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Effect of Nitric Acid Concentration on the Optical Properties of Titanium Dioxide Nanoparticles TiO_2

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ABSTRACT

A sample of TiO_2 nanostructured was prepared using 8 molarity concentration of HNO3 diluted acid the preparation had been done by depending on hydrothermal method and using autoclave reactor with 100cc Teflon volume, at temperature (140 ˚C), duration (10 h). The optical properties, morphology and crystal structure of the nanostructure synthesized was investigated by using Field Emission Scanning Electron Microscope (FESEM), UV-V scanning, and the results revealed that the prepared specimen was rutile phase at mentioned acid molarity, temperature and duration, the morphology imaging of this sample tell us that the mean radius of the TiO_2 nano particles was about (117.1-148.3 nm).UV-V results revealed that TiO_2 nanoparticles have indirect allowed band gab about 3.2 e.V and have refractive index about 1.1 -1.5..

1. Introduction

The Titanium dioxide-nanoparticles have a large area of interest as they have a large number of applications[1]: nonlinear-optics, spectrally selective coating for solar energy absorption, intercalation-materials for electrical batteries- optical-receptors, catalyst in-chemical reactions, antibacterial materials, paining optical materials, photonic devices, gases sensors, cosmetics,etc... [2].

TiO_2 chemically stable material and good electrical semiconductors [3]. The prepared composite have many crystal structure: Anatase , rutile and brookite, the rutile form is the most chemically stable of than the another's structures but when it comes to Nano- sale range anatase is the most stably formation the two others phases, because of the higher surface energy is needed when Rutile is starting to formation[4] As well known that the Anatase has the best Solar- Electric Conversion Efficiency(SECE) and photocatalytic than Rutile type because of it's special electronic structures as larger band gab and fast electron mobility [5].Photo - catalytic performance are affect by some factors like crystallization process, by composition , grain-surface properties , crystallinity, morphology and particles sizes[6]. Rutile phase has better photo activity for optical - electronics

applications depends on some modifications , and have higher refractive index that provide slight scattering inside the crystal structure planes[7]. There is many methods we can use such as sol-gel, precipitation, anodization, and hydrothermal method to prepare a various morphologies of oxide or dioxide nanostructures[8]. Hydrothermal is the preferred feasible method especially in this research because it give a best controlling ability of morphological and crystallization information properties just when replacing conditions of preparation like durations, Solvent kind, temperature, and atmospheric pressures, and addition to that different types of phase and morphological scales can be prepared at just one step using strong acid and low temperature with hydrothermal method[9].

2. Materials and theoretical method's

There is so many different methods for preparing chemical composites, every method of those is specialized for preparing a particular structure, but here we will depend on the most common using preparing method for Nano – materials that method is called the hydrothermal method it is depend on a solutions reactions – based approach [10].Hydrothermal method is have many advantages and the import one which very useful in reactions is that we can prepare the nano particles under a wide range of temperature from rooms temperatures to extreme temperature [11].If we wont to controlling the morphological structure and do a surfactant to the obtained nano grains either lower pressures or higher pressures can be applied to the reactor depending on the vaporing pressures of the main composition with the reactor, there is magnificent features of mentioned and used preparation method comparing to others where it can generate nanomaterials that aren't stable at increased temperature .Nano – structured in high vapor pressure can be produced by hydrothermal autoclave with minimizing the losing in the raw material [12]. To Prepare Titanium dioxide we already had been using row materials (precursors) that we need to make the appropriate reaction so that give us a pure TiO_2 and this materials is as :

1- Titanium -Tetra-Iso -Propoxide (TTIP).
2- Nitric acid (HNO_3) has 65% concentration and the molarity is 16 M.
3- Distilled water.
4- Ethanol.
5- Ethylene glycol (EG).

2.1. Sample preparation

At first we poured 25 cc of nitric acid with 25 cc of deionized water inside a beaker, this process makes the nitric acid diluted, After that we added 2.5cc of TTIP (Titanium Tetra Iso-Propoxide), inside the beaker that full of diluted acid H2O=25 cc, and HNO3= 25 cc, (table.1 show all the information about the needed precursors), and stirred the mixture by magnetic stirrer which is designed for mixing fluids of different viscosity with the help of a stir bar that spins very quickly[13]. for 15 minutes to dissolving the TTIP completely, after that we poured the clean and transparent solution inside the Teflon of 100 cc volume and put in the autoclave that we closed with hand and wrench, then transferred to the furnace and left for 10 hour at temperature of (140°c), and after that cooling down (getting cold) to room temperature, we opened the autoclave and after that wished and centrifuged with the deionized water and ethanol for several times to remove other materials from the main product .After wishing we drying the product with putting in oven at 70 °c for 12 hour. After drying we calcinated the product in oven at 700°c for 12 hour. In this synthesis we add ethylene glycol as a surfactant, where the surfactant is a material that limit growth of particles in some directions[14].

