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Gas Sensitivity of ITO Composite Prepared by Sol-Gel Method

Abstract- *Indium oxide and indium tin oxide composite (ITO) were prepared by sol-gel dip-coating (SGDC) technique. The particles annealed at (200 ˚C, 400 ˚C). The structure and surface morphology of particles were characterized by X-ray diffraction (XRD), Atomic Force Microscope (AFM), FT-IR and UV/visible measurements. The XRD and AFM indicate decreasing in the particle size and improve of optical and electrical properties of composite with increasing of tin oxide addition. The hall measurement were used to obtain information about the type of conductivity of indium oxide and indium tin oxide thin films and carrier concentration and mobility and resistivity, the results of Hall measurements show that the In_2O_3 and ITO composite have n-type. The thin film of composite ITO at composition (80:20) mole ratio has high sensitivity toward CO gas compared with pure indium oxide.*

Keywords- *Indium oxide, Indium tin oxide composite, sol-gel, XRD, AFM, sensor.*

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1. Introduction

Composite thin films are prepared by combining two or more different substances in order to enhanced properties and structures. Composite films made up of either mixed metal oxides, metal-metal oxide, polymers mixed with metal oxides or metals, were prepared and examined for their application as active materials for gas sensors[(1)]. Metallic oxides like (In_2O_3, ZnO, TiO_2, and SnO_2) are commonly utilized as the sensing matters in chemical sensors, and their gas sensing properties have been studied for more than four decades[(2)]. In_2O_3 –ITO thin films have been prepared by metal organic chemical vapor deposition [(3)], sputtering, laser deposition and sol – gel method. The sol –gel method offers many advantages such as highly homogeneous thin films, large area coating, absence of the need for vacuum, low cost, and high flexibility [(4)]. In this paper, by using sol–gel method, In_2O_3 – ITO thin films were fabricated and their electrical and optical properties were investigated for several atomic ratios of In_2O_3: ITO (80:20 and 60:40) mole ratio**.**

2. Experimental

*I. Preparation of Indium Oxide particles***.**

Indium oxide particles were synthesized by the sol–gel method. Indium nitrate monohydrate ($In(NO_3)_3.H_2O$) (0.3 M) dissolved in distilled water and the solution was stirred in glass beaker with the help of a magnetic stirrer at 25 ˚C for 20 minute to ensure completely dissolved. Meanwhile, 0.6 M of sodium hydroxide (NaOH) was dissolved in distilled water in another glass beaker with the help of a magnetic stirrer at 25 ˚C for 20 minute to ensure completely dissolved. The basic solution (NaOH) was slowly added in drop by drop (3 drops in minute) to the $In(NO_3)_3.H_2O$ solution under constant stirring until the pH up to more than 8, and precipitation occurred. The precipitate washed with distilled water (about 5 times) and then with ethanol (2 times), and then the precipitate was dried in oven at 200 ˚C for 90 min (white precipitate), and yellow precipitate convert when annealing at 400 ˚C. The general reaction equations are:

1. $2In(NO_3)_3.H_2O+6NaOH \rightarrow 2In(OH)_3+ NaNO_3+ 2H_2O$

2. $2In(OH)_3 \rightarrow In_2O_3 + 3H_2O$

The final equation is:

3. $2In(NO_3)_3.H_2O + 6NaOH \rightarrow In_2O_3 + 6NaNO_3 + 5H_2O$

II. Preparation of SnO_2 particle

The particles of tin dioxide was prepared by the method of sol-gel. In a typical procedure, (0.44 M) stannous chloride dihydrate ($SnCl_2.2H_2O$) solution was stirred with a magnetic stirrer for 20 min in the beaker, the solution becomes colorless. Ammonium hydroxide (NH_4OH) was slowly added (3 drops/minute) until the final solution has

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a pH value (up to more than 8). The mixture was washed with distilled water to get rid of unwanted soluble salts, centrifuged, about (5 times) and then with ethanol absolute (2 times), and finally dried at 200 °C for 90 min after this the precipitate becomes pale yellow powder of tin dioxide. The general suggested reaction between stannous chloride dihydrate and ammonium hydroxide solution are:

