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# Synthesis and Characterization of ZnO Nanoparticles

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## ABSTRACT

ZnO nanoparticles with particle size less than 50nm are synthesized by simple sol gel method. These nanoparticles can be used as a source layer for the extraction of electrons in heterojunction organic solar cells. Zinc acetate is used as a precursor material in this case. X-Ray powder Diffraction, Ellipsometery and Scanning Electron Microscopy are used to study the crystal structure, optical properties and surface morphology of the synthesized nanoparticles, respectively. The presence of (100), (002) and (101) planes in the XRD graphs strongly indicates that ZnO has wurtzite structure even under as-synthesized conditions. Surface morphology was studied by SEM which indicates that the nanoparticles are of spherical shape with size less than 100 nm. Large area growth of these nanoparticles is also observed with uniform size distribution. A remarkable decrease in the transmission values is observed by increasing the pH from 2 to 9. Refractive index ~ 1.5 is observed at 350nm for all of the samples except the one synthesized with pH 9.

## 1. INTRODUCTION

Zinc oxide is a direct band gap II-VI semiconductor having band gap energy of 3.37eV and it has a large exciton binding energy (60meV) which allows the excitonic emission even at room temperature (Lihitkar 2012). Zinc oxide is the topic of interest in these days due to its presence in much unique and important morphology like, nanorods, nanoflowers, nanowires, nanodendrites and nanoparticles (Singh 2012, Ling-min 2012, Cu 2012, Xu 2012, Darroudia 2013). Zinc Oxide nanostructures have gained much interest due to their potential applications in solar cell (Ibrahem 2013), varistirs (Hirose 2012), sensors (Rai 2012, Erola 2010) and in piezoelectric devices (Kumara 2012). Among these nanostructures zinc oxide nanoparticles gained researchers interest due to their quasi one dimensional structure. These nanoparticles have diameter in the range of tens of hundreds of nanometer. This reduction in size changes and improves its physical properties hence gives different results as compared to the bulk zinc oxide (Zak 2011).

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ZnO nanoparticles based solar cells provide low cost solar electricity. Zinc Oxide is the important candidate for the extraction layer in organic solar cells due to the reason that its energy levels fit very well to the requirement of an electron injection layer for getting better efficiency. The wide band gap of ZnO ensures high transmittance in the relevant spectral regime as well as its highest occupied orbital states are matched with the work function of the desired material and its valance band is deep below lowest un-occupied orbitals states of the polymers used previously for extraction layers (Stubhan 2011).

Chu (2012) reported that ZnO nanocrystals can be used as electron transport layer in inverted bulk heterojunction (BHJ) solar cell without annealing the samples that can give high efficiency up to 6.7%. Sun (2011) also reported the use of ZnO thin films as electron transport layer in air stable inverted bulk heterojunction (BHJ) solar cell whereas the applied annealing temperature is low. They attained the 6% efficiency. Comparison of the different solvents for different extraction layers is also helpful for making ZnO useful in organic solar cells as Oh (2011) reported the role of solvents and annealing temperature in extraction layers of ZnO nanoparticles by sol-gel method. Li (2012) reported applications of various morphologies of ZnO in Organic solar cells, and gives factors affecting on results obtained by this. Thickness of the extraction layer for electron extraction and for hole extraction is also important for getting the high efficiency of the synthesized solar cell. Stubhan (2011) reported that by using ZnO nanoparticles and Aluminium doped ZnO solar cells gives larger efficiency with compareable thichnesss of the extraction layer as less than 30 nm.

There are various methods for the synthesis of ZnO nanoparticles, like co-precipitation (Kripala 2011), chemical vapour synthesis (Bacsa 2009), Solid state reaction method (Martin-González 2010), sputtering (Li 2010), and sol gel method (You 2012). We used sol gel method for the synthesis of ZnO nanoparticles as by sol gel process we can get controlled stoichiometry preparation of the precursor solutions along with large area growth. Also it is a low cost simple method (Znaidi 2010).

