

# **Fabrication and Characterization of Chemically Prepared ZnO Nanotubes based Sensors**

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## **ABSTRACT**

Gas sensors have gained much attention due to changes in climate and environment caused by industrial outcomes. Zinc Oxide (ZnO) is a well-known wide band gap semiconductor and it might be suitable for gas sensors. ZnO nanotubes are synthesized by sol-gel technique using anodic aluminum oxide (AAO) templates with pore size of ~200 nm. A silicon un-doped substrate (5x10 mm<sup>2</sup> dimensions) is used for deposition of ZnO nanotubes. The structural properties are observed using Bruker D8 Advance X-ray diffractometer, whereas morphology of ZnO nanotubes is observed by SEM. Gas sensing properties have been performed by using KEITHLEY 2400 source meter for as-grown and annealed samples under different conditions. Device showed high efficiency / sensitivity of 75% at room temperature. The selectivity of sensor was observed very high for acetone. The response time and recovery time that has been measured as 20 min and 11 min, respectively.

## **1. INTRODUCTION**

Recently, environmental regulations on risky volatile organic compounds (VOC) have been stricter around the globe. Acetone is a common product in chemical reagent industry taken as an example of VOC (Choi et al. 2009, Hazra et al. 2014). Acetone can affect human body and can damage the nervous system by acute poisoning. In low value of concentration, the damage of acetone is not so much high, but at higher concentration, it can lead to coma or even death. That's the reason why it is so much important to detect acetone gas in environment for the chemical industry workers (Xu et al. 2007). Semiconductor based gas sensors used for detection of VOC have been studied worldwide. Many semiconductors have been used as gas sensors such as ZnO (Acharyya 2016), Fe<sub>2</sub>O<sub>3</sub> (Sutka 2016), SnO<sub>2</sub> (Degler et al. 2016), TiO<sub>2</sub> (Liu et al. 2016) etc.

ZnO is widely explored because of its unique properties such as wide bandgap and numerous nanostructures that makes it preferable for use in field effect transistors (FETs), lasers, photocatalysis sensors and photovoltaic. ZnO has been synthesized in various nanostructures i.e. nanoparticles, nanorods, nanobelts, nanotubes, nanowires etc. showing a very high surface-to-volume ratio, enhanced electrical characteristics and slow electron-hole recombination rate. Among all of these nanostructures, nanotubes provide distinctive properties such as low grain boundary, 1-D carrier transport, quantum confinement and high surface-to-volume ratio because of

availability of both inner and outer side for interaction with species (Xu et al. 2007).

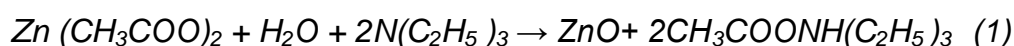
In nanotube-based sensors, the transport of electrons between the electrodes occurs along the length of nanotubes, which contains large numbers of grains. As a result, this type of 1-D nanostructure prevents electrons to get trapped in any site and also prevents the loss in electron mobility (caused by many scattering mechanisms that take place in 2-D transportation of electron) (Demczyk et al. 2002, Kayani et al. 2015). These properties enhance transport response properties of the sensors. These unique features invite worldwide chemical researchers for development of gas sensors with various ZnO nanostructures targeting different kinds of VOC detections (Wang et al. 2008).

There are various synthesis techniques like electro-deposition, hydrothermal and atomic layer deposition that have been already investigated for ZnO nanotubes. Most of the ZnO NTs based gas sensors for alcohol works on very high temperature (200°C-400°C) that causes more power consumption and is not reliable for long term use. Cho et al. (2012) produced ZnO nanotubes based ethanol gas sensor by using atomic layer deposition technique (the wall thickness of ZnO nanotubes ~10 nm). The best working temperature of device was found to be 450°C with a high response of almost 99% at 100 ppm of ethanol gas. The authors of this work also gave the idea of co-relation between wall thickness and sensor response. Feng et al. (2015) described the synthesis of ZnO NTs sono-chemically and the response of sensor was measured ~59% at 500°C for ethanol. Acharyya (2016) produced ZnO nanotubes by a two-step process of electro-deposition and electrochemical etching. Best optimum temperature was found as 75°C for alcohol sensing properties. Authors also described the effect of humidity that caused the decrease in resistance of ZnO nanotubes.

