Research Article

Synthesis and Characterization of Nanostructure Tio₂/Anthraquenone (AQ) Prepared by Sol-Gel Method

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Abstract

Sol–gel technique conducted to synthesize nano titanium dioxide with anthraquenone (AQ) relatively in acidic pH. Nanoparticles were characterized using techniques like, Scanning Electrion Microscope (SEM), Atomic Force Microscope (AFM), UV-Visible Spectrioscopy, X-ray diffraction (XRD), Fourier transform infrared (FT-IR), SEM picture display that the TiO₂/AQ is spherical in style, the band gap of TiO₂/AQ nanoparticle is (3.05eV), BET and BJH analysis provides Pore volume and specific Surface area and the kinetic studie Suggest that the reaction is pseudo first order and the rate of reaction was reduce with rising initial concentration for p-Nitrotolune.

Keywords: sol–gel, Nanoparticles, Atomic Force Microscope, Nanostructure.

الخلاصـة

تم خلال البحث الحالي دراسة تحضير الدقائق النانوية لثنائي اوكسيد التيتانيوم مع انثراكوينون بطريقة الهلام-جل) واستخدمت التقنيات الاشعة السينية ومجهر الماسح الالكتروني ومجهر القوة الذرية ومطياف الاشعة فوق البنفسجية والاشعة تحت الحمراء و تم دراسة خصائص وتشخيص المادة النانوية المحضرة ووجد ان الدقائق النانوية كروية الشكل ذات حجوم مختلفة ان فجوة الطاقة للمادة النانوية لايجاد المساحة السطحية وحجم المسام. BET, BJH وقد استخدم تحليل 3.05 eV كما درس تأثير الكفاءة الضوئية لتجزئة بارا نايتروتولوين في المحاليل المائية وكان التفاعل من المرتبة الاولى الكاذبة وسرعة التفاعل تنخفض بزيادة التركيز الابتدائي.

Introduction

In the other few years, major efforts have been synthetic to convert the band structure of TiO₂ to shift its absorption border across the visible light region and site its band borders at proper placement, thus clement, its photocatalytic efficiency one way of doing thus is to dope TiO₂ with each anions or cations [1].

Titanium dioxide have three crystal kind rutile, anatase, and brookite of these various, anatase TiO₂ has been most excessively use as a widespread catalyst in order that of its diverse fitness, like as visual and electronic ownership, crest photo-catalytic efficiency, least cost, nontoxicity and while chemical stabilization. The catalytic activity of TiO₂ is likely on its dependent on the crystal size the minimal the particles, the great will be its surface area [2].

The sol-gel method is the extreme succeeded for providing nanosized metal oxide semiconductor, sol-gel derived TiO₂ powder has been report to show height, catalytic efficiency due to their end texture broad surface and height porosity [3] [4].

The sol-gel method is a depressed temperature way extreme hard used to acquire best ceramic [5]. Several methods used to improve the stability of nanoparticles, like torpidity of semiconductor and cap by kind organic or inorganic category.

Through these methods, polymer cap in a chemical way advanced to synthesize nanoparticles with high surface stability, and also have significant effect on the morphology and optic property of nanoparticle, doping of TiO₂ have been an important access in energy gap engineering to charge the optic repayment of semiconductor photo catalyst [6].

More way has been based for titanium dioxide synthesis like sol-gel method, hydrothermal technique, chemical steam deposition, direct oxidation and all the other.

The sol-gel method is one of the extreme used techniques led to its chance of deriving single metasTable frame at depressed reaction temperatures and stellar chemical homogeneity [7].

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Material and Methodologies

Whole reagents used were of analytical stage purity and was obtained from Merck chemical Reagent Co. LTD. titanium tetra isopropoxide (TTIP) and anthraquenone (Sigma, Aldrich), ethanol absolute (Merck) while deionization water consumed for the concoction of nanoparticle by the sol-gel method.

