

The Effect of Crystal Violet and CuO Respectively on Photocatalytic Cracking of n- Pentadecane Using Zinc Oxide and Visible Light

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Abstract

The photocracking of n - pentadecane ($C_{15}H_{32}$) using : 1st, Sensitized Zinc Oxide by crystal violet. 2nd, Copper Oxide and Zinc Oxide as mixed semiconductors with visible light have been investigated. The reaction was carried out in the photocatalytic cell 20cm.³ with a quartz window to received the irradiation generated from Modified Halogenated Lamp 400-700 nm.. The photocatalytic cell was surrounded by thermostated water jacket. Many parameters on the photocatalytic cracking processes have been explored in order to find the optimum conditions for the above two systems, such as, the concentration of crystal violet (dye) sensitizer deposited on ZnO, different ratios of both oxides, the effect of the particles size of catalysts, air flow rate and the effect of temperature.

The main photolytic products were light hydrocarbons (alkanes) and light oxygenated alkanes (carbonyl) which identified by Gas Chromatographic using FID detector and IR spectrophotometric techniques. Also, both semiconductors, their mixture and sensitized ZnO were studied by XRD diffraction.

A reaction mechanism for photocracking processes have been suggested.

الخلاصة

تم دراسة التجزئة الضوئية المحفزة للنورمال بنتاديكان باستخدام: أولاً "أكسيد الخارصين المحسس بصيغة البنفسج البلوري. ثانياً "مزيج من أكسيد الخارصين مع أكسيد النحاس بنسب مختلفة.

استخدمت خلية تفاعل سعة (20) سم³ لدراسة الفعالية الضوئية للعوامل المساعدة المحفزة باستخدام ضوء صادر من مصباح هالوجيني (400-700) نانومتر خلال نافذة من الكوارتز قطرها (2) سم. خلية التفاعل محاطة بمنظم حراري يعتمد على تيار ماء. للحصول على أعلى كفاءة للعامل المساعد المحسس بصيغة البنفسج البلوري و لمزيج أكسيد الخارصين وأكسيد النحاس فقد تم إجراء عدة تجارب لدراسة تأثيرهما على سرعة عملية التجزئة الضوئية للنورمال بنتاديكان مثل تغير كمية المحسس الضوئي إلى أكسيد الخارصين في العامل المساعد الأول و تغير نسب أكسيد النحاس إلى أكسيد الخارصين في العامل المساعد الثاني. كذلك تم دراسة تأثير حجم دقائق العوامل المساعدة و سرعة تيار الهواء المار في خلية التفاعل و تأثير درجة الحرارة على مسار وسرعة التجزئة الضوئية للنورمال بنتاديكان. وجد أن أهم نتائج التفسير الضوئي للنورمال بنتاديكان هي الكانات خفيفة وهيدروكربونات مقابلة مؤكسدة (كاربونيل) تم تشخيصها باستخدام تقنية كروماتوغرافيا الغاز ومطيافيه الأشعة تحت الحمراء. كما درست العوامل المساعدة بعد انتهاء عملية التفسير الضوئي بواسطة حيود الأشعة السينية.

بضوء النتائج التي تم الحصول عليها تم اقتراح ميكانيكية التجزئة الضوئية للنورمال بنتاديكان بتوافر المحسس الضوئي و أكسيد النحاس.

Introduction

The n-type semiconductors particles with appropriate band gap illumination act as short circuited microelectrodes and the photogenerated electrons and holes can initiate redox processes of the absorbed substrates (Pichat *et al* 1979 , Lifongo *et al* 2004). Several researchers have used different semiconductors as photocatalysts (Hidaka *et al* 1986, Ibanez *et al* 2003): The direct excitation of semiconductor oxide following illumination are shown in figure 1:

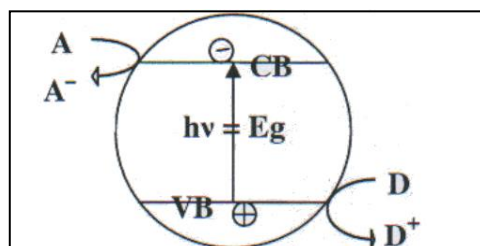


Figure 1 : Photoinduced charge transfer processes at a semiconductor particles.

The utility of semiconductor oxide can improve enormously by optical sensitization towards visible light . This behavior was proposed by Vinodgopal et al 1994 , this can be achieved by surface doping or dye sensitization of semiconductor powder . In each case the mechanism of sensitization seems to involve charge injection from the excited state of the dye molecules in the conduction band of the semiconductor as shown in figure 2 :

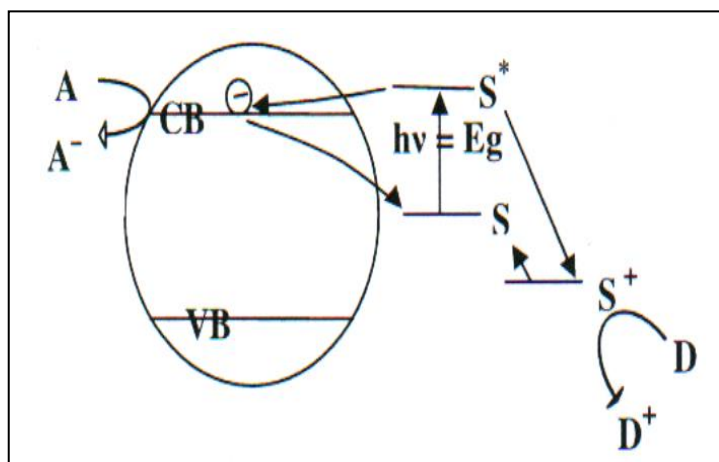


Figure 2 : Charge transfer processes at semiconductor particle interface by charge injection from excited state of the adsorbed molecule (dye) into the conduction band of the semiconductor .