With the aim of high sensitivity even at low concentration of acetone vapors at possibly low temperature (preferable at room temperature), the motivation of present work was to produce and utilize ZnO Wurtzite phase nanotubes as gas sensing material. Sol-gel and AAO templates were used to synthesize the array of template-assisted growth of ZnO nanotubes with diameter of 200 nm.

## 2. Experimental Techniques

A low cost sol-gel technique was used for synthesis of template-assisted growth of ZnO nanotubes. The AAO templates had the pore size of 200 nm. For the preparation of ZnO sol hydrated zinc acetate, trimethylamine, deionized water and isopropyl alcohol were used, according to the following chemical reaction Eq. 1



The detailed synthesis procedure of ZnO through sol-gel process has already been reported by our group. (Riaz et al. 2011) For the fabrication of ZnO nanotubes, dip-coating technique was used to pour zinc oxide sol into the AAO template. First, the AAO template was annealed at 150°C for 30 minutes. Then that AAO template was

dissolved in ZnO solution for 20 minutes. Later that template was again annealed at 300°C for 1 hour. Ultrasonic energy was applied for 10 min for removal of nanotubes from their AAO template by using IPA.

A silicon substrate was used for fabrication of ZnO nanotubes based gas sensor. The substrate was first cleaned with deionized water, acetone and IPA in Kerry's ultrasonic bath apparatus and was then oxidized. Si/SiO<sub>2</sub> substrate of size 5x10 mm<sup>2</sup> was used. On the Si/SiO<sub>2</sub> Al electrodes were deposited independently. For the electrode deposition resistive heat evaporation was done using RF magnetron sputtering and evaporation unit. Proper masking was applied for the desired pattern of electrodes. Then, for fabrication of gas sensor, ZnO nanotubes were deposited on the substrate between the electrodes.

### 3. Results and Discussion

Bruker D8 Advanced Diffractometer (CuK $\alpha$  = 0.154nm, Ni filter) was used to analyze ZnO NTs. The observed pattern (Fig. 1) shows hexagonal wurtzite ZnO structure with intense characteristic (101) plane at 36.14° along with (002), (100), (110), (112) and (103) planes at 34.7°, 31.7°, 68.9° and 61.1° [JCPDS Card No. 5-0664]. The peak at (002) shows preferred alignment along c-axis of the NTs. The crystallite size was found by Debey Scherer formula given in Eq. (2)