1. $SnCI_2 \cdot 2H_2O + 2NH_4OH \rightarrow Sn(OH)_2 + 2NH_4CI + 2H_2O$
2. $Sn(OH)_2 \rightarrow SnO + H_2O$
3. $SnO + 1/2\ O_2 \rightarrow SnO_2$

The overall equation is:

$SnCI_2 \cdot 2H_2O + 2NH_4OH + 1/2O_2 \rightarrow SnO_2 + 2NH_4CI + 3H_2O$

III. Solution preparation to deposited thin film

ITO thin films at different compositions In:Sn (80:20 and 60:40 mole ratio) were deposited by the sol-gel dip coating. SnO_2 and In_2O_3 oxides were dissolved in mixed solution of poly ethylene glycol (2-4 drops) and distilled water. The two solutions were mixed (at 60 °C) and stirred for 2 hours, as shown in table (1). The films were obtained by dipping quartz glasses in SnO_2/In_2O_3- solution and then they were dried at 200 °C.

Table 1: The amount of SnO_2 and In_2O_3 and their mole ratio.

In_2O_3 solution Mole	SnO_2 solution mole	Mixture solution (ml)	Ratio%(In_2O_3/ SnO_2)
0.80	0.20	20	80
0.60	0.40	20	60

The thin films forming via deposited by dip coating technique. The quartz substrate is immersed in the dispersion and then withdrawn at a constant speed. The substrate stayed in the solution (about 30 sec) and then dried for 5 minute at 100 °C. The thickness of the film can be controlled by the number of the dip, the number of dipping about (10- 25 time).

3. Results and Discussions

I. Analysis of XRD of particles

For characterization of indium oxide, X-ray diffractometer using Cu-Kα radiation (λ = 1.54050 °A). XRD spectra were recorded by scanning 2θ in the range (20–60) deg. X–ray diffraction measurement has been done and compared with the JCPDS cards no. (21-1272) for In_2O_3. X-ray diffraction was used to determine the phase structure of the as-synthesized $In(OH)_3$ and its thermally manufactured products (In_2O_3). Figure (1- a) show the diffraction patterns of $In(OH)_3$ at (200°C) are occurred at 2θ values of approximately 22.4493, 31.9450, 51.4601 and 56.5230° corresponding to (200) ,(220) ,(420) and (422) respectively. All the diffraction peaks of these XRD patterns could be perfectly indexed to those of body-centre cubic $In(OH)_3$ according to the (JCPDS Card No. 01-076-1463). Whereas at (400°C) four diffraction plans appears for indium oxide (211), (222), (400) and (440) located at 2Θ= 21.5644, 30.6921, 35.5649 and 51.0914° respectively, as shown in figure (1- b), that are close to the values of the reference data JCPDS card (no: 06-0416). All the spectra show that particles are polycrystalline with a cubic structure and the final products exhibited excellent crystallinity. By the heat treatment to the atoms the defects and the grain boundaries in the In_2O_3 decreasing and this lead to decreases (FWHM) of the reflection peaks and the crystallite size of the particles increases, as shown in, this contribute to the improving the crystallinity of particles[5]. The lattice constant increases with annealing temperature, this could be attributed to increasing in interplanar distance (d) due to excess oxidization process. Table (2) shows all the obtained results of the XRD measurements of indium oxide. The lattice constant close calculated values to the standard lattice constant of $In(OH)_3$ and In_2O_3 (a_o=7.974 and a_o =10.117 Aº respectively).

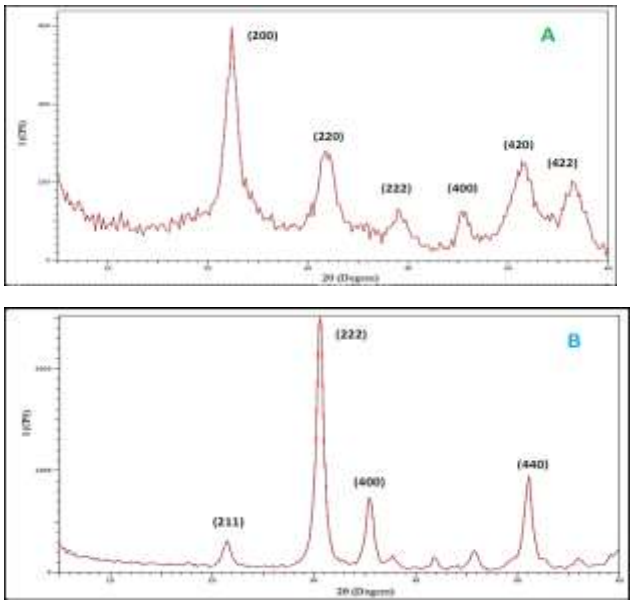

Figure 1: XRD patterns of the particles (a): $In(OH)_3$ at 200 °C (b): In_2O_3 at 400 °C