Vinodgopal and Kamat 1995 have succeeded in enhancing the rate of photocatalytic degradation of organic compounds and managed to improve the photocurrent stability by using coupled semiconductors . This principle of charge separation in each semiconductors system is shown in figure 3 :

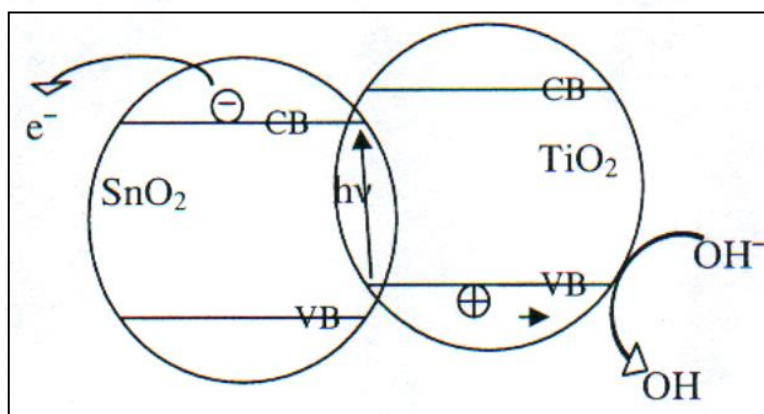


Figure 3 : The principle of charge separation in a coupled semiconductor systems.

Al – Sayyed *et al* 1991, Nasr *et al* 1995 , Garcia *et al* 2002 , Arabatziz *et al* 2003 and Bssekhouad *et al* 2004 were have suggested that the organic molecules and metal oxide may extend the range of photocatalysis to longer wave length.

The aim of the present work is a comparative study between the photocatalytic cracking of n- pentadecane using Znic Oxide sensitized by Crystal Violet and Zinc Oxide with the Copper Oxide as mixed semiconductors with visible light in both systems .

Experimental

A. Chemicals:

- 1- Zinc Oxide: Band gap (3.4) ev, purity 99%, particles size 100 mesh supplied by Fluka AG. This is further grinded to smaller particles size of 200, 300 and 400 mesh.
- 2- Crystal Violet: It is supplied by B.D.H. Chemical Ltd. Pool, England, with purity 99% and used as supplied.
- 3- Methane and ethane were supplied by Varian, diluted to 1% helium gas . Propane and butane gases were obtained from Petroleum Reserch and Development Center, Baghdad, with high purity in a liquid form under pressure. N- pentane to normal hexadecane were supplied by Fluka AG with purity 99.8 - 99.9% . The gases from methane to butane and 0.2 cm³ from n-pentane to n-hexadecane hydrocarbones were used , to find the retention time of each hydrocarbones , using the gas – Chromatographic analysis as shown in figure 4 .

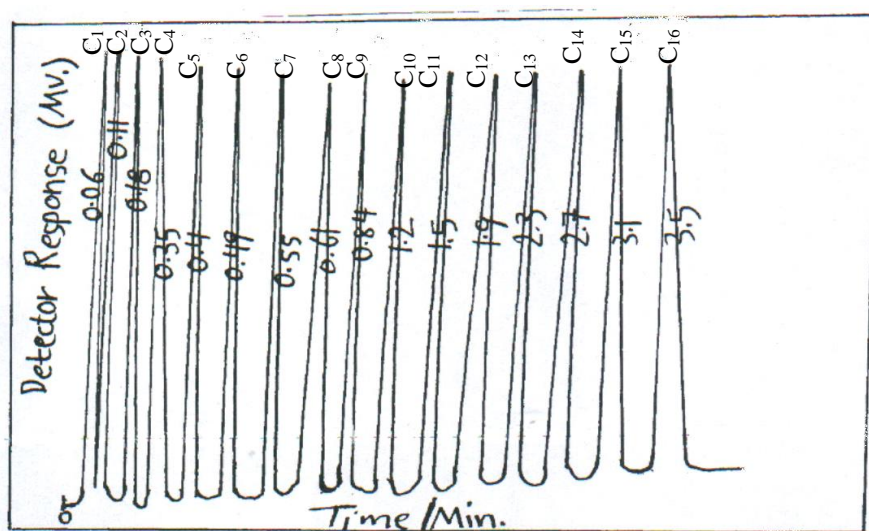


Figure 4 : Gas-Chromatogram of methane to n-hexadecane separated on OV1 column, detected by FID, column initial temp., 459 K for one min. to 590 K for one min. 10 C° /min, rate flow 30 cm³/min ., injection-temp. 450 K, detector temp. 590 K, sample size 0.5μ I. , carrier gas is nitrogen.

4- Gases used for photochemical reaction : Nitrogen and hydrogen gases were supplied by Al- Mansor Company , Iraq, used as received . Air was obtained from a comprssor existing in the laborory filtered by passing it through a special filter to remove the trace of small solid particles and humidity. All gases are saturated with the same hydrocarbon.

B- Apparatus:

- 1- Gas-Chromatograph supplied by Pye Unicom series 304 with Flame Ionization Detector and Computing Integrator type PU 481 Philips for data analysis chromatographic. Column type OV1 with methyl silicone and molecular seveice (mesh size 100-120) and 1.5 m. length and 0.4 mm. In diameter was used for analysis.
- 2-IR-spectra using Perkin–Elmer 1330 KBr disc.
- 3-X-Ray Diffraction type D5000 with CuK_{∞} radiation supplied by Siemens, Germany, was used to study the ZnO, CuO and their mixture after photoysis.

C-Preparation of catalysts:

1-Sensitized ZnO: The sensitized ZnO by crystal violet was prepared by suspending 1.2 gm. ZnO in 250 cm^3 of aqueous solutions containing different weight of crystal violet (0.1, 0.2, 0.4, 0.6, 0.8, 1.2 and 1.5)gm., each mixture was fluhed with air at flow rate of $30 \text{ cm}^3/\text{min.}$ at 298 K.

The suspension mixture was irradiated for two hours in a photolysis cell supplied with modified halogenated lamp as in Figure 5 . The irradiated products was separated by filtration and washed several times with distilled water until the color of crystal violet was disappeared from washing . It was dried over night at 350 K . The sensitized ZnO was sieved to mesh size 100, 200, 300, and 400 mesh using Karl Kolb DW 4188 stainless steel sieves (only four sieves exist).

