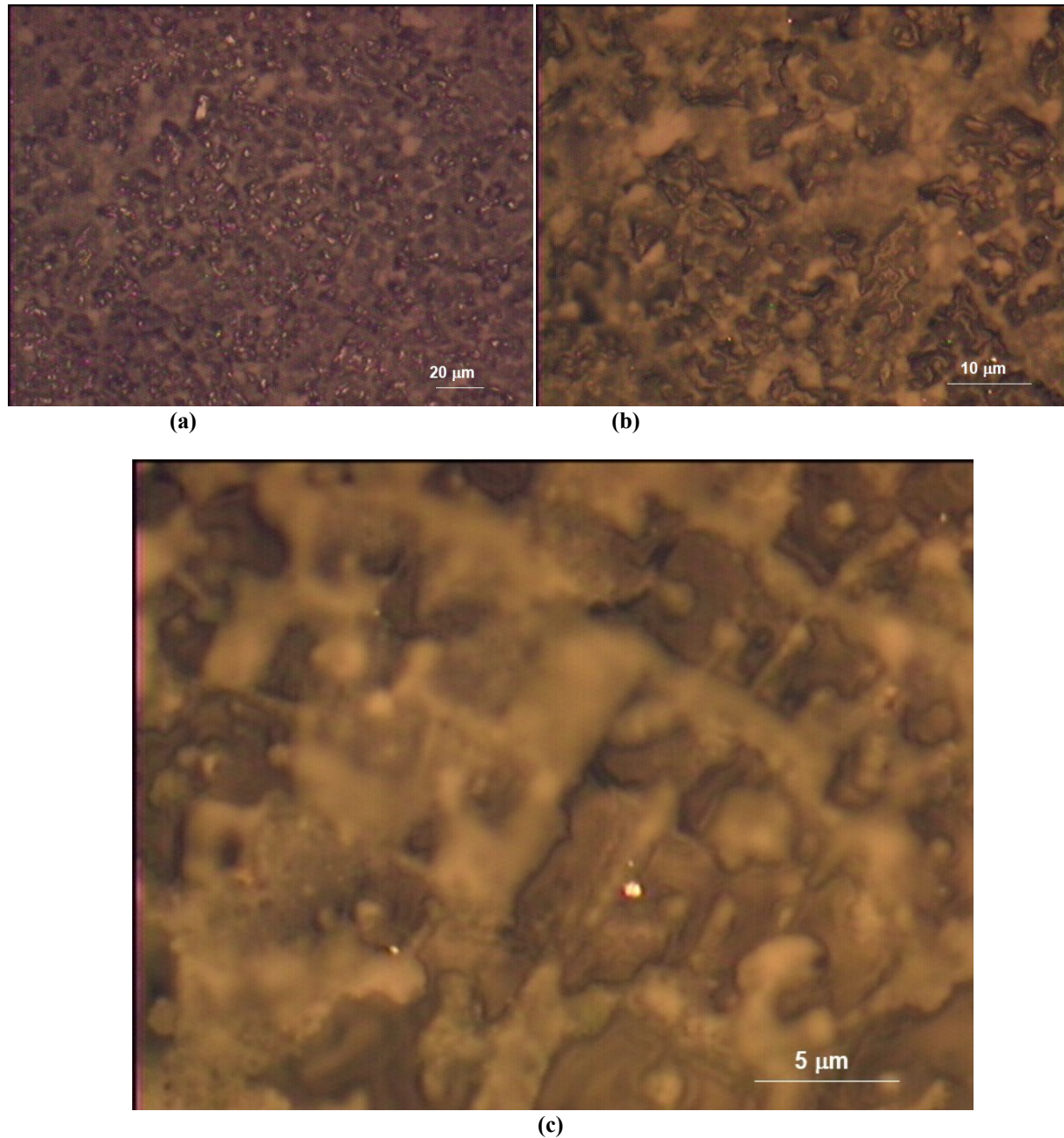
**Fig. 1** shows a disk-shaped sample of urea-NiO<sub>2</sub>-MnO<sub>2</sub> composite. Since urea composite melts in the range of 133 °C, various shaped composites could be casted simply by pouring the mixture into different shaped containers placed on hot plate prior to cooling in an ice water bath. Unlike the case of ethylene carbonate based composites [7], urea-NiO<sub>2</sub> -MnO<sub>2</sub> composite did not show rod or needle morphology. Because of absence of rod and needle formation during solidification, good mixing could be achieved for shaped composite. A comparison of the un doped urea-NiO<sub>2</sub> composite and urea-NiO<sub>2</sub> -MnO<sub>2</sub> composite showed that MnO<sub>2</sub> doped composite has better mechanical properties for fabrication and electrode bonding. It has better stability for the silver diffusion. For current-voltage measurements at various frequencies, stability of several electrode materials was evaluated. Silver paste was stable and we used for the detailed electrical measurements of the irradiated and non-irradiated composites.