Table.1 shows the precursors used to prepare the specimen of TiO_2

Material	Amount	Type
TTIP	2.5 cc	-

HNO_3(diluted to 8 M)	25 cc	Acid
Distilled water	25 cc	-
Ethylene glycol(EG)	0.055 cc	Surfactant

3. UV-V and FESEM Characterization

Optical properties are a measure of a substance's interaction with light, and include, Refraction index, reflection, absorption, polarization, and transmittance. Since light is electromagnetic waves most optical phenomena can be calculated using the classic electromagnetic description of light [15].The absorbancy and transmittances spectra Ultra Violet-Visible were calculated with using (Shimadzu -Japan's, Model 1800.0) calculation wave length was in the range(190. to 1100.) nm, to characterize these optical properties of TiO_2 nanoparticles, and so Field Emission Electronic Microscopy (FESEM -Nova Nano sem),Operating voltage magnitude used at value of(18 K.V) to obtain information about the morphology of the nanostructure.

4. Results and discussion

4.1. UV-V analysis

Figure (1) shows the UV–vis transmittance spectra of TiO_2 nanoparticles prepared at 140 ˚C where the figure shows a small transmittance at short wave lengths where the transmittance is 17% at this 384nm edge(smaller value of T at these wave length), and start to increasing after this value up to 55% at 1050nm. If a Semi –conductor structure composite absorbing a photonic beam that carrying a magnitude of energy at the same of its optical band-gab E_g or greater that that value some of electrons in the electronics levels will do transitions from Valence band (VB) moving to Conducting band (CB).[16]. Figure (2) show absorption and as well known the absorbance is inversely proportional with transmittance [17].As shown in fig 2 the absorbance have a higher percent at 384 nm which is about 80% and after that starting to decrease as the wave length decrease where absorbance dimensioned to 27% at the greatest wave length 1100nm.