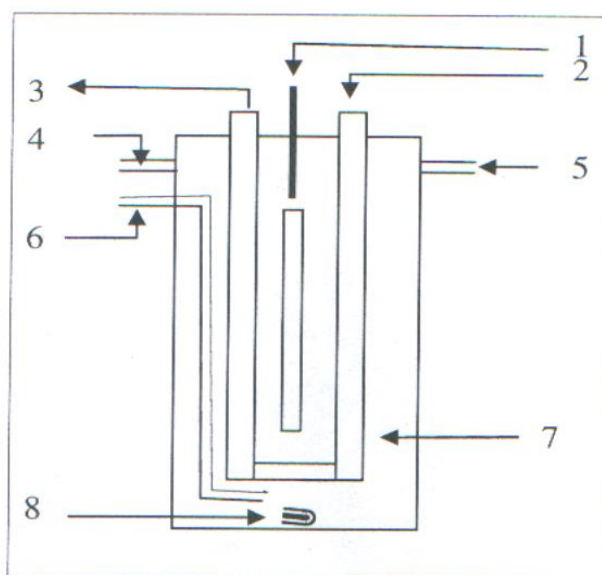


Figure 5: Main parts of the photolytic cell used in photocatalytic degradation of satueated hydrocabons:

1- lamp 2 - water cooling inlet 3 – water cooling outlet 4 - vent
5 - in-out sampling 6-gas entry 7- reaction chamber 8 - mangnetic stirrer

2-Mixture semicondutors:

All the percentahe ratio of semicondutors were prepared by direct mixing and heating at 673 K for 3 hours,Which listed in Table 1:

Table 1:Percentage ration of mixed semiconductors.

Metal oxide	Percentage ratio						
ZnO	0.0	10.0	25.0	50.0	75.0	90.0	100.0
CuO	100.0	90.0	75.0	50.0	25.0	10.0	0.0

D - Methds: Photocatalytic cracking of n-pentadecane was curried out in pyrex static reactor with quartz window to received the irradiation generated from modified halogenated lamp (400-700) nm . In all experiments 20 cm³ of n-pentadecane was used with 0.1 gm. of semiconductors oxides required. The solution was suspended by a magnetic stirrer, and air was saturated with n-pentadecane before being passed through the photolysis cell with rate 2.5 cm³/min. as in figure 6 .

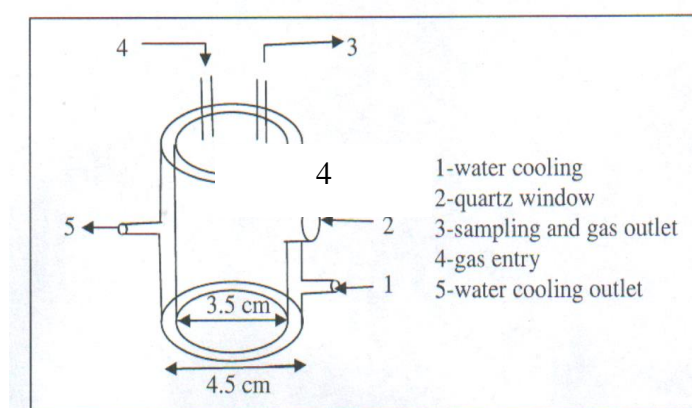


Figure 6 : Photolysis cell.

Periodically (0.25)cm³ samples of reaction mixture were with drown by microsyinge and centrifuged to separate solid catalysts .

Results and Discussion

1- structural Characterization :

The naked and prepared sensitized ZnO were characterized by :
A-XRD spectrum :

Figure 7 – a show the ZnO XRD spectrum with specific 2θ and intensity, while the deposition of crystal violet on the surface of ZnO give new spectrum 7 – b which indicate a shift in 2θ and reduce its intensity, also this precipitation of crystal violet on the surface of ZnO leads to appear of new peak 2θ in spectrum not exist in the original spectrum , this may due to the distortion of the crystal lattice of ZnO. Also the figure show crystal violet spectrum 7 – c .

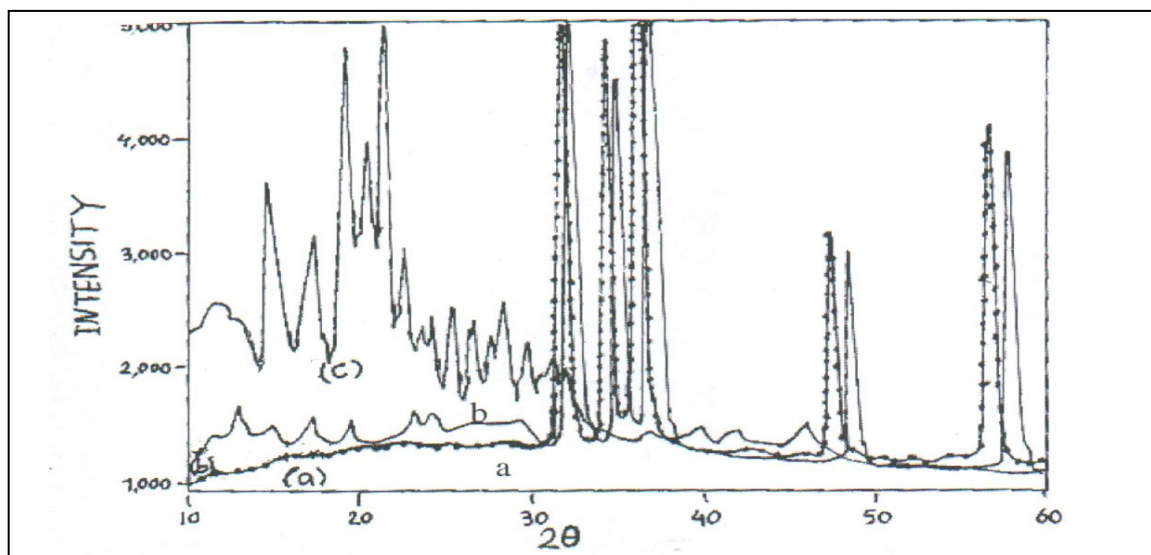
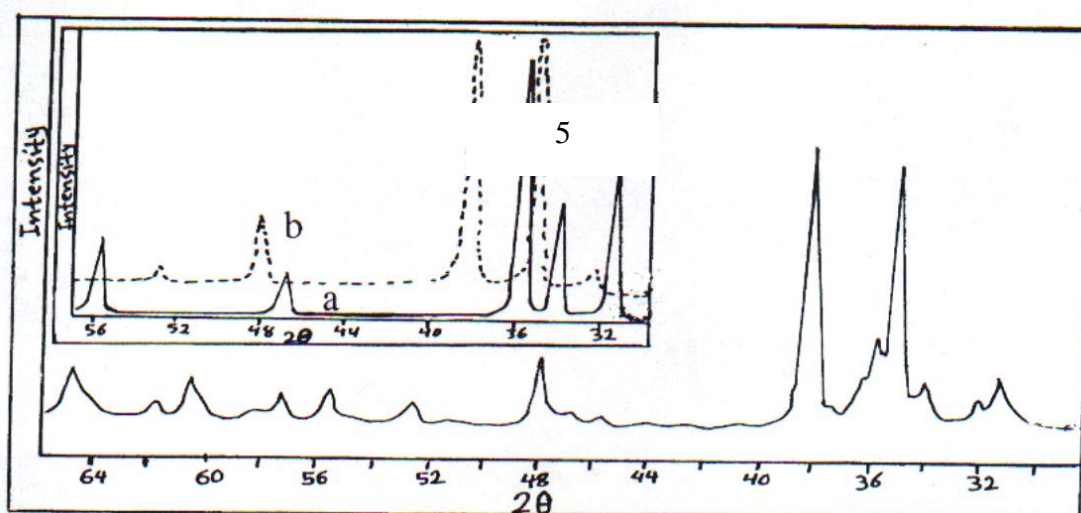