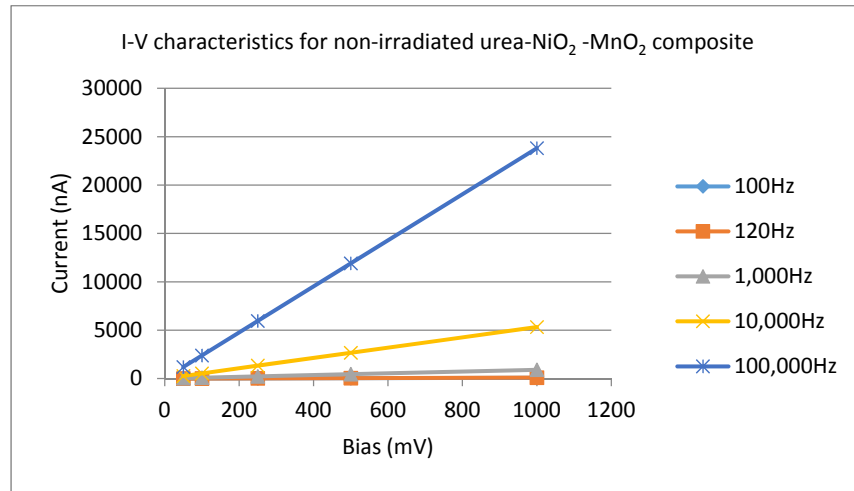
**Fig. 1** As prepared non-irradiated urea-NiO<sub>2</sub>-MnO<sub>2</sub> composite

The micro morphology of the non-irradiated composite showed that shiny particles of the metal oxides were distributed between small crystallites of urea. In some portion of the composite, there were micrometer size particles

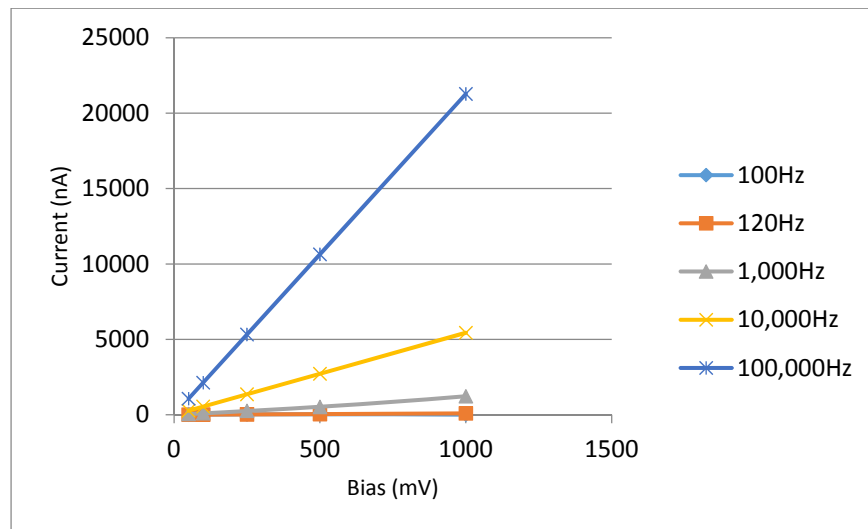
while as in some portion extremely small particles were observed. This indicates that localized undercooling difference was the cause of the size of urea crystals in the composite. **Fig. 2** shows the morphology of the composite at several magnifications. The high magnification sample (c) shows some glassy behavior of the composite. As shown in **Fig. 2(b)**, the morphology appeared as colony structures developed in the early stage of curing. However, after few hours, we observed that grains disappeared for a large portion of the composite.



