# Catalyzed oxidative degradation of methyl orange over Au catalyst prepared by ionic liquid-polymer modified silica