Figure 7 : XRD spectrum of : (a) ZnO (b) Sensitized ZnO (c) Crystal Violet .

Figure 8 – a - b shows the XRD spectra of ZnO,CuO and their mixture (50% ZnO+50%CuO). While the spectrume of the figure 8 - c was which indicated a new sigbificant peak 2 θ located at (65, 62, 60, 48, 36, 34, and 31). Which may indicate the transformation of crystal structure by heat treatment due to the formation of a new bonding between these oxides that may cause an extension in light absorption spectral of the semiconductors to visible region .



**Figure 8 : X-Ray powder diffraction spectrum for (50% ZnO)+50%CuO.
The insert spectrum (a) Solid line for ZnO (b) Dotted line for CuO.**

The appearance of new peaks in the figure 7 - b and figure 8 - c may represent the transformation of crystal structure of zinc oxide by crystal violet adsorption and by the formation of new bond between the zinc oxide and copper oxide by heat treatment . The modification of zinc oxide in two system may cause the extended light absorption to visible light.

B – IR spectra:

Figure 9 show the IR spectra : (a) Naked ZnO (b) Sensitized ZnO (c) Crystal violet. From these spectrum we can see clearly the presence of crystal violet on the

surface of ZnO by the appearance of specific peak in $(1000-1500) \text{ cm}^{-1}$ which return to crystal violer , not present in the spectrum of naked ZnO.

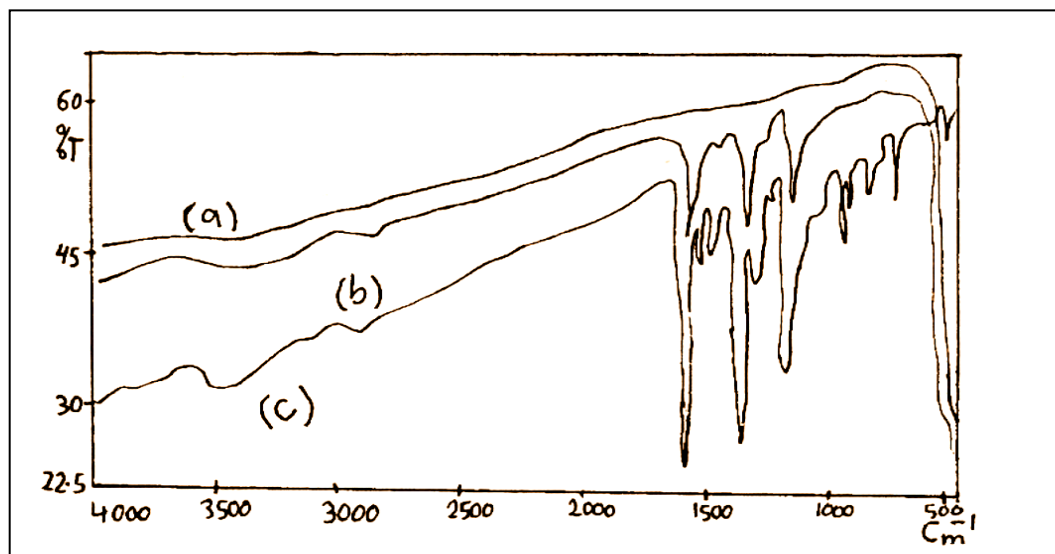


Figure 9 : IR spectrum for: (a) ZnO (b) Sensitized ZnO (c) Crystal Violet

2 – Preliminary experiments:

These experiments were made to determine the conditions necessary for photolytic activity before and after adsorption of sensitizer. The experiments results of the photocracking of n - pentadecane at 298 K at different conditions are given in table 2 .

Table (2) : The effect of different conditions on photocracking of n- pentadecane at (298) k and (5) hours irradiation.

Exp. No.	Hydro-carbons	Retenti-on Time	Conc.(mol./lit.)		Experiments conditions	Reaction products
			(0.0)hr.s	(5.0)hr.s		
1	n-C ₁₅	3.5	3.720	3.720	n - C ₁₅ + air	No Products
2	n-C ₁₅	3.5	3.720	3.720	n - C ₁₅ + air + ZnO	No Products
3	n-C ₁₅	3.5	3.720	3.720	n - C ₁₅ + air + light	No Products
4	n-C ₁₅	3.5	3.720	3.720	n-C ₁₅ + air + malachite green	No Products
5	n-C ₁₅	3.5	3.720	3.720	n - C ₁₅ + air + light	No Products
6	n-C ₁₅	3.5	3.720	3.660	n-C ₁₅ + air + malachite green	See Products
	n-C ₇	0.61	0.000	0.025	+ light	
	n-C ₈	0.84	0.000	0.035		
7	n-C ₁₅	3.5	3.720	3.400	n - C ₁₅ + air + sensitized ZnO + light	Detectable change see conc. Of light hydrocarbons
	n-C ₆	0.55	0.000	0.041		
	n-C ₇	0.61	0.000	0.089		
	n-C ₈	0.84	0.000	0.120		
	n-C ₉	1.2	0.000	0.050		
	n-C ₁₀	1.5	0.000	0.020		
8	n-C ₁₅	3.5	3.720	3.720	n - C ₁₅ + air + CuO	No Products
9	n-C ₁₅	3.5	3.720	3.720	n-C ₁₅ + air + CuO + light	No Products
10	n-C ₁₅	3.5	3.720	3.630	n-C ₁₅ + air + (10 % CuO + 90 % ZnO) + light	See Products
	n-C ₇	0.61	0.000	0.032		
	n-C ₈	0.84	0.000	0.058		
11	n-C ₁₅	3.5	3.720	3.500	n-C ₁₅ + air + (25 % CuO + 75 % ZnO) + light	See Products
	n-C ₆	0.55	0.000	0.030		
	n-C ₇	0.61	0.000	0.070		
	n-C ₈	0.84	0.000	0.100		
	n-C ₉	1.2	0.000	0.020		
12	n-C ₁₅	3.5	3.720	3.410	n-C ₁₅ + air + (50 %CuO + 50 % ZnO) + light	Detectable change see conc. Of light hydrocarbons
	n-C ₆	0.55	0.000	0.040		
	n-C ₇	0.61	0.000	0.150		
	n-C ₈	0.84	0.000	0.110		
	n-C ₉	1.2	0.000	0.010		
13	n-C ₁₅	3.5	3.720	3.480	n-C ₁₅ + air + (75 % CuO + 25 % ZnO) + light	See Products
	n-C ₆	0.55	0.000	0.020		
	n-C ₇	0.61	0.000	0.082		
	n-C ₈	0.84	0.000	0.118		
	n-C ₉	1.2	0.000	0.020		
14	n-C ₁₅	3.5	3.720	3.640	n-C ₁₅ + air + (90 % CuO + 10 % ZnO) + light	See Products
	n-C ₇	0.61	0.000	0.030		
	n-C ₈	0.84	0.000	0.050		