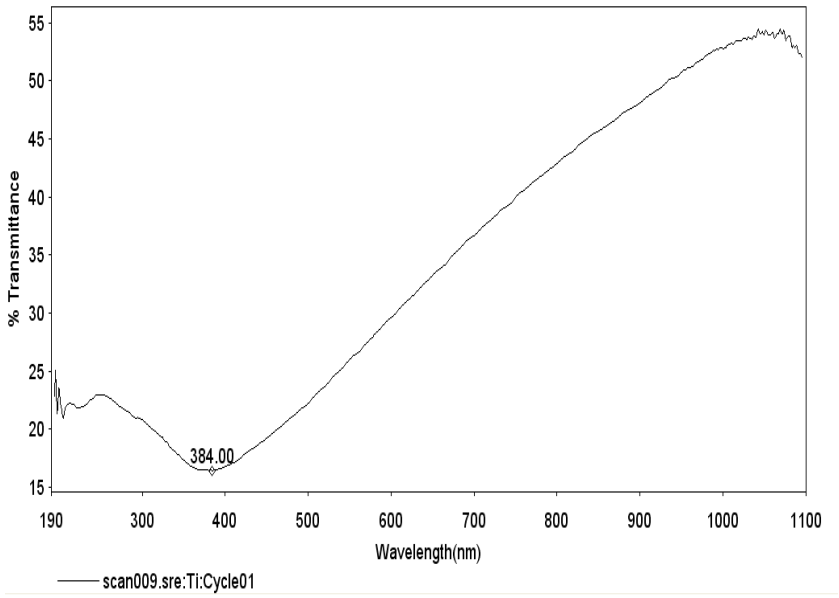

Figure.1: UV-V transmittance spectra

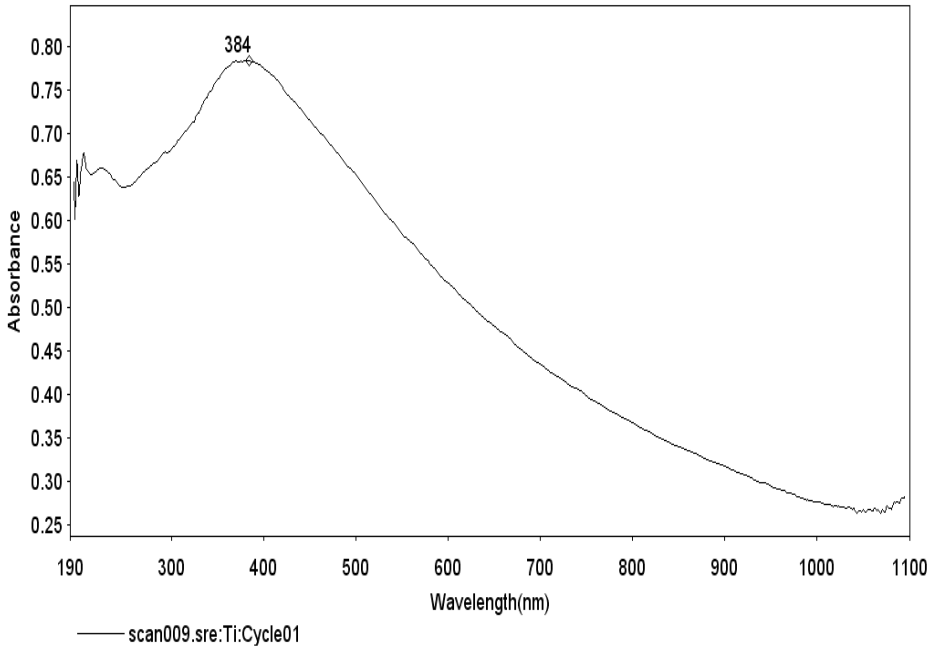

Figure.2: UV-V absorbance spectra

Refractive index have relationship is shown in fig (3)it is variant depending on wave length where it non-linear and have less value 1.1 at 384nm and greater value 1.5 at 800nm, this result of refractive index (n) agree with the studies of research [18].

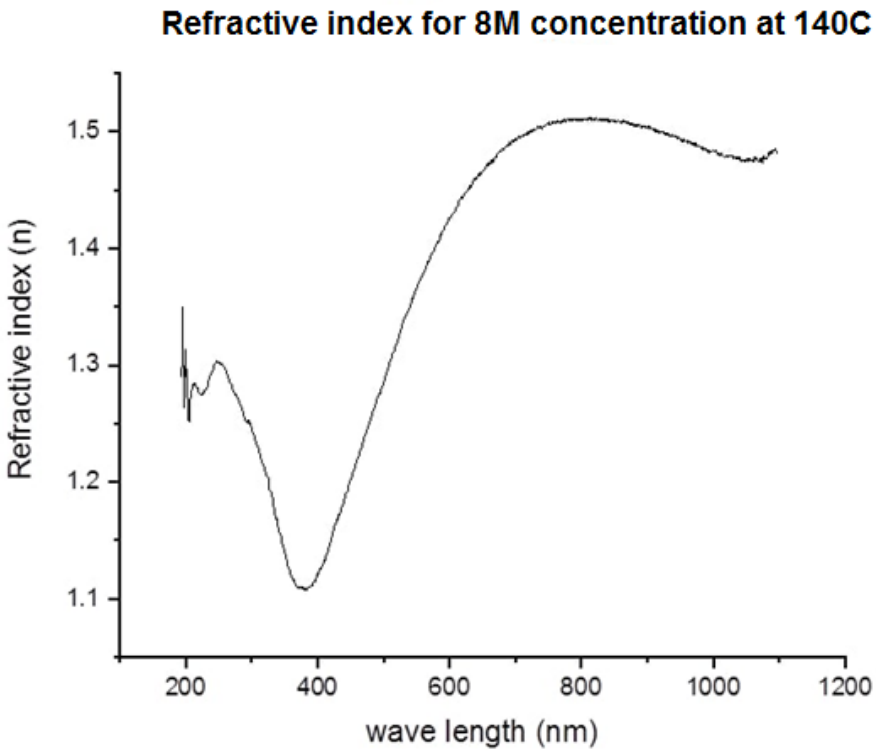

Figure .3Refractive index for specimen prepared of 8M HNO3 concentration=140C,using origin software.