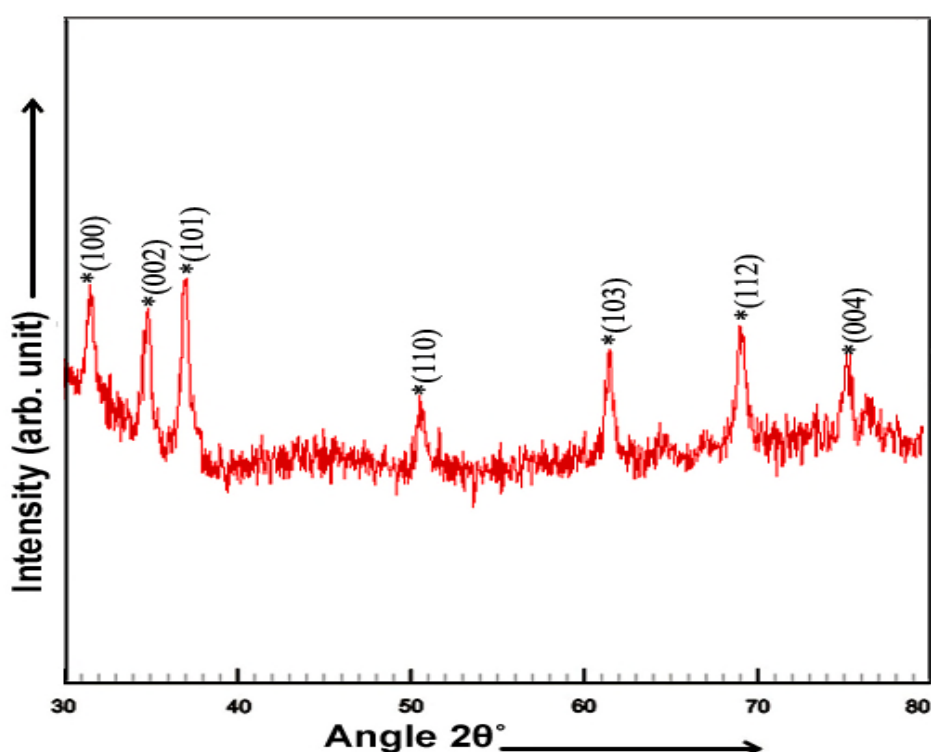


Fig.1 XRD pattern of observed peaks of ZnO nanotubes

$$D = \frac{k\lambda}{B \cos\theta} \quad (2)$$

Where, D is the crystallite size, k is a constant whose value is 0.94,  $\lambda$  is the wavelength of the X-rays used, B is FWHM of the peak while  $\theta$  is the angle of diffraction.

Lattice constants 'a' and 'c' of wurtzite hexagonal ZnO were also calculated and are in agreement with standard values. [JCPDS-5-0664]. Crystallite size ~ 1.485 nm was calculated using Debye Scherer formula.

After annealing the NTs, I-V characteristics were taken at room temperature (Fig. 4). I-V characteristics confirmed an ohmic nature of the deposited structures. The oxygen vacancies and Zn interstitial play an important role as shallow donor in ZnO. They help in adsorption of gases along these vacancies (Cho, 2012). The ZnO NTs have shown fair response to gases by the adsorption on oxygen vacancies on the surface of ZnO NTs. Current annealing method used for annealing the sensor. High voltage and large current flow from the thin layer of nanotubes produce heat in the deposited film. It is due to the power dissipation occurring in nanotubes layers. Due to heat produced in sample the trap levels and in-homogeneity of sensors reduces whereas the current flow in the sensor increases.

The sensitivity of NTs is given by Eq. (3)

$$\frac{R_{air}R_{gas}}{R_{air}} \times 100 \quad (3)$$

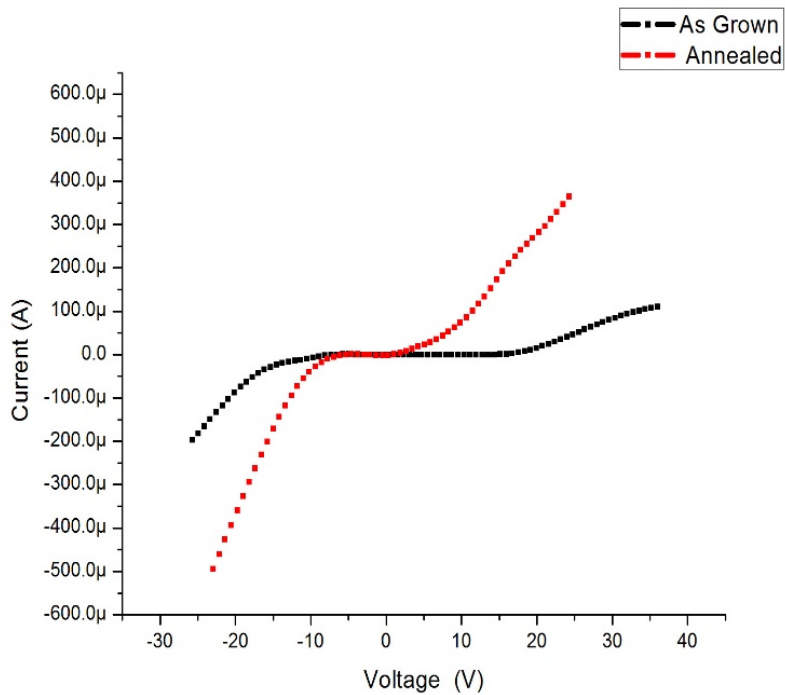


Fig. 4: I-V Characteristics Curve for ZnO nanotubes as deposited and annealed sensors.

For acetone gas sensing with ZnO nanotubes, the sample has been tested for one hour. For checking of consistency of device, test has been repeated 3 times. 50 ml acetone was placed in the chamber while the measurements were taken. Fig. 5 shows the change in current in presence of acetone.

The ZnO NTs device was placed in test chamber in the presence of acetone for almost one hour. The sensitivity of the device varies with change in time. Initially at the start the sensitivity has zero value. It increases almost linearly and then after some time it become constants up to some extent, and then starts decreasing. The behavior of sensitivity against time shows the saturation of device. The maximum response of device has been measured 97% at 20 voltage and 40 minutes time (Fig. 6).