3 – The effect of crystal violet concentration and the percentage ratio of CuO to ZnO on photocracking of n – pentadecane.

For this purpose several sensitized ZnO samples using crystal violet dye concentration ranged from (0.1 – 1.5) gm./lit. . These sensitized ZnO have been used to monitor the rate of photocracking process of n-pentadecane. Results are shows in figure 10 .

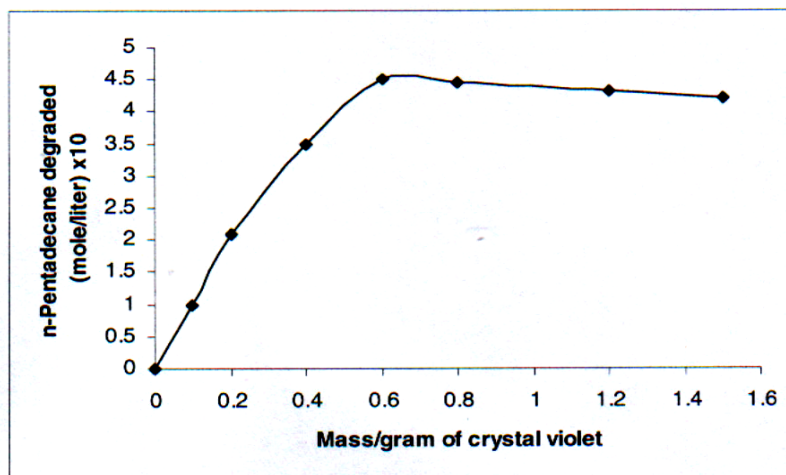


Figure 10: The effect of crystal violet concentration fixed on ZnO 1.2 gm. on photocracking of n- pentadecane using visible light.

Figure 10 shows that the rate of photocracking processes increases as the concentration of crystal violet deposited on the ZnO increases until the concentration become 0.6 gm. then gradually decrease. This behavior could be suggested by the idea that the concentration of 0.6 gm. of crystal violet on 1.2 gm. of ZnO in the optimum concentration to cover the largest area of the concentration ZnO particle, therefore, absorbed maximum exiting photons to generate highr concentration of the activated sensitized ZnO semicoductors. Another reason, for this behavior is the strong absorption of light by crystal violet . Other suggestion , that the sample which contain high concentration than 0.6 gm.of crystal violet on 1.2 gm. of ZnO this prevents the penetration of light through the successive layers of dye on the ZnO surface is weak to generate the required excited state of the crystal violet deposited on ZnO.

While the rate of photocracking of n-pentadecane increases as the efficiency of electron transfer from each semiconductors to each others was taken as in figure 11.

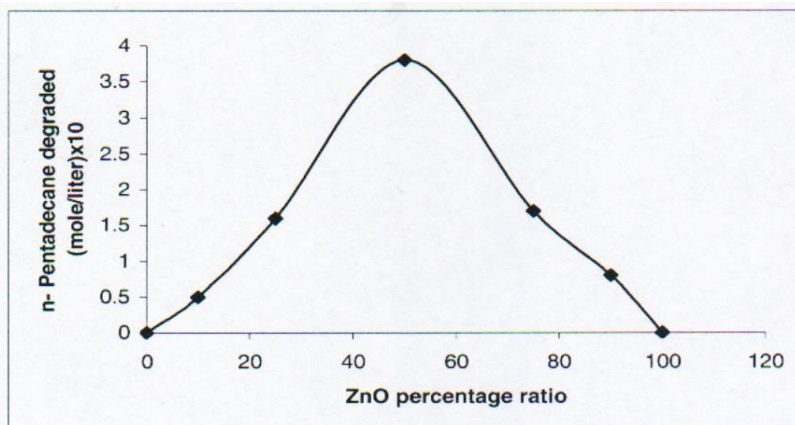


Figure 11: The effect of semiconductors percentage ratio on photocracking of n-pentadecane using visible light.

This may be explained by that particle of ZnO deposited or precipitate on CuO particle which gives rise to active ZnO-CuO groups that acts as electron-hole separation centers as in figure 3. The electrons transfer from the ZnO valance band to CuO conduction band at the interface contact region improve the charge separation and thus enhances the photocatalytic activity of degradation . Also the improvement of efficiency in photodegradation of n - pentadecane was due to increasing in photoconductivity of solution by using differnt ratios. The suggestion of decreasing in the efficiency of photodegradation of n-pentadecane in 1st and 5th percentage ratio of semiconductors rather than 3rd percentage ratio was explained by that the excess CuO particles in 1st percentage ratio and ZnO particles in 5th percentage ratio prevent the light from passing through all layers to reach the active ZnO - CuO groups in the reaction vessel.

Figure 10 shows that the rate of photocracking of n- pentadecane was higher than the of photocracking of n-pentadecane using copuled semiconductors as in figure 11, this may explained by that the absorption of visible light by crystal violet was generated more active site for photocracking processes rather there copulas semiconductors.