Fig.(2 a and b) show the X-ray diffraction patterns ITO particles annealed at 400 °C at different compositions (In:Sn=80:20, 60:40) mole ratio. The strongest peaks of ITO (20% mole SnO_2) particles appeared approximately at 2Θ= 21.539, 30.638,

35.484 and 51.083° which are corresponding to (211), (222), (400) and (440) respectively. When at concentration (40% mole SnO_2) four different located peak appears at 2Θ= 21.577, 30.701, 35.550 and 51.158° corresponding to reflection planes (211), (222), (400) and (440) respectively.
None of the spectra indicated any characteristic peaks of SnO_2, which means that the tin atoms were doped substitutionally into the In_2O_3 lattice and this agree with reference[6]. The results show polycrystalline of ITO structure according to the (JCPDS card no:06-416) and the ITO particles shows high intensity diffraction peak in plane (222) and this agree with reference [10]. From the results we notice when the content of SnO_2 in In_2O_3 augment the FWHM increases and the main grain size decreases whereas the lattice constant decreases because addition SnO_2, and this agree with reference[7]. The values of the FWHM and the main grain size(G.S) and interplanar distance (D) of the samples are given in the Table (3).

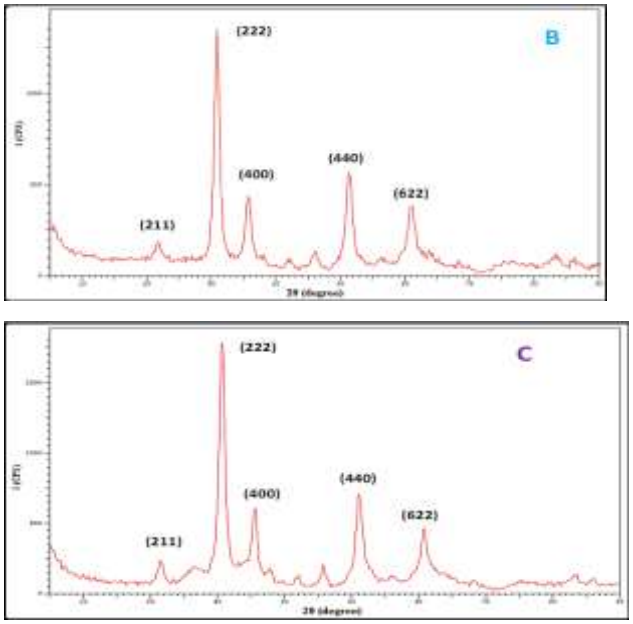

Figure 2: XRD patterns of the particles (a):ITO 20% (b): ITO 40% mole at 400 °C

II. Fourier Transform Infrared Spectroscopy (FTIR).

FTIR is a powerful tool for the identification of the molecular mechanism associated with the formation of the oxide. FTIR spectrum of the prepared material ($In(OH)_3$) show a large absorption band around 3500 cm^{-1} characteristic of OH stretching absorbed water, because of the difficulty of removing the water residue completely[8]. Two main intense peaks centered at 775 and 503 cm^{-1} were observed, which is characteristic of the In-O(H) and In-O stretching respectively. The most prominent absorption bands detected after thermal annealing at (400°C) are quite similar, with the main absorption bands at 3420 cm^{-1} due to water and low wave number bands (601, 567, 540, 491 and 457 cm^{-1}) which are due to the indium-oxygen bond. These results are in general agreement with those of thermal analysis[9].