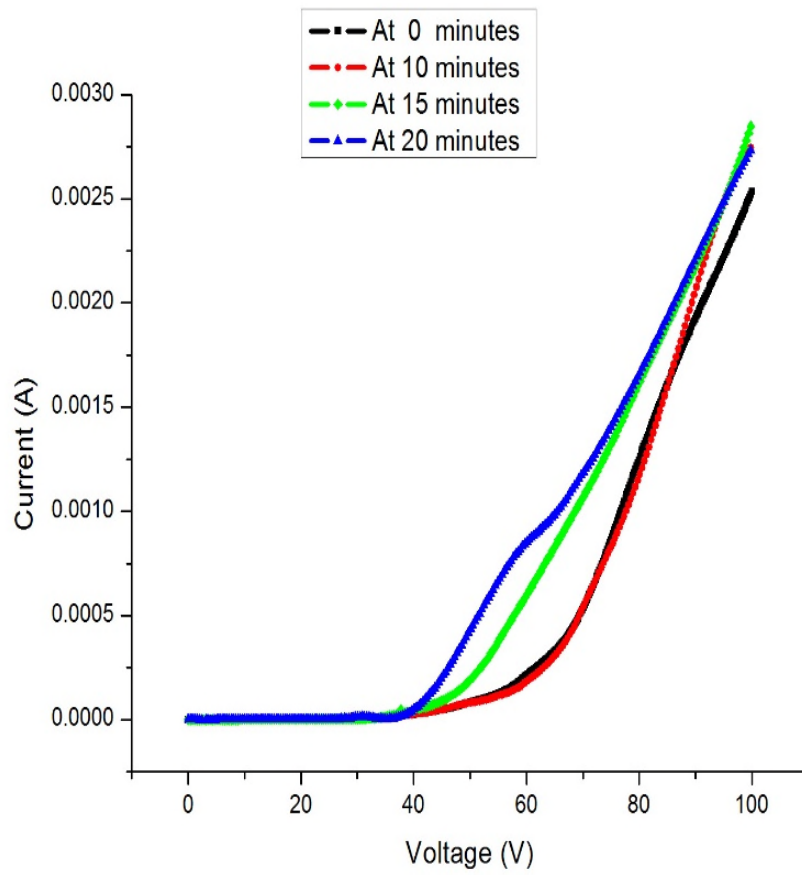


Fig. 5: I-V in Presence of Acetone

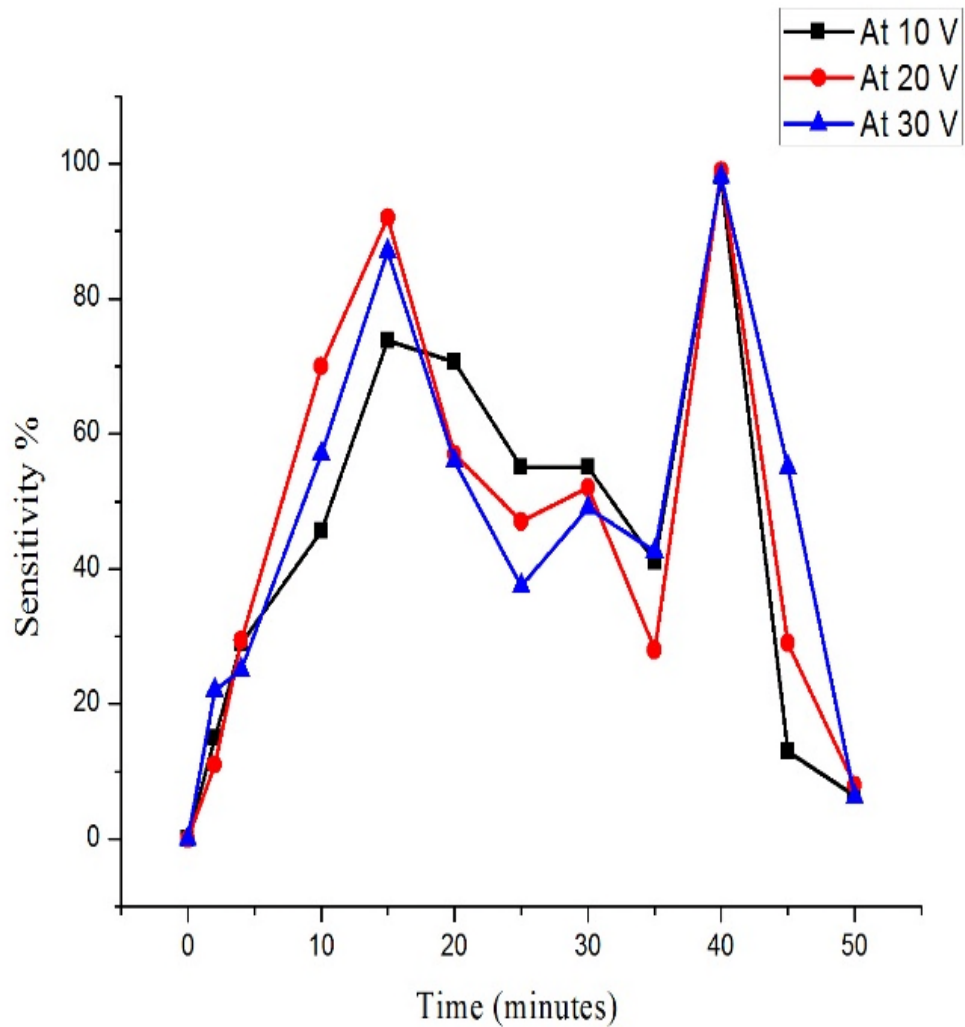


Fig. 6: Relation between time and Sensitivity of ZnO NTs sensor

By using ZnO nanotubes based gas sensor, acetone, ethanol and IPA vapors were detected with different sensitivity and response time. It was experimentally observed and also measured that sensor has the maximum sensitivity and fast response time for acetone. Fig. 7 shows the statistical data of sensitivity of device.