4- Mass effect of sensitized ZnO and mixed semiconductors on photocracking of n - pentadecane using visible light.

The rate of photocracking processes of n – pentadecane increases and reach 4.6 mole / liter as the concentration of sensitized ZnO increases as a function of 5 hours irradiation of each experiment until the concentration become 4.8 gram/liter ther gradually decreases as in figure 12 .

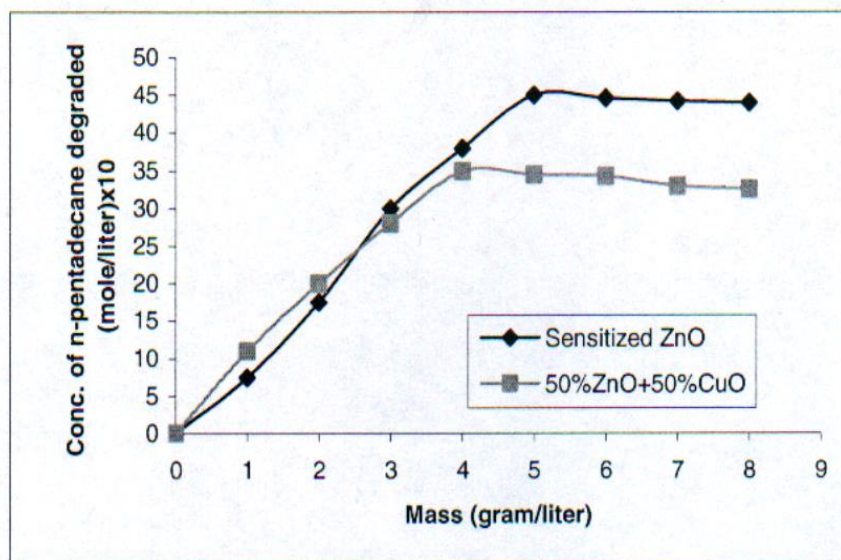


Figure 12: Mass effect of sensitized ZnO and mixed semiconductors on photocracking of n-pentadecane using visible light.

This behavior could be explained by the idea that the concentration of 4.8 gram/liter of sensitized ZnO provides the highest absorption of light by sensitized ZnO and assures a homogeneous absorption of light through the layers of reaction vessel. The decrease in the efficiency of photodegradation process at the concentration of sensitized ZnO higher than 4.8 gm/lit., might be explained by the strong absorption

of light through the first successive layers of solution and prevent light from passing through all other layers in the reaction vessel. This effects were studied by Sung - Suh *et al* 2004.

Also figure 12 shows that the concentration of degraded n-pentadecane at constant irradiation time 5.0 hours increases with increasing the concentration of semiconductors mixture and reaches a max. value 3.5 mole/ liter at concentration 4.0 gm./lit of the semiconductors mixture. This behavior could be explained by the idea that the concentration of 4.0 gram / liter of mixed catalysts is the optimum concentration to cover the largers area of loading (ZnO–CuO) junctions , therefore absorbed maximum exciting photons to generate higher concentration of activated species of (ZnO–CuO) . The concentration of (ZnO–CuO) more than 4.0 gram /liter prevents the the penetration of light through the successive solution layers to generate the required excited state of the active species of (ZnO CuO).

5- The effect of sensitized ZnO and coupled semiconductors (50% ZnO+50% CuO) particles size on photocatalytic cracking of n-pentadecane:

The effect of the particles size of the sensitized ZnO and coupled semiconductores (50% ZnO+50%CuO) on the rate of photodegradation of n-pentadecane has been studied by four different samples of both catalysts. For this purpose 0.6 gm of crystal violet deposit on 1.2 gm. of ZnO and coupled semiconductores (50%ZnO+50% CuO) were used with mesh size (100,200,300,and 400) respectively as in figure 13 .

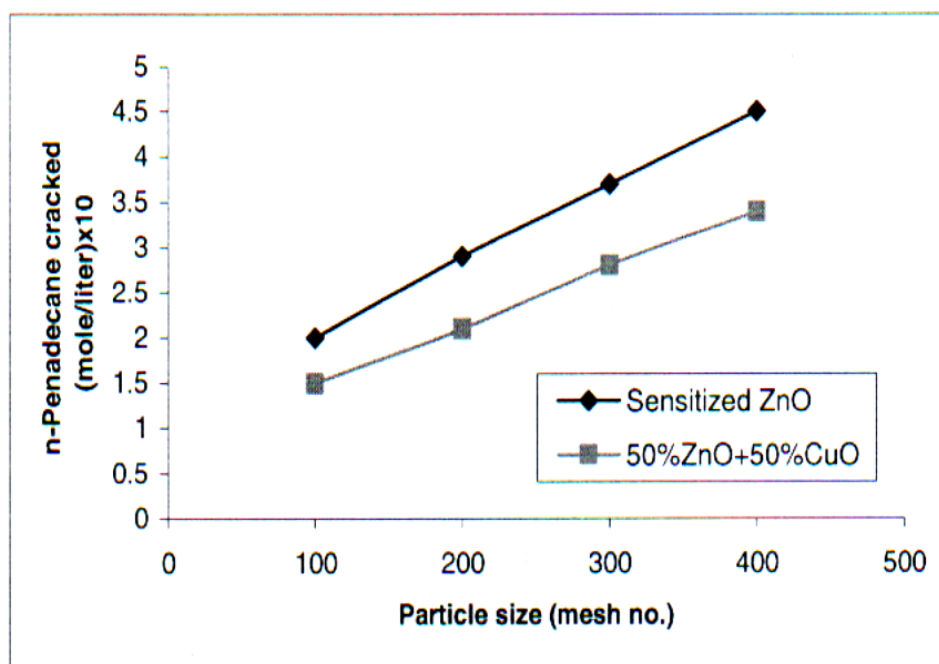


Figure 13: The effect of particles size on photocatalytic cracking of n-pentadecane at 298 K.

The result in figure 13 shows that the rate of photodegradation of n-pentadecane increases with particle size decreases (mesh size incese) for both catalysts. This is expected , that the surface area and the active sites of the activated catalysts by light are larger when the particle size decrease.