The optical energy band gab E_g could be measured for the prepared sample of TiO2 if we applied the experimental T-auc relation which states [19]:

$(\alpha hv)^n = A(hv - Eg)$ ……..(1)

in this relation α, is the extinction coefficient, h is the constant of plank, v is the frequency of the light waves measured in Hz, A is the absorbent waves constant and it equals to one (A= 1), (hv) is the photonic energy, and E_g is the optical band gab, and (n) number is taking many values its depend on the transition position, when the transition is indirect and allowed n =2, for direct allowed transitions n = $\frac{1}{2}$, but when the transition is indirect and forbidden it will be (n) = 3, and n = $\frac{3}{2}$, at direct forbidden transitions [20]. By plotting $(\alpha vh)^n$ versus the photon energy (vh), the band gap energy of the prepared specimen can be obtained by Tauc method, where the intercept of the tangent to this plot will be given a good approximation of Eg in eV for the prepared sample as shown in figure (4). In this work, the n was took the value (2) indicating the indirect allowed transition between the bands so equation (1) will be in that case as below:

……..(2)) $\alpha hv)^2 = A(hv–E)$

Indirect band gab Eg was equal to 3.2 e.V calculated by taking the extrapolation of curve $(\alpha hv)^2$ versus hv using origin program, that value of band gab was agree to the standard value of E_g which mentioned in the studies of research [21].

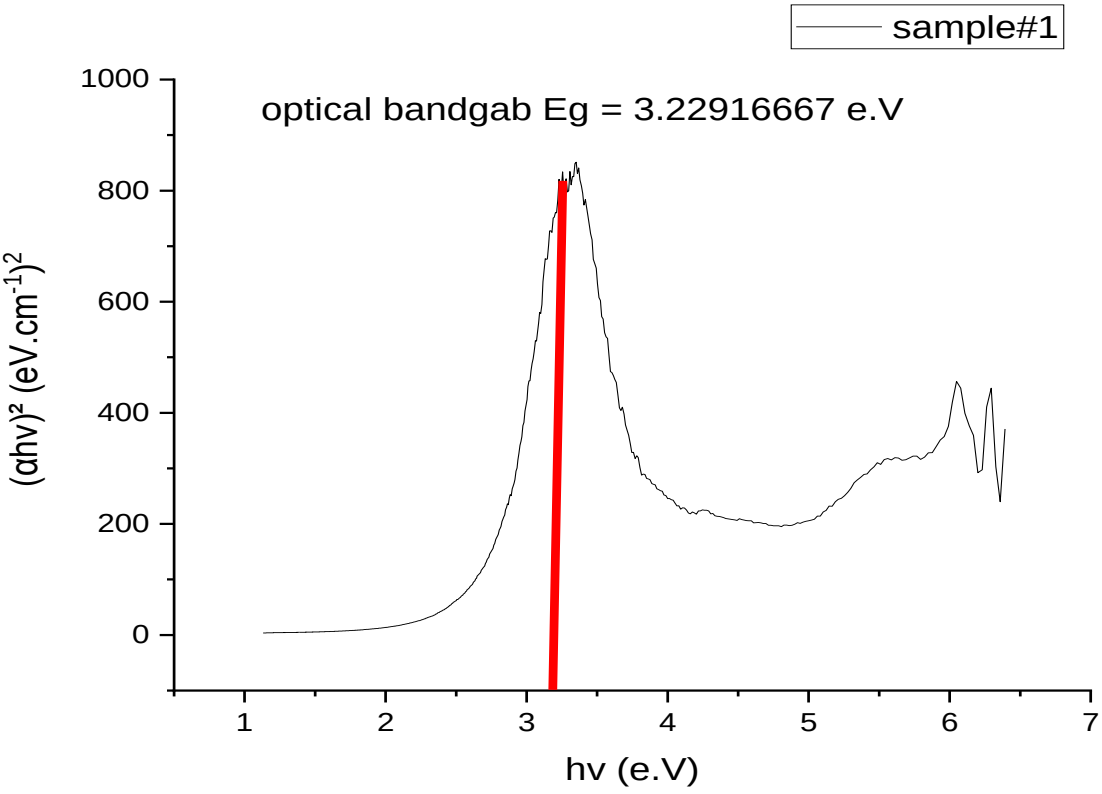

Figure. 4 (αhv)2 versus hv show direct band gab energy

4.2. FESEM Analysis

The represented FESEM Images for titanium dioxide nano-particles prepared, with assisting of strong acid HNO3 using hydrothermal preparation as can see in figure.(5). The scanning electron microscopy tests showed that the morphological information of synthesizes specimen have an irregular semispherical nano structure particles (3D structures. The imaging reveals that the nano grains have a different diameters and length of the grains with average range for length (117.1 –

148.3 nm) respectively at 8 M concentration of HNO3 and 140 ˚C temperature heating, these data were calculated by (Image.j.program). Moreover due to a chelating properties of the (EG, O-H Groups), so fast growth with a slower nucleation rate of the crystal building favor the rolling process of the titanium dioxide layers with a three dimensions structure like as Nano grains, these results about morphological information are all comes to agree with the results in research [22].