The properties of ZnO nanostructures prepared by sol gel method can be influenced due to many factors like temperature, aging time and pH. The pH of the synthesized sol plays an important role in the morphology of the ZnO nanostructures. As variation in pH influences hydrolysis and condensation behavior of the sol (Alias 2010)

We report here in this paper the synthesis and characterization of ZnO nanoparticles with an average size of particles less than 50 nm. Sol-gel method is used for the synthesis with the variation in pH. Centrifugation is used in order to enhance the properties of the synthesized ZnO nanoparticles.

## 2. EXPERIMENTAL DETAILS

Zinc Oxide Nanoparticles in the form of nanopowder and thin films were synthesized by low cost sol-gel method. Zinc acetate dihydrate [$Zn(CH_3COO)_2.2H_2O$] was used as precursor materials for ZnO sol. Deionized water, IPA (Isopropyl Alcohol) and TEA (Tri Ethyl Acetate) were used as solvents. Zinc Oxide sol was synthesized by the sol gel method as reported somewhere else by (Riaz 2011). We get transparent ZnO sol with pH 6. Thin films of the prepared Zinc Oxide were prepared by spin coating on glass substrates and these substrates firstly were cleaned by detergent, and then in Isopropanol alcohol and acetone by using ultrasonic cleaner. Thin films of desired thickness were obtained by coating at 3000 rpm for 10 sec.

Zinc Oxide nanopowder as shown in Fig. 1 was also synthesized by the same sol-gel method. NaOH was used as precipitating agent in this case as well as to maintain the pH of the sol. In final transparent ZnO sol drop wise addition of NaOH with magnetic stirring at 60°C for 20 minutes gives white milky precipitates. These precipitates were centrifuged and washed with deionized water several times and then dried at 70°C to get ZnO nanoparticles.


Fig.1 ZnO nanopowder with variation on pH

Structural and magnetic properties of the prepared nanoparticles were studied after characterization by X-Ray diffrectometer, Scanning electron microscopy and Vibrating sample magnetometer. Optical properties of the ZnO nanoparticles were studied by JA Woollam Spectroscopic Ellipsometer to calculate band gap, wavelength and refractive index. Rigaku D/MAX-II A X-ray diffractometer operated at 35 kV and 20 mA, using CuKα radiation with wavelength of 1.5405Ǻ in the Bragg's diffraction angle '2Ө' ranging from 20° to 80° was used to study structural properties. The size and morphology of the prepared particles were obtained by using a Hitachi S3400N Scanning electron microscope (SEM). And magnetic properties were studied by Lakeshore 7407 Vibrating sample magnetometer.

## 3. RESULTS AND DISCUSSIONS

### *3.1 XRD patterns*

Fig. 2 illustrates the XRD patterns of ZnO nanoparticles synthesized by the sol-gel method with variation in pH values (2, 3, 4, 7, 8, 9, 10). The samples prepared at pH 2, 3 and 4 have no intense ZnO peaks which is due to the high concentration of H+ ions and low concentration of OH− ions in the prepared sols. Due to the presence of equal no of H+ and OH− ions in the sols with pH 7, broad peaks are observed. The samples prepared with the pH values 8, 9 and 10 have intense peaks representing the clear formation of ZnO. The highest ZnO intensity peak was observed at pH 9 as a adequate amount of $OH^-$ is existing to form ZnO.

All peaks show the formation of the hexagonal wurtzite structure of ZnO nanoparticles which is with accordance to the JCPDS card no 36-1451. The cell parameters c = 5.205Å and a = 3.249 Å are also confirmed by the JCPDS data. These results are also in accordance with results presented by Alias (2010). Absence of the peaks representing other phases as well as absence of impurities is also observed which strongly suggest the formation of the high purity ZnO. It is also observed that all peaks of the ZnO nanoparticles (with basic medium) are higher than those (with basic medium). Moreover, full width half-maximum height values for the ZnO nanoparticles with basic medium are also larger, implying that the basic nature tends to reduce the crystalline structure. This is also in agreement to the results presented by Alias (2010). The crystallite size "D" for ZnO Nanoparticle was calculated using the Debye–Scherer formula which is given in Eq. (1).

$$D = \frac{k\lambda}{B\cos\theta} \tag{1}$$

where *k* is Sherrer constant, *B* is the full width at half-maximum, *λ* is the X-ray wavelength, and *θ* is the Bragg diffraction angle.