6-The effect of crystal violet and copper oxide on catalytic cracking of n-pentadecane using ZnO and visible light for 25 hours irradiation time at 298 K:

Figure 14 shows that the effect of the crystal violet sensitized and copper as coupled semiconductors in the present photocatalytic systems, also indicates the variation of the concentration of n-pentadecane compounds with time irradiation 25 hours in the presence or absence of crystal violet and copper oxide respectively. From Figure 14, its clear that the concentration of n-pentadecane (mole/liter) unchanged by using ZnO or CuO alone in photodegradation under visible light for 25 hours irradiation, while in the same Figure appears a significant change in the concentration of n-pentadecane (mole/liter) for the same irradiation time, that reflects the activity of sensitized ZnO and the coupled semiconductor (50%ZnO+50%CuO)in photocracking of n-pentadecane.

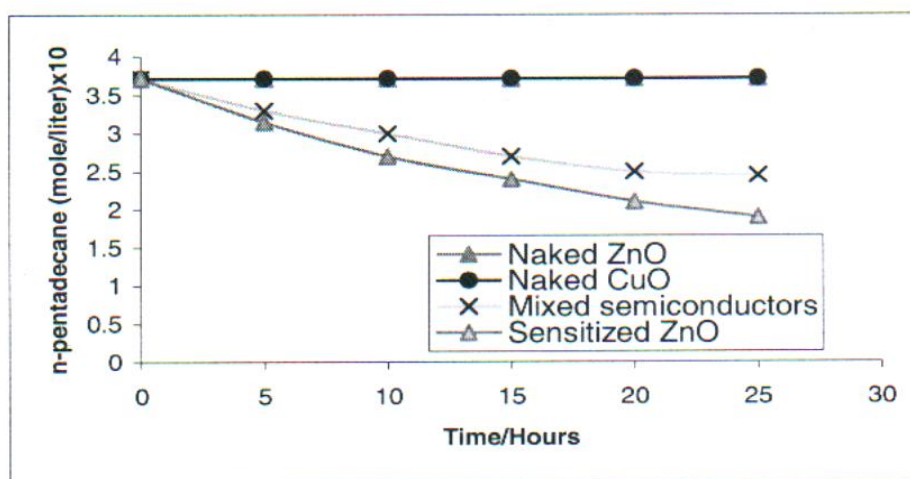


Figure 14: The effect of irradiation time on catalytic degradation of n-pentadecane.

The irradiation of n-pentadecane by using sensitized ZnO and mixde semiconductors (50% ZnO + 50% CuO) with visible light 25 hours was analyzed by gaschromatographic technique as in figure 15.

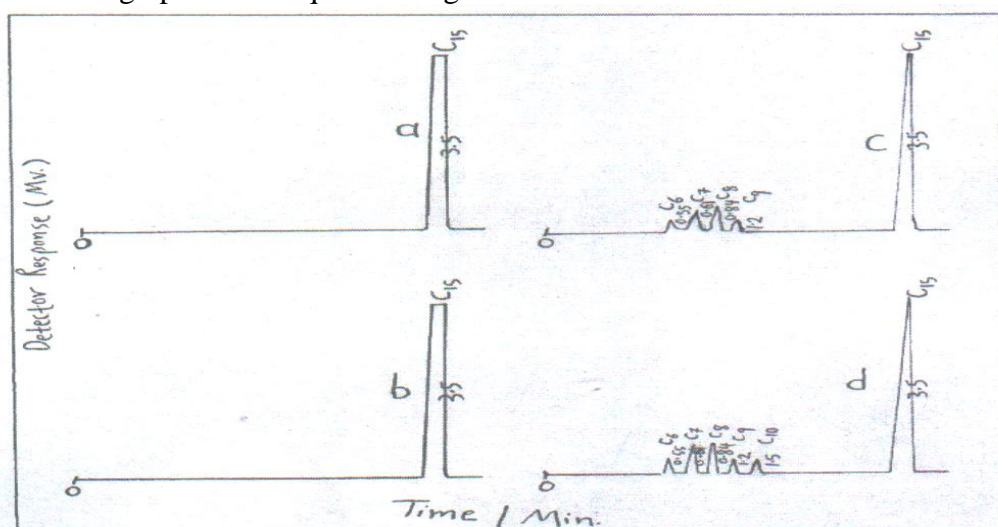


Figure 15 :Gas chromatogram of n- pentadecane and generated light hydrocarbons at 298K after 25 hours irradiation.

- a-n-pentadecane before irradiation. b- n-pentadecane with ZnO or CuO.
c- n-pentadecane with mixde semiconductors (50%ZnO +50%CuO).
d- n-pentadecane with sensitized ZnO.

Figure 15 – c - d shows the generation of new light hydrocarbons compounds such as: C₆ , C₇ , C₈ , C₉ and C₁₀ when the sensitized ZnO and the mixed oxides (50%ZnO +50% CuO) were used as photocatalysts, while the light hydrocarbons not appear by using irradiation n-pentadecane with either ZnO or CuO alone after 25 hours irradiation.

From the initial concentration of n-pentadecane = 3.720 mole / liter and its initial peaks area = 100% , the concentration (mole/liter) of these generated light hydrocarbons after 25 hours irradiation can be caculated from its corresponding peaks area percentage (%) as in simple relation:

$$C_o / (p. a. \%)_o = C_t / (p. a. \%)_t$$

$$\text{Then } C_t = C_o \times (p. a. \%)_t / (p. a. \%)_o$$

Then from the peaks area percentage (p.a.%)_t after 25 hours irradiation of each light hydrocarbons generated , and initial concentration of n- pentadecane (C₀ =3.720 mole/litr) and its initial peaks area percentage [(p.a. %) _o =100], can be determine the concentration (C_t = mole /liter) of these generated light hydrocarbons as in table3.