The peaks at 3421, 1629 cm^{-1} of the ITO (20 % mole) annealed in 400 °C correspond to stretching vibration and bending of O–H band respectively. The absorption peak of Sn-O is near to 1150 cm^{-1} , while peaks at 781-430 cm^{-1} corresponding to (In-O) stretching . While the peaks at 3448 and 1633 cm^{-1} of the ITO (40 %) annealing in 400 °C, correspond to stretching vibration and bending of O–H band respectively. while peaks at 775-430 cm^{-1} corresponding to (In-O) stretching .

III.The Results AFM of In_2O_3 and IZO Particles

The surface morphology of In_2O_3 particles preparation by sol-gel method (annealed at 400 °C) was analyzed by using atomic force microscope. Figure (3) shows images 3D and the granularity accumulation distribution chart of In_2O_3 particles annealed at 400 °C. The average grain size was (96.6 nm).

The AFM images 3D and the granularity accumulation distribution chart of ITO (20% and 40% mole ITO) annealed at 400 °C are shown in Figures (4- a and b). The average grain size of ITO is about (86.97-94.44 nm). The AFM results of ITO show that has a smaller particles diameter compared with pure In_2O_3. This may due to the rearrangement of atom and reduction in the vacancy defect. These results agrees with reference[10].

IV. Optical Properties

Optical transmission data is more important in evaluating the optical properties of metallic oxides thin films. High transparency in the visible region is required in application for optoelectronic devices [11].

1. Transmittance Results of (In_2O_3 and IZO)

The effect the different annealing temperature (200 and 400 °C) for (90 min) on In_2O_3 thin films is shown in figure (5-a), that the films have high transmission reach to 68.6%. With the increasing annealing temperature the transmittance is slightly increased within this spectral range, this result agrees with reference [12] . The optical transmittance spectra of for ITO at different compositions (In:Sn=80:20 and 60:40 mole) and were annealed at 400 °C. The figure (5-b) show the samples are highly transparent in the visible region of films ITO (20 and 40%) is about (67.6-73.6 %) this result agrees with reference [10].

Table 2 : The XRD results of indium oxide particles.

Annealing Temp. 90min	2θ (deg)	hkl	FWHM (β) (deg)	Grain Size (A°)	Lattice constant (A°)	d (A°)
200 °C As-prepared	22.4493	200	1.5794	51.280326	7.914459	3.95722
	31.945	220	1.9994	41.328914	7.917615	2.79929
	51.460	420	2.6985	32.679875	7.935119	1.77434
	56.5230	422	2.42340	37.218146	7.969824	1.62683
400 °C	21.5644	211	0.9438	85.68619	10.08595	4.11757
	30.6921	222	0.8439	97.61838	10.08280	2.91065
	35.5649	400	0.8732	95.54383	10.08894	2.52223
	51.0914	440	0.9498	92.70432	10.10473	1.78282

Table 3:The obtained results of the XDR for ITO particles at 20 , 40 % mole at annealing temperature 400 °C.

Samples	2θ (deg)	hkl	FWHM (β) (deg)	Grain Size (A°)	Lattice constant (A°)	d (A°)
SnO_2 20 % mole	21.5393	211	1.1328	71.38705	10.09757	4.12231
	30.6382	222	1.0565	77.96453	10.10012	2.91565
	35.4844	400	1.1137	74.89458	10.11109	2.52777
	51.0836	440	1.1829	74.43377	10.10617	1.7865
SnO_2 40 % mole	21.577	211	1.037	77.9868	10.08013	4.11519
	30.7015	222	1.0957	75.18664	10.07979	2.90978
	35.5506	400	1.0837	76.98213	10.09287	2.52321
	51.1583	440	1.2631	69.72936	10.09241	1.784103

2. Hall Measurements of (In_2O_3)

The hall measurement were used to obtain information about the type of conductivity of indium oxide thin films and carrier concentration and mobility and resistivity. The thin films annealed at different temperature (200, 400 °C) for 90 min, the results indicated to that the indium oxide have conductivity (n–type). On the other hand we noticed the carrier concentration increases versus increasing annealing temperature and this agree with reference[13]. Meanwhile the Hall mobility and Hall coefficient decreases with increasing temperature as shown in table (4). The decreasing of Hall mobilities can be explained by scattering in semiconductors [14]

3. Hall Measurements of (ITO)

The results of Hall measurements show that ITO at composition (In:Sn 80:20 and 60:40 % mole) have a negative Hall coefficient (RH) values which confirm that the ITO particles are n-type semiconductors. The hall coefficient value decreases with increasing the additive metallic oxide (SnO_2) into indium oxide. All data related to the Hall measurements are listed in table (4).