Fig. 3 shows SEM image of ZnO nanoparticles prepared with pH 8. Spherical nanoparticles with diameter ~80 nm were observed.

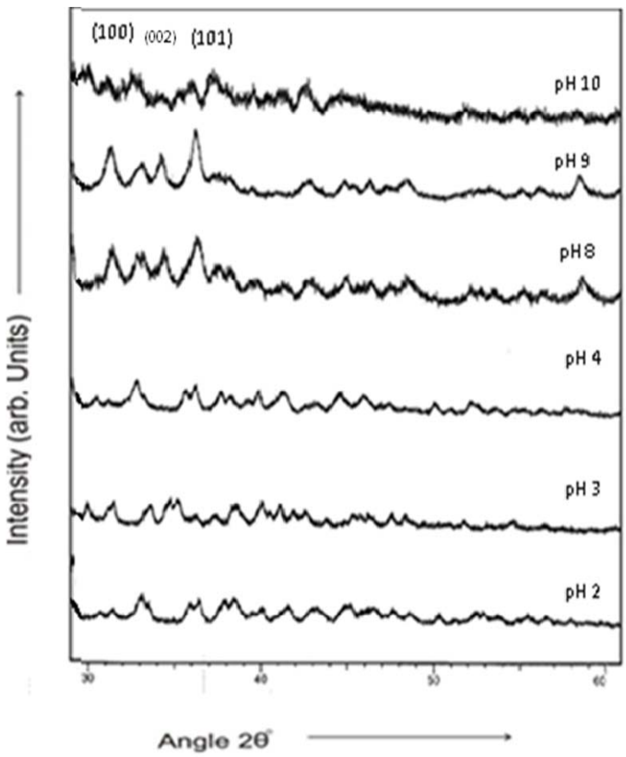


Fig. 2 XRD of ZnO nanoparticles at different pH levels

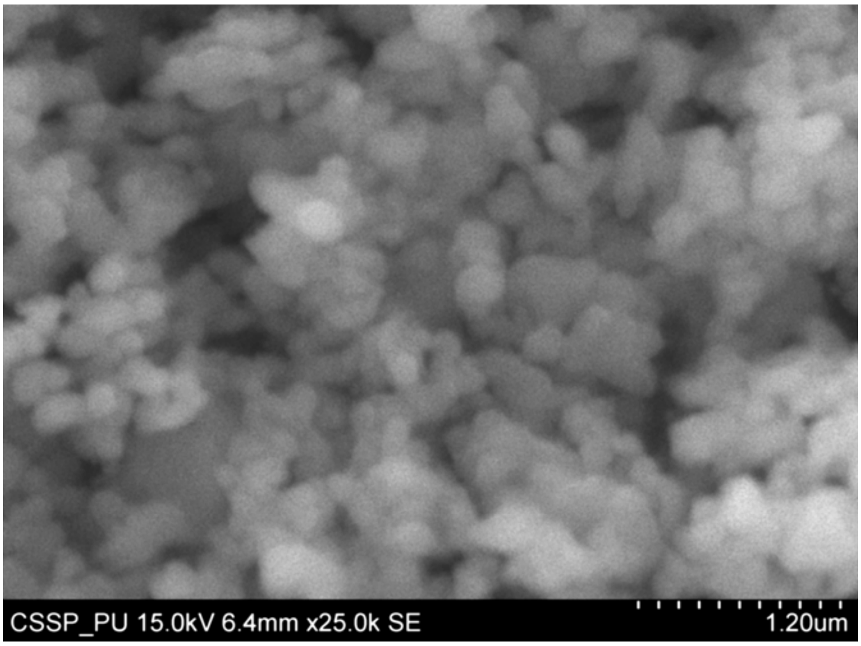

Fig. 3 SEM images of ZnO nanoparticles at pH 8

### *3.2 Optical Properties*

Fig. 4 shows transmission spectrum of ZnO nanoparticles prepared with variation of pH. All the samples have transmittance from visible range to infrared region. ZnO nanoparticles with pH 8 has more uniform transmittance in the whole range of near infrared and visible as compared with the samples prepared with pH 2, 3 and 4,7, 9 and 10. From the above results, it can be known that ZnO thin films prepared by sol–gel