Characterization

The prepared crystalline nanoparticles structure was characterized using Surface morphology by using SEM (Sigma). UV-visible absorption spectrum of nanocrystal was recorded in the wave length range (200-800nm) using two quartz cells of (10mm) path way with double beam spectrophotometer (100 Conc/Varian. USA) and the mean, particle space was measured employing atomic force microscope (AFM) AA300 scanning probe microscope angstrom Advanced Inc. The surface area of nanoparticle was calculated by employing Instrument NOVA station A by nitrogen

Nano Particles Preparation

(a) Assembly of titanium dioxide was acquired from titanium tetra isopropoxide (TTIP) which were settled in absolute ethanol and deionization water the admixture were designed in expression of a molar ratio of TTIP: H_2O = 1: 4 Nitric acid was consumed to detect pH=4 and for hold the hydrolysis operation of the solution.The sol was busily whiskered for 60 min in require to brew a homogenous sol. After 24 hour the sol was convert into gel to acquire nanoparticle, the gel was dried under 80^0C till 2 hours to vaporize water and organic material to the upper range, then the dry gel was calcination at different temperatures for 2 hours were subsequently carried outside to acquire coveted titanium dioxide nanoparticles [7] [8]
(b) Anthraquienone/TiO_2 was prepared by capped technique (TiO_2 with Anthraquienone) by Sol-Gel. (0.2 gm) anthraquienone was dissolved in absolute ethanol and hydrolyze through addition of step (A) solution down fixed stirring at room temperature for 40 minute then cooled at room temperature, separated by centrifuge for 15 min, the absolute ethanol and water with washed and the resultant material was aging for 24 hour and dried at 80^oC for 4 hours.

Results and Discussion

The study surface roughness and characteristics of AQ doped TiO_2 nanoparticles Surface morphology photographs was recorded by using SEM, AFM, surface area and XRD.

X-rays the crystal texture of the acquired powder was describe by powder X-ray diffraction (XRD) analyses. As it is indicate in Figure 1, the diffraction peaks that indexed as the anatase phase for titanium dioxide accord to the JCPDS card No., 21-1276.

The main diffraction peaks at 2θ=25.34, 37.80, 48.07, 53.80 and 55.07 ^{0} are belong to (101), (004), (200), (105) and (211) planes of the TiO_2 tetragonal phase, Figure 1 shows a powerful peak agree at 2 θ = 25.34^O which correspond to the (101) reflection, while another characteristic peak (004), (200), (105) and (211) correspond to various crystalline planes.In the status of the sample acquired with the use of the AQ, the XRD patterns display weakened peak occurring at 2 θ =23.5, 27.4, 62.7, 68.9, 70, and $75.12^θ$ corresponds to the AQ structure. The analyses of the datum due to the conclusion that the increment of AQ at the stage of titanium dioxide syntheses, titanium dioxide sample with the addition of AQ caused worthy changes in crystals characteristic. It mean sample designed with the tiny addition of AQ are characterized with the large crystallite sizes was (24.19 nm) calculated using Scherrer formula.

$$D = K \lambda/B \, COS \, \theta \qquad (1)$$

Where D is the crustallite volume, λ is wavelength of the X-ray wherever D is the crustallite volume, radiation (Cu K α = 0.15418 nm), K is the Scherrer constant and B is the fall widths at half maximums height, θ is the Bragg diffraction angles. Our observations are in agreement with Stefanska *et al.* [9] studies effect of increment of acetyl acetone as chelating factor on the property.
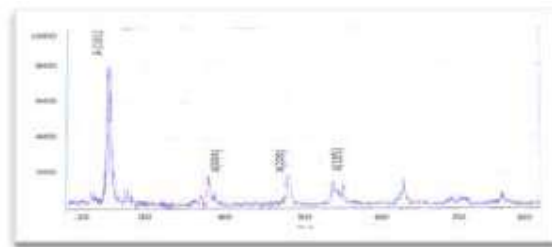

Figure 1: X-ray diffraction (XRD) of TiO_2/AQ nanoparticle.