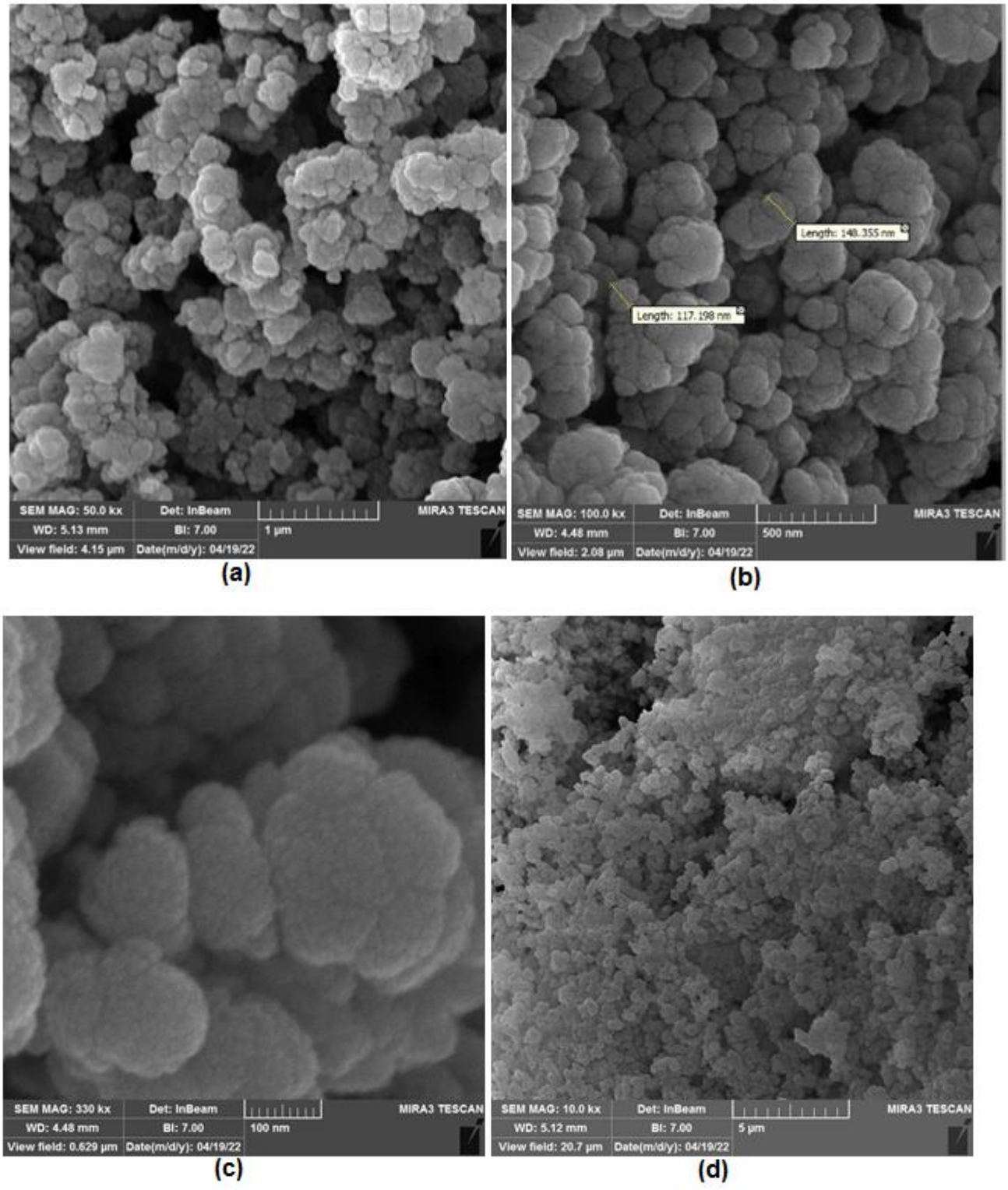

Figure. 5 FESEM Images for TiO_2 nanoparticles specimen prepared at 8M concentration of HNO3, Temperature = 140 ˚C, Heating time (T)= 10h, Where (a) image of morphology surface at 1 micro meter zoom,(b) at 500nm zoom, (c) at 100 nm zoom, (d) at 5 micrometer.

5. Conclusion:

The prepared sample have a stable rutile structure when it have little heating time while the heating more than 10 h can producing another phases(anatase, brookite), rutile is the most stable phase and have an irregular spherical 3D structure and the nano particles of TiO_2 have indirect allowed band gab 3.2 e.V which is good semiconductor and high refractive index can reach to 1.5 and also the nano particles is a transparent having a little transmittance at low wavelengths and high absorbance at low wavelengths .

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