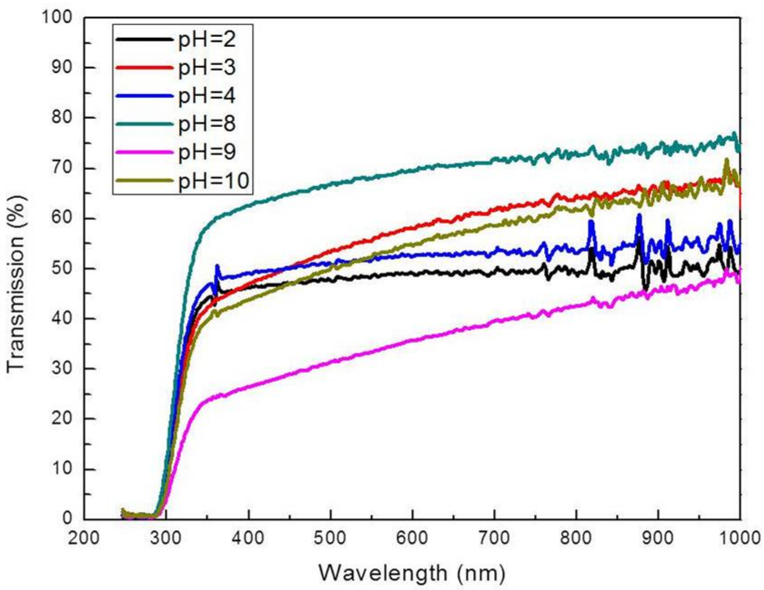

Fig. 4 Optical Transmittance spectra of ZnO nanoparticles with variation in pH

method have transmittance in the visible and infrared range, which can be used as transparent window materials in many optoelectronic devices (Sun 2011).

The transmission properties are observed to be improved for ZnO nanoparticles with basic medium. Due to Quantum confinement effect, surface to volume ratio increased that plays important role to increase the transmittance of ZnO nanoparticles. As by increasing pH, particle size tends to reduce which is also in accordance with the XRD results.

Figs. 5 and 6 show plots of refractive index *n* and extinction coefficient *k* of ZnO nanoparticles on glass substrate as a function of wavelength. These are derived after model fitting the data obtained by Spectroscopic Ellipsometer. In the designing optical