SEM morphologies of the Nano crystalline AQ doped TiO_2 is depicted in Figure 2 shows SEM image of the prepared nanoparticle obtained by sol-gel method was showed spherical structure. The average diameter of TiO_2/AQ nanoparticle is clear nanostructure can be seen having (65 nm). The nanoparticle seen by SEM picture depends of a number of crystallite that is seen by TEM picture 200 nm.
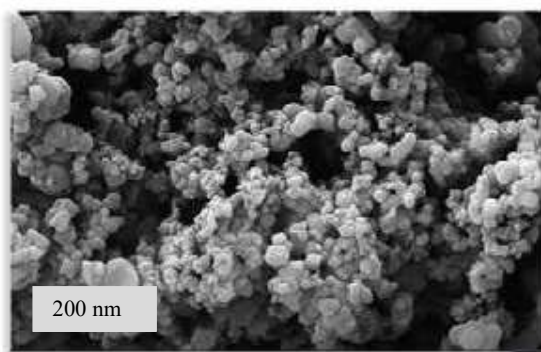

Figure 2: SEM image of TiO2 /AQ nanoparticle

AFM imaging Figure 3 display that the average diameter of the particle were (73.34 nm) that diameter was huge than the value acquired from SEM picture analyses (65 nm).The Root Mean Square lead to be 2.33 nm on the plain TiO_2/AQ surface. It is fully known that AFM gives stellar resolution for higher resolution imaging [10].

Figure 3: AFM 2, 3D topography map of TiO2/AQ nanoparticle.

TEM pictures of sol-gel derive nanoparticle is show in Figure 4 express spherical structure can be seen that have a diameter of (30 nm).The particle size measure through TEM was ordinarily in approval with those determined by XRD although some agglomeration current, led to tip surface energy of the particle. Stefanska *et al.* [9] studied TiO_2 particles prepared with acetylacetone as chelating factor addition display spherical particle and tight size division.
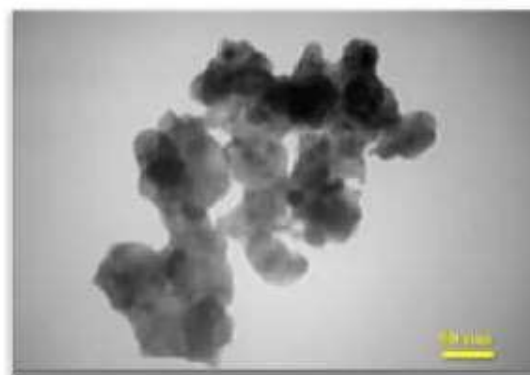

Figure 4: TEM image of TiO2/AQ nanoparticle.

FTIR spectra of nanoparticles of anthraqunone and TiO_2 were recorded to study the functional group and biding sites.

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FTIR spectra of AQ is shown in Figure 5, the assignments of absorption band in the spectra as the band located at 1672.3 cm^{-1} and 690 cm^{-1} are led to the stretching and bending vibration of the C= C bond. The band at 1631.83 cm^{-1} in spectra was led to the bending vibration of the C=O bond It can be seen in the band at 1573.97 cm^{-1} indicating a presence of C-C bond and 1330 cm^{-1} was led to C-H bond.

The FTIR spectrum of TiO$_2$/AQ is shown in Figure 6 a band was appeared at 633, 603cm^{-1} was referred to Ti-O bending mode.

The band at 1450.22 cm^{-1} agrees to the Ti-O-Ti bonding. While the bands at 1672, 1573, 1330, 1168, and 690 cm-1 has been reduced after nanoparticle TiO$_2$/AQ formation. The band at 2350 cm^{-1} was due to C=O stretching vibration and a very small bend appeared at 1406.15 cm^{-1}.

Figure 5: FTIR spectrum of AQ.

Figure 6: FTIR spectra of TiO2/AQ nanoparticle.

Determination of Band Gap of Tio$_2$/AQ Nanoparticle

The band of bulk anatase is 3.2 eV after doping by AQ a tiny change were spotted led to the existence of anatase nanocrystallite the absorbance that seem at energies below the band gap energy while AQ were present in content results in higher insparency in the visible region which leads to higher dispersity, and smaller particle size [11]. The band gap was determined by using Tauc Equation [12] is described accordingly:

$$(\alpha h\nu)^{1/n} = A \, (h\nu - E_g) \qquad (2)$$

Where A is a constant, α is absorption coefficient, and Eg is the energy gap of material and exponent (n) consist on the kind of transition. To determine the likely transition $(\alpha h\nu)1/n$ vs hv is plot and congruent band gap was acquired from extrapolate the part of the graph on hv axis as the energy gap value of TiO$_2$/AQ is found to be (3.05 eV).