**Fig. 2** Morphology of non-irradiated urea-NiO<sub>2</sub>-MnO<sub>2</sub> composite at different magnification. The high magnification sample (c) shows some glassy behavior of the composite



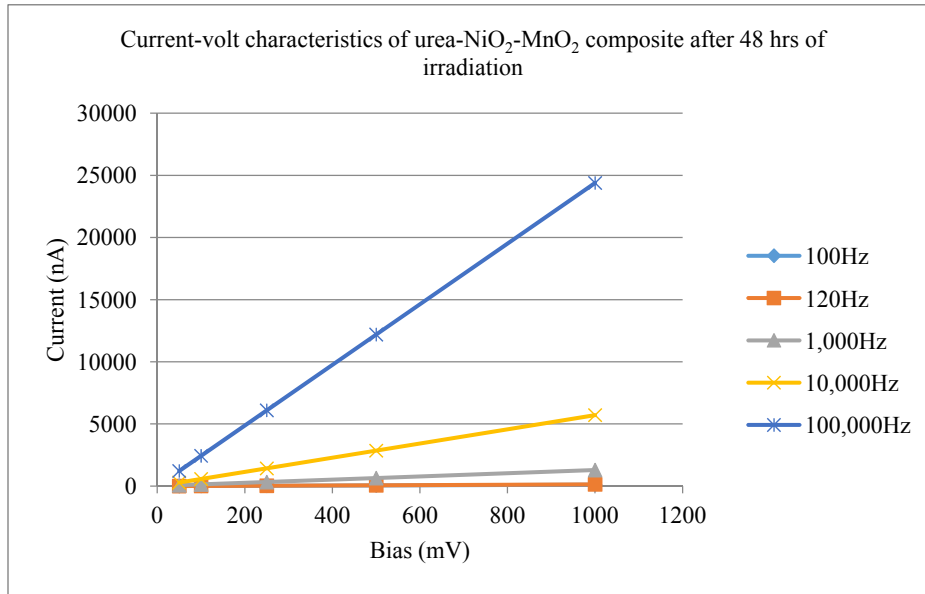
**Fig. 3.** Current-voltage characteristics of the urea-NiO<sub>2</sub>-MnO<sub>2</sub> composite at several frequencies



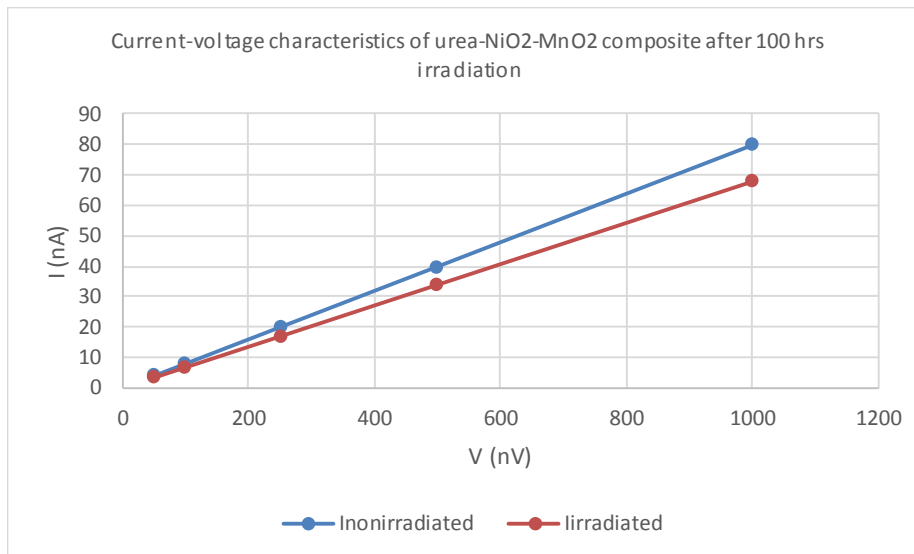
**Fig. 4.** Current-voltage characteristics of 100 hours aged urea-NiO<sub>2</sub>-MnO<sub>2</sub> composite at several frequencies