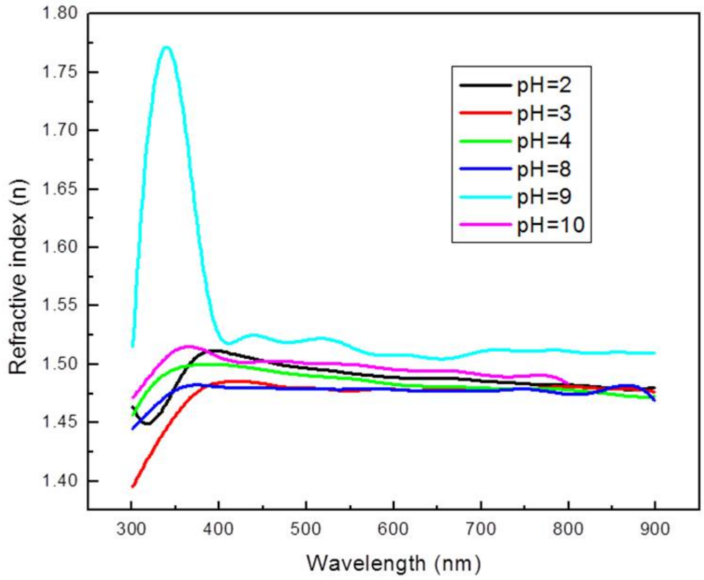


Fig. 5 Refractive index of ZnO nanoparticles on glass substrate

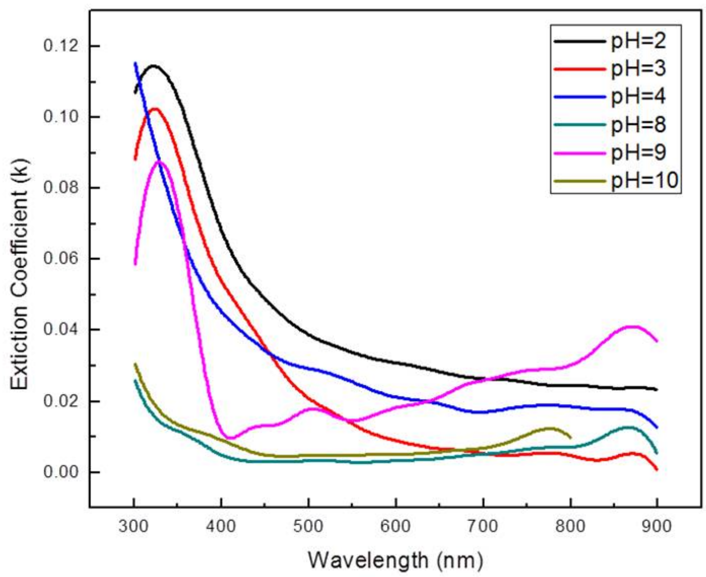


Fig. 6 Extinction coefficient of ZnO nanoparticles on glass substrate

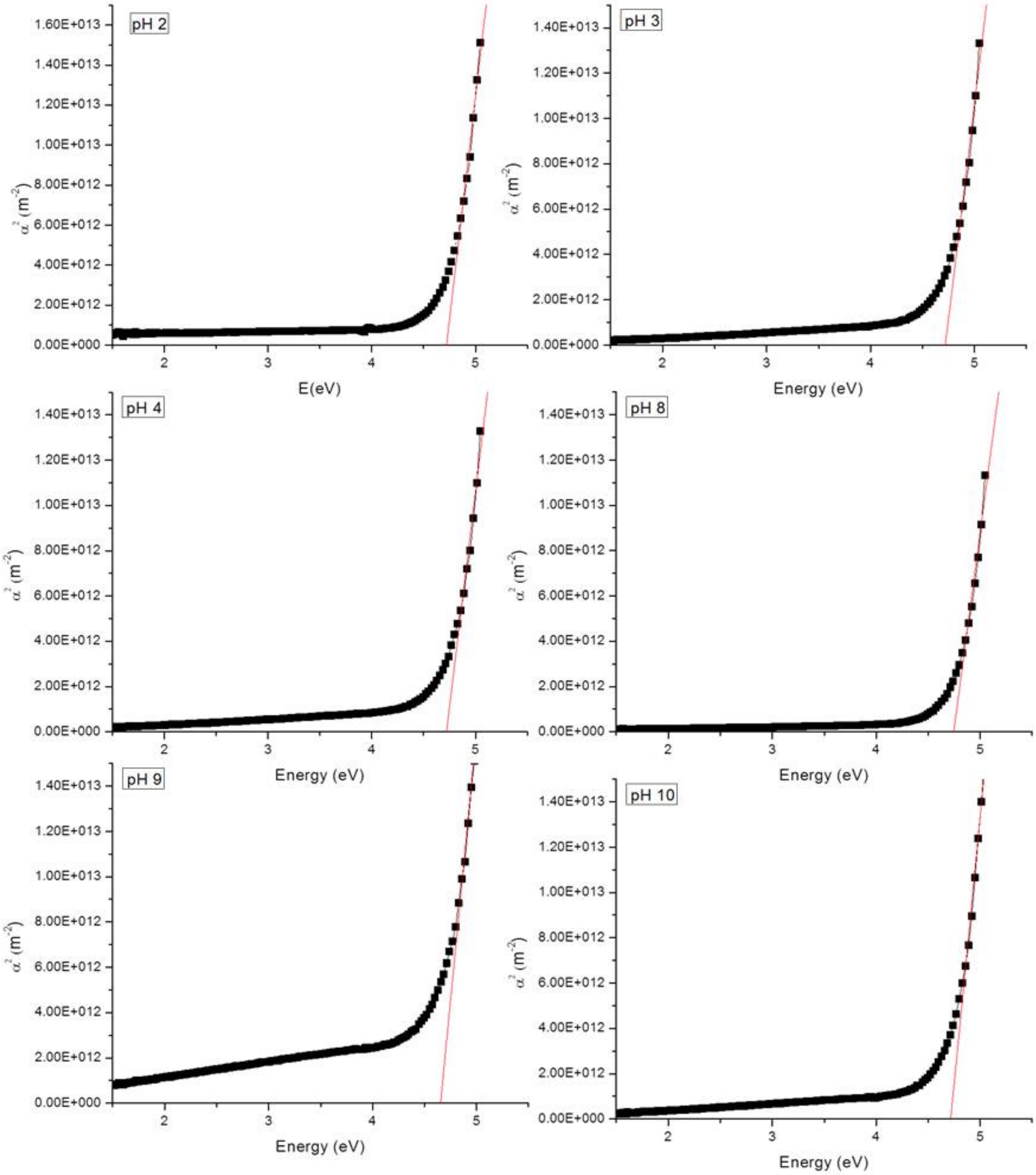

Fig. 7 Optical band gap energy estimation of ZnO film with variation in pH

devices as well as in optical communication, refractive index dispersion plays an important role. The ZnO thin films refractive indices in the wavelength range of 300-900nm is found to be from 1.78 to 1.48. The maximum value of refractive index is for the sample prepared with pH 8. Value of n is less than reported value which might be due to smaller thickness of films and dominant substrate effect.

Extinction coefficient "*k*" of ZnO nanoparticles with variation in pH is in the range of 0.11 to 0.3 in the wavelength range of 300-900 nm. Extinction coefficient is directly related to absorption and transmission is inversely proportion to absorption. Due to transparent material extension coefficient is approximately zero. Optical properties are enhances by high transmission. The variation in the extinction coefficient *k* is also reported by Dinh (2008), according to which the extinction coefficient *k* equivalents to zero for wavelengths greater than 500 nm and then sudden increase was observed in the range from 350 nm to 500 nm.

Large band gap materials are getting interest for optoelectronics at room temperature. The optical band gap energy of zinc oxide nanoparticles was calculated. The absorption coefficient was calculated using Eq. (2)