Surface Area and Porosity of Tio$_2$ /AQ Nanoparticles

BET and BJH methods were conducted for determination of surface area analysis and porosity analysis. That AQ doped TiO$_2$ resulted in break down of the mesoporous surface area decrease to 15.96 m^2.g^{-1} The situation of that band is influenced by the coordinate geometry round the titanium atom and by the existence of adsorbent as shown in Table 1, Table 2, and Figure 7. Note that TiO$_2$ in the case of doping with AQ less surface area while increase average pore diameter from 104.2 A^o to 365.5A^o.

Komarneni *et al.* [13] determined the surface area of anatase and doped polyvinylpyrrolidone (PVP) during microwave–hydrothermal method which was equal (77 m^2.g^{-1}) because the presence of PVP did not disperse anatase.

Table 1: Surface area and pore size of TiO2/AQ

Pore vol. cm^3.g^{-1}	Pore diam. A^o	Avg. pore diam. A^o	Surface area m^2.g^{-1}	Sample
0.3528	87.70	104.2	129.8	TiO$_2$
0.1498	30.79	365.5	15.96	AQ/TiO$_2$

Figure 7: Surface area of TiO2/AQ.

Table 2: Surface area and pore volume of TiO2/AQ

BJH Pore Size Distribution Desorption

Kinetic Study

Influence of Concentration of Nanoparticle Tio₂/AQ

The removal efficiency of concentration of TiO$_2$/AQ on para-nitrotolune photodegradation is illustrated in Figure 8.

It indicates the decay of p-N.T increased with loading of catalyst up to (0.075 g/l) and 96 % degradation efficiency. The optimum of catalyst load TiO2/AQ nanoparticle was calculated during the scope of 0.025 g/l to 0.25 g/l at pH 5.7 and initial concentration of p-N.T ($1*10^{-4}$ M). The efficiency of p-N.T photodegradation is reduced at higher concentration of catalyst (0.25g/l). The explanation of this phenomenon is that light intensity will be decreased by the suspension of catalyst at high concentration and radical generated is decrease [14].
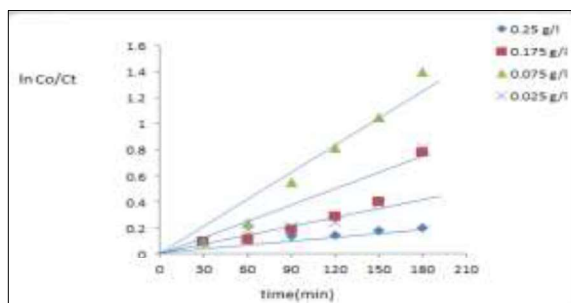

Figure 8: Different loading of nanoparticle TiO2/AQ, P-N.T (1x10-4).

Effect of Initial Concentration of P-Nitrotolune

Photodecomposition reaction seemed to obey a pseudo first − order reaction kinetics, as the results obtained fitted this reaction Equation. The influence is of changing p-NT concentration at scope (1-7 x10^{-4}M).

The rate constant of the photoreactions were (0.0103 min^{-1}) in the presence of catalysis at pH

5.7 The degradation efficiency of p-N.T was as maximum value at $1x10^{-4}$ M where as concentration more than $1x10^{-4}$ M degradation efficiency decreased within 180 min at same conditions of experiment as shown in Figure 9. More molecules covering the surface of TiO_2 /AQ reduce of photon absorption. This result has effects on hydroxyl radicles generation which decreases the efficiency degradation

At substrate concentrations, yet the photonic activity reduce and TiO_2 /AQ surface turn into saturated main to catalyst extinction [15].