Also IR spectrophotometric technique was used to identify the photocatalytic products (functional group) created during the photocracking of n-pentadecane after 25 hours irradiation as in figure 16:

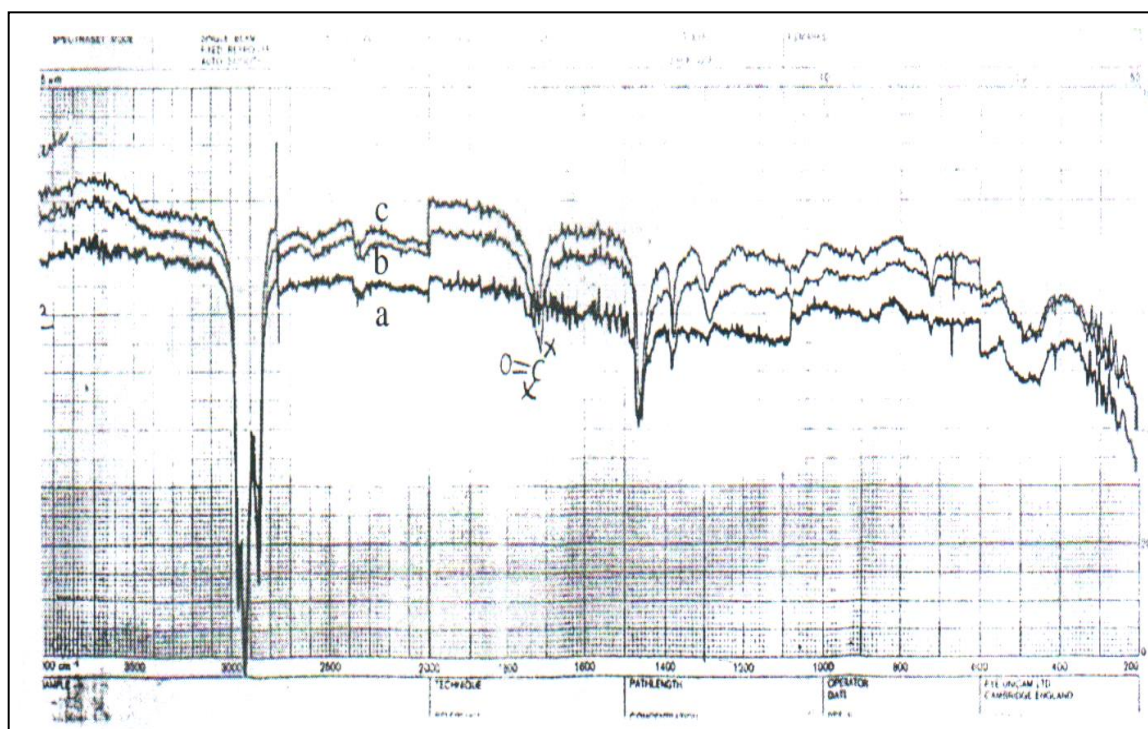


Figure 16: IR spectrum for:
a- n-pentadecane befor irradiation
b- n-pentadecane after 25 hours irradiation using sensitized ZnO.
c - n-pentadecane after 25 hours irradiation using mixde semiconductors (50%ZnO +50%CuO) catalyst.

Figure 16–b-c shows the (-CO-) stretching vibration of aliphatic carbonyl compounds at 1720 cm⁻¹ , which is not present in the original substrate n-pentadecane and in both photocatalytic system spectra using ZnO and CuO individual as in figure 16 – a .

Proposed Reaction Mechanism

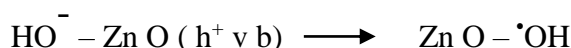
Figure 2 shows , sensitizer (crystal violet) adsorbed on ZnO surface , upon irradiation absorbed visible light and generate electrons and holes.

ZnO – sensitizer $\xrightarrow{\text{visible light}}$ ZnO – sensitizer^{1*} or ZnO – sensitizer^{3*}
 Excited sensitizer singlet or triplet are injected photoelectron in conduction band of ZnO as in equation:



Figure 3 depicts, that the ZnO absorbs visible light and generated electrons and holes.

The valence band photogenerated holes in sensitizer figure 2 and ZnO in figure 3 are free to react with (⁻OH) adsorbed on the ZnO surface to create hydroxyl radical ($\dot{\text{O}}\text{H}$).

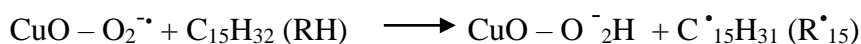
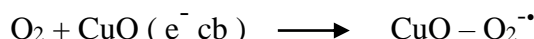


The electrons are injected in conduction band of ZnO in the 1st sensitized catalyst and in the conduction band of CuO in the mixed oxide and radicals are produced.



The presence of empty CuO conduction band can help to prevent the recombination between the electron – hole pairs, by attracting the ZnO valence band photoelectron. Improve charge separation in coupled colloidal semiconductors system such as TiO₂ / CdS and ZnO / CdS have also demonstrated. Thus , recombination is avoided between (e / h).

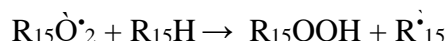
The ZnO in the 1st and CuO in the 2nd catalysts conduction bands electrons react with electron acceptors , such as oxygen (Vinodgopal et al 1994), creating radical ($\text{O}_2^{\cdot-}$, O^{\cdot}). These radicals ($\text{O}_2^{\cdot-}$, O^{\cdot} and $\dot{\text{O}}\text{H}$) present extremely strong oxidizing properties are able to abstract in initial step a hydrogen atom from any carbon in the chain (n-pentadecane) except from carbon one(C₁).



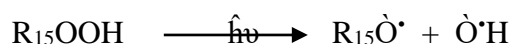
According to the results obtained by Gas Chromatography chromatogram and IR spectroscopy, the most probable propagation steps involve , that the alkyl radicals was react with molecular oxygen forming peroxy radicals which stabilize themselves as hydroperoxides by the incorporation of hydrogen atom.,the more suggested propagation steps are:

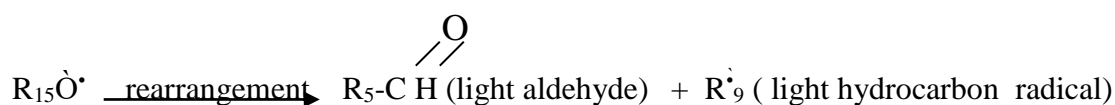


The peroxy radicals followed by hydrogen abstraction form the backbone of other C₁₅H₃₂ molecules and repeated fast oxygen addition :



The hydroperoxide species is well-known to decompose photochemically with high quantum yield to $\text{R}_{15}\dot{\text{O}}^{\cdot}$ and $\dot{\text{O}}\text{H}$ radicals :





R_9^{\cdot} (light hydrocarbon radical) + $R_{15}H \rightarrow R_9H$ (saturated light hydrocarbon) + R_{15}^{\cdot}
Alkyl radical react fast with O_2 :



Peroxyradical terminate to form light alkanes and light carbonyl compounds.

Referece

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