$$\alpha = \frac{1}{t}\ln T \qquad (2)$$

Where *T* is the transmittance of the Zinc oxide nanoparticles deposited on glass substrate and t is the film thickness.

The plots giving band gap energy estimation between $(\alpha hu)^2$ versus *hu* in the UV–visible region are shown in Fig. 7. The linear part of the plot has been extrapolated towards energy axis. The intercept value on the energy axis has been found to be 4.26 eV in the case of sample prepared with ph 4. Band gap of ZnO thin film obtained in the present work is observed to be greater than that of bulk ZnO it might be attributed to the smaller particle sizes as compared to bulk material. As band gap decreases with the decrease particles size. It is also stated that pH influence particle size as with the increase of pH particle size reduces. The reduction in particle size influences in the absorption of the UV light. ZnO nanoparticles with larger band gap could widely be used in many optoelectronic devices (Yadav 2010).

## 3. CONCLUSIONS

ZnO nanoparticles powders have been successfully synthesized by the sol–gel technique at different pH values using centrifugation. All of the samples have good structural and optical properties. ZnO synthesized at pH 8 has the best properties. XRD results in the formation of the hexagonal wurtzite structure of ZnO nanoparticles. Influence of pH is studied which shows that with the increase in pH of the sol particle size reduces.

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