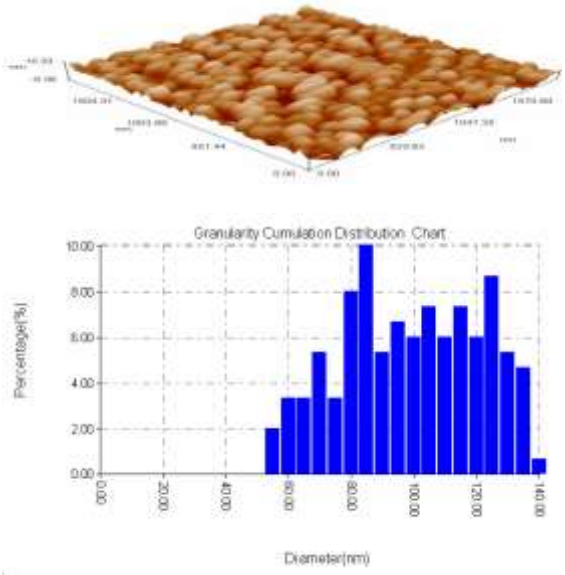

Figure 3: AFM images 3D and B- granularity cumulation distribution chart of In_2O_3 annealed at 400 °C.

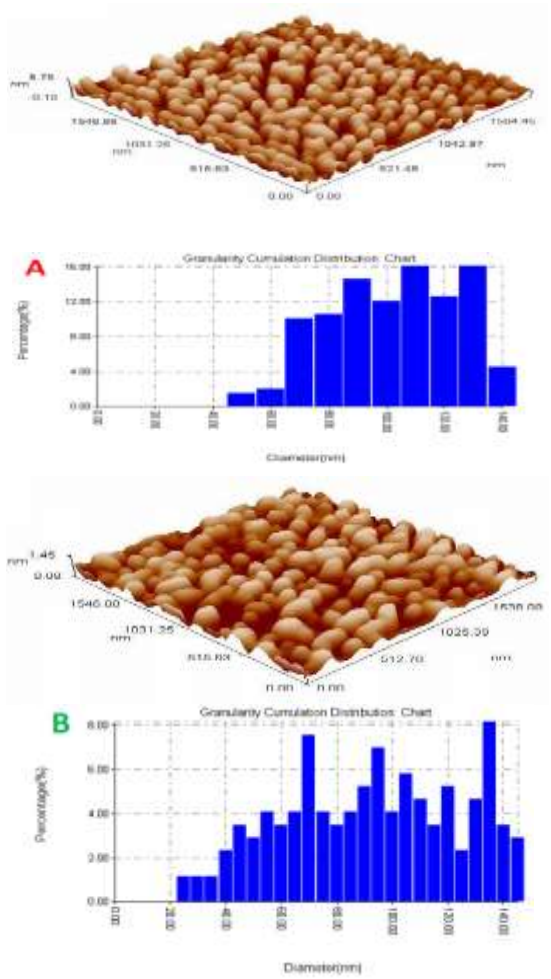

Figure 4: AFM images 3D and Granularity accumulation distribution chart of ITO particles (a) ITO 20% (b) ITO 40% annealed at 400 ˚C