1/rate was plotted versus 1/Co based on the data as shown in Figure 10 1/rate correlated to 1/Co well, so the degradation of 4-N.T catalyzed TiO_2/AQ fitted with the Langmuir Hinshelwood (L-H) kinetic model according to Equation 1.

$$1/r = 1/k + 1/kKCo \qquad (3)$$

Where k and K are estimated $(416.67 x10^{-7}$ M^{-1} $min^{-1})$ and $(266.397$ $M^{-1})$ respectively. The high value of adsorption constant (K) indicates to a stronger adsorption on sits at TiO_2 surface.
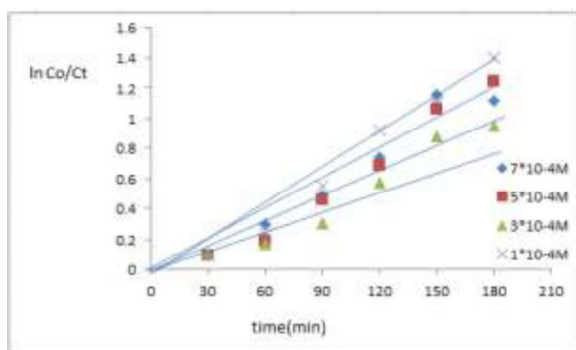

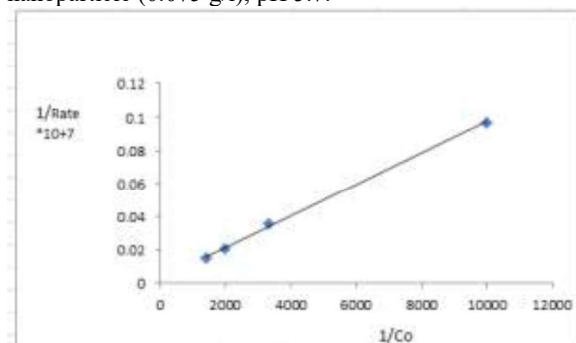Figure 9: Different concentration of p-N.T, TiO2/AQ nanoparticle (0.075 g/l), pH 5.7.

Figure 10: plot of the reverse of the initial rate of p-N.T in TiO2/AQ nanoparticle (0.075g/l) against the reverse of the initial p-N.T concentration.

Effect of PH Value (Tio₂/AQ)

The photocatalytic treatment of p-N.T in the presence of the nanoparticle (TiO_2/AQ) proved to be quite effective one the degradation and mineralization of the toxicity.The rate of photocatalytic degradation was studied in the pH range (3-9) by UV-light, TiO2/AQ) loading 0.075 g/l and initial concentration of p-N.T ($1x$ 10^{-4}M). The maximum degradation was obtained at pH value 5.7 as shown in Figure 11. As pH raise, this will increase the degeneration activity over to pH 5.7, the extreme 96% degeneration activity were acquired at pH 5.7 can be explain by surface charges on the various photocatalyst.
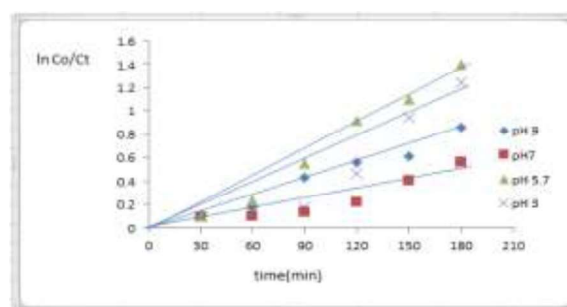

Figure 11: Different pH of TiO2 /AQ (0.075g/l), p-N.T (1x10-4M)

Effect of Temperature on Photo degradation of P-N.T by Tio₂/AQ Nanoparticle.