**Fig. 3** shows the current -voltage relationship for the freshly prepared non-irradiated composite at different frequencies. Same sample was kept at room temperature for more than 100 hours to evaluate its stability and effect of oxygen in atmosphere. The data observed for identical bias and frequencies are plotted in **Fig. 4**. There was no significant difference in current-voltage characteristics. This showed that urea-NiO<sub>2</sub>-MnO<sub>2</sub> composite was stable in the atmosphere and electrical properties did not change. **Fig. 5** shows results of the composites which was irradiated for 48 hours with Cs-137 source. The resistance of the urea-NiO<sub>2</sub>-MnO<sub>2</sub> composite at bias voltage of 50 mV to 1000mV and 100Hz to 100000Hz frequency range was measured and current was determined for both non-irradiated and irradiated composites. Current - voltage data for 50 mV to 1000mV bias, and the frequency range of 100Hz to 100,000Hz frequency showed identical behavior. **Fig. 6** show the I-V characteristics of non-irradiated and irradiated composites at 100Hz. The difference in current is significantly lower [7] compared to the urea-NiO<sub>2</sub> composite which did not have MnO<sub>2</sub> doping. When the irradiated composite was kept again in atmosphere, it achieved the current -voltage characteristic (**Fig. 7**) of the non-irradiated composite. **Fig. 7** shows the I-V results of

the irradiated sample which was placed for 48 hours in atmosphere after irradiation. The data showed that its electrical characteristics are almost identical to that of non-irradiated composite and MnO<sub>2</sub> helps in recovery.



**Fig. 5.** I-V characteristics of irradiated urea-NiO<sub>2</sub>-MnO<sub>2</sub> composite which was placed in atmosphere for 48 hrs. for recovery.



**Fig. 6.** A comparison of I-V characteristics of as prepared and irradiated MnO<sub>2</sub> doped composite at 100Hz

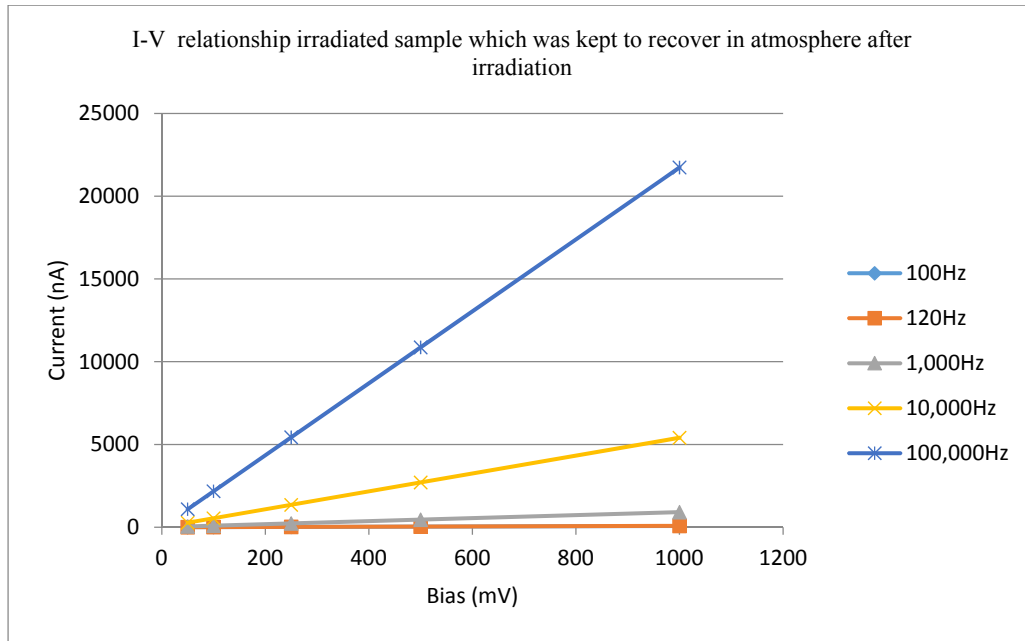


Fig. 7. I-V characteristics of urea-NiO<sub>2</sub>-MnO<sub>2</sub> composite which was placed in atmosphere for 48 hours after irradiation

#### 4. SUMMARY

Urea-NiO<sub>2</sub>-MnO<sub>2</sub> composite demonstrated significant difference in current-voltage characteristics due to the exposure of  $\gamma$ -radiation even at very low energy of the Cs-137 radiation source. Addition of MnO<sub>2</sub> in the urea-NiO<sub>2</sub> composite reduces the detection sensitivity. However, Urea-NiO<sub>2</sub>-MnO<sub>2</sub> composite recovers the current-voltage characteristics of the non-irradiated composite when kept in the open atmosphere. Frequency had very pronounced effect on the resistivity and hence the current for a bias voltage applied to the composite.

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