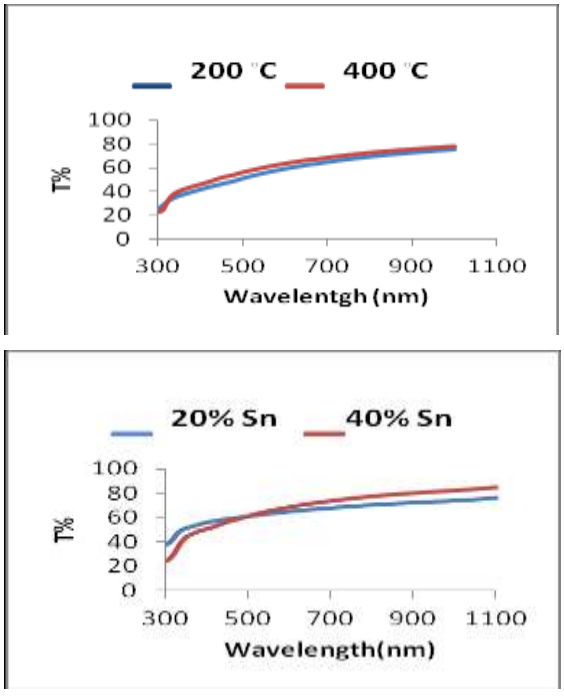

Figure 5: UV-VIS transmittance spectra of In_2O_3 thin films: (a) at different annealing temperature (200 and 400 ˚C), (b) at different compositions (20 and 40%mole) with Tin Oxide.

Table 4: The obtained results of Hall measurement of In_2O_3 and ITO.

Sample thin	R_H (cm^3/C)	μ_H ($cm^2/v.s$)	Carrier concentration (cm^3)
In_2O_3 pure	1.5×10^6	3.4×10	4.05×10^{12}
In:Sn =80:20	1.2×10^6	1.2×10^4	4.8×10^{12}
In:Sn 60:40	6.8×10	6.8×10^2	2.8×10^{17}

V. Sensing Properties

The sensing properties of In_2O_3, ITO thin films for CO gas were studied as function to operating time at temperature 50 ˚C. The films have been deposited on quartz substrate by dip coating technique. The concentration of CO gas was (5ppm).

The sensitivity for CO gas via In_2O_3, ITO thin films is calculated by measuring variation of resistance of the films in air and in presence gas at temperature 50 ˚C**.** The resistance of surface change in presence gas versus over certain time range is measured by using equation (1)**.** the sensitivity of indium oxide is found to be maximum when the annealing temperature was 400 ˚C.

$$S = |[(R_g - R_a)/R_a] \times 100\%| \quad \ldots(1)$$

Where (R_a) and (R_g) are the electric resistance of the sensor in air and in presence of gas respectively.

The sensing materials have to be annealed at various temperatures to achieve crystallization and structural evolution. A sufficient degree of crystallinity is required to attain the desired electronic properties for gas sensor application. It is observed that the sensitivity increases from 200 to 400 ˚C and then decreases with the further increase in the annealing temperatures. It is shown that the maximum sensitivity of (87%) to CO at annealing temperatures 400. The results agree with reference [15]. The sensitivity of ITO thin film at concentrations (20% mole SnO_2) and annealed at 400 ˚C increases compared with pure indium oxide as shown in Fig (6). This may be due to excess in the additive contained lead to decrease in the grain size. Consequently an increase in adsorption and increasing in sensitivity [16,17] can be detected.

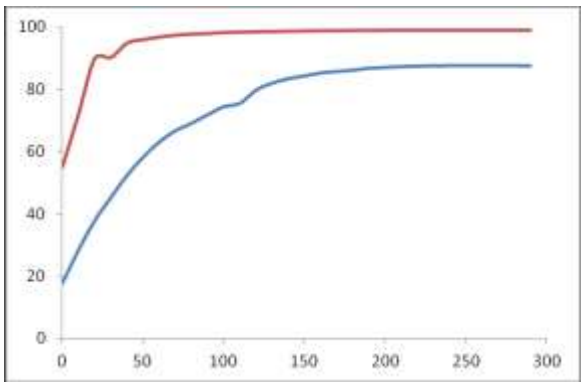

Figure 6: Sensitivity of In_2O_3 and ITO thin films annealed at 400 ˚C for CO gas.(where X-axis is sensitivity and Y-axis is time(sec)).

4. Conclusion

Based on the results of this study, the main conclusion can be summarized as follow :

The XRD indicated to that the In_2O_3 and ITO particles have polycrystalline structure with strongest peak (222) and good crystallinity which increases with the increase of annealing temperature. Meanwhile the results of AFM shows that the grain size increases with increasing annealing temperature. The results of Hall measurements showed that In_2O_3, ITO thin films have a negative Hall coefficient (RH) values which confirm that films are (n-type). The thin films were used as gas sensor for carbon monoxide, best sensitivity of pure In_2O_3 thin films to CO gas can be obtained at annealing temperature 400 ˚C. The best sensitivity obtained of composition (In:Sn=80:20 mole) which is higher than pure In_2O_3.

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