The rate constant was evaluated at each temperature their results are shown in Figure 12. The photocatalytic degradation reaction for p-NT has been load out by convert the reaction temperature from 288k to 318 k The temperature effect of photodegradation of 4-N.T at initial concentration ($1x10^{-4}$ M), pH 5.7, and (0.075 g/l) of TiO_2 /AQ at 298 K a higher degradation efficiency 96 %. There are in approval with the Arrhenius Equation for that the rate constant ln k must rise linear for reciprocal temperature. Arrhenius land of the reaction rate constant against reverse temperature give a straight line from which the activation energy obtained equal (17.908 kJ/mol), their results are shown in Figure 13.
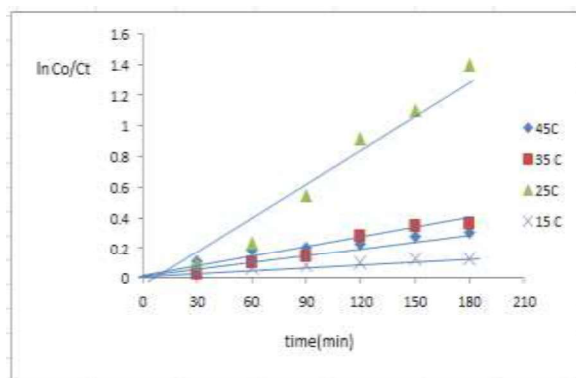
Figure 12: Different temperature of nanoparticle TiO2/AQ (0.075g/l), p-N.T (1x10-4M), pH5.7

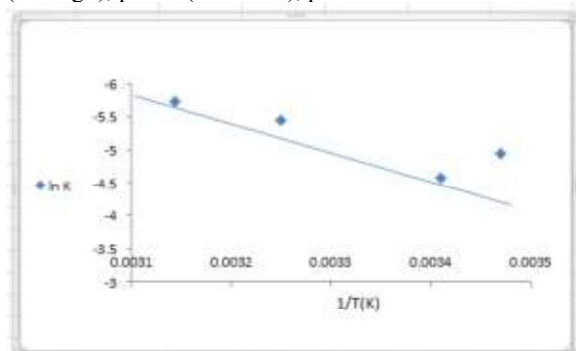Figure 14: Different light sources for p-N.T (1x10-4M), nanoparticle TiO2/AQ and pH5.7

Conclusion

TiO$_2$/AQ nanoparticles synthesized through sol-gel method, the addition of AQ in the method of nanoparticle production cause important changes in texture. X-ray diffraction measurement revealed that the particle size was (24.19nm) of TiO$_2$/AQ. The SEM and TEM were showed the formation of spherical shaped nanoparticle. A considerable reduction in pore volume and surface area are proportional to that of the pure titanium dioxide. It is apparent that the band gap shifts towards lower values in presents AQ is found (3.05 eV) that indicates numbers of free electrons is available for charge conduction. The TiO$_2$ /AQ prepare by sol-gel technique exhibit relatively high photocatalytic efficiency in the photo degeneration of p-NT. The photo degeneration of p-nitrotoleune when 0.075 gm.l^{-1} of TiO$_2$/AQ nanoparticle at pH 5.7 by150 watt that photocatalyst degenerate p-NT up to 96%.

Figure 13: Arrhenius plot for the degradation of p-N.T (1x10-4M)irradiatednanoparticle TiO2/AQ (0.075g/l)

Effect of Different Light Sources

The photodegradation of p-N.T were load out under the irradiation of light of three various sources UV lamp (150 watt), visible light (300 watt) and sun light, photocatalytic reaction rate rely largely on the radiation absorption of the photocatalyst.

The photo degeneration activity of p-N.T were found to be extreme at optimal reaction provision pH 5.7, 1x10^{-4} M of p-N.T and 0.075 g/l amount of TiO2/AQ, down that term in matter, to ensure the diminution in concentration of p-N.T by the photocatalyst. It was spotted that photolysis occupy space by UV-light were lead to be 96%. The 96% photo degeneration was completed under another light source during 180mins; their results are show in Figure 14.
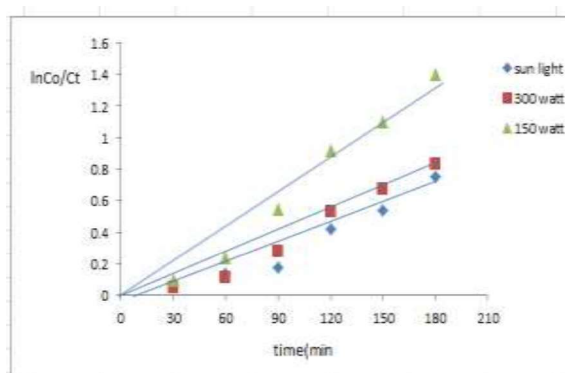
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