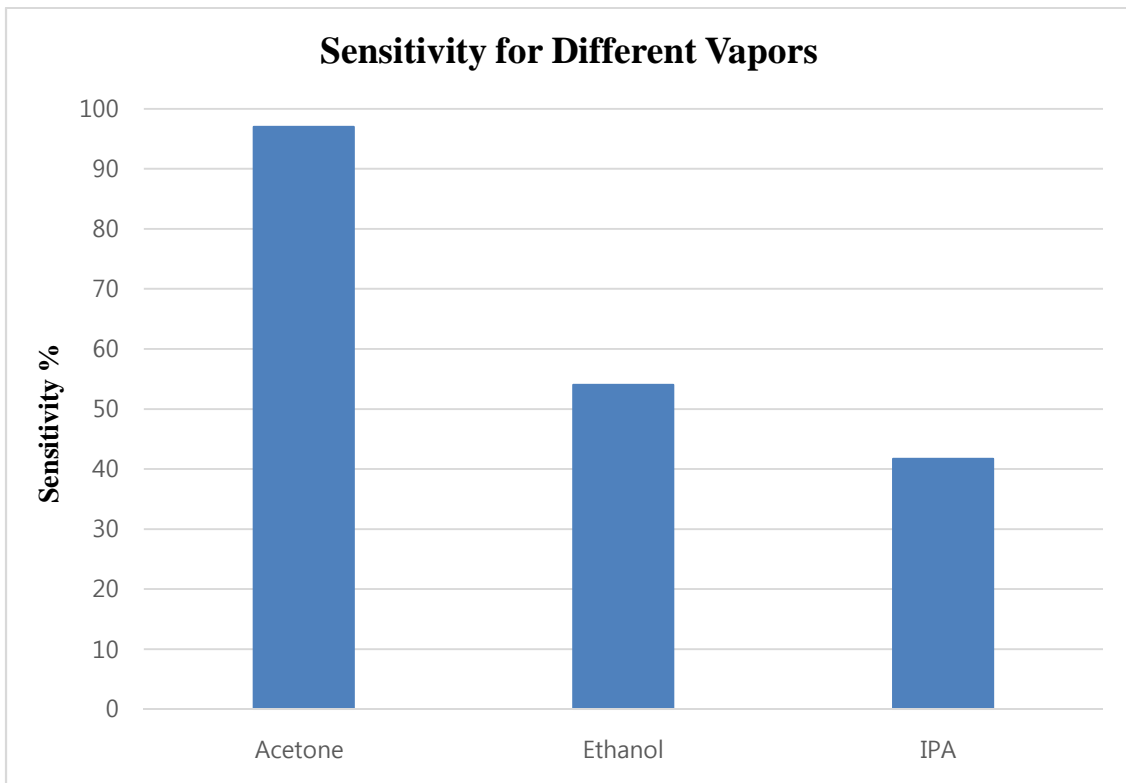


Fig. 7: Sensitivity for Acetone, Ethanol and IPA of ZnO NTs based device

One of the achievements of our work is to produce ZnO nanotubes based gas sensor with very high sensitivity or efficiency at room temperature as compared to previously reported work. In Fig. 8 the comparison of our work with reported ZnO nanotubes based gas sensors sensitivity has been shown.



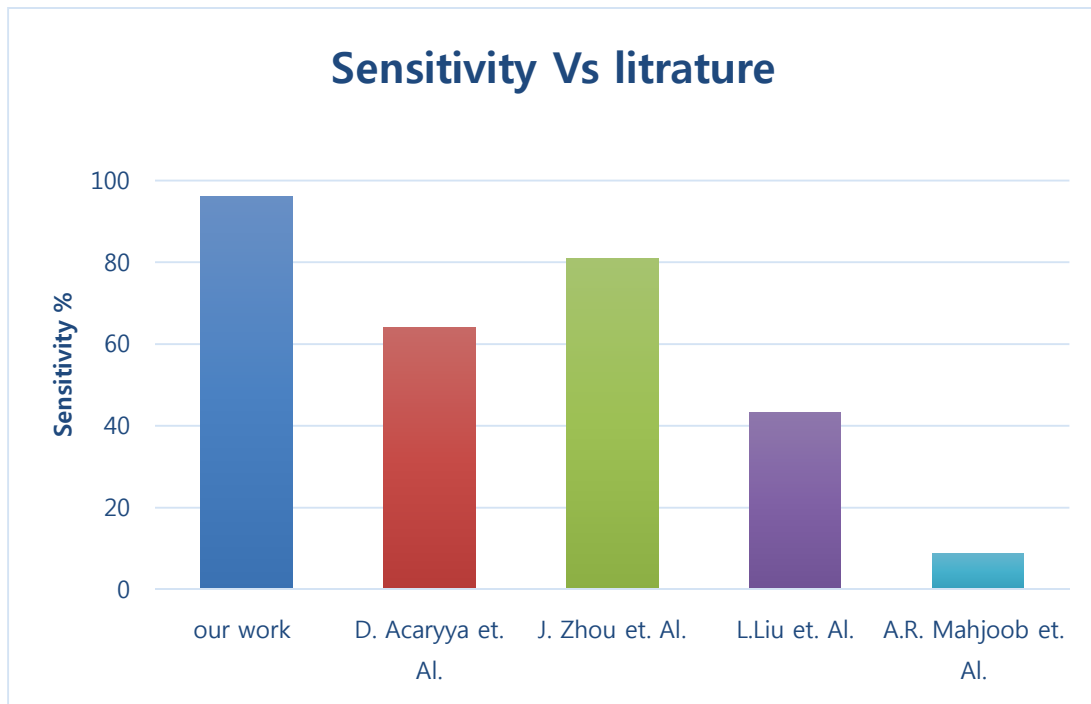


Fig. 8: Sensitivity of Different Sensors with Literature Review

#### 4. CONCLUSIONS

ZnO nanotubes based gas and chemical vapors sensor had been fabricated and characterized for acetone, isopropyl alcohol and for ethanol. ZnO nanotubes were synthesized by template assisted sol-gel growth technique. Anodic Aluminum Oxide (AAO) with pore size of 200 nm, was used as template for this purpose. Vapor sensing performance of device had been done using various repeated times for acetone, IPA and ethanol, and the sensitivity of device had been measured. Our device showed a very high sensitivity for acetone vapors compared to other vapors. The measured sensitivity for acetone, IPA and ethanol was 97, 41.7 and 54, respectively. Response time and recovery time of device was normally average of 15 and 20 min, respectively. The main advantage of our device is its working ability at room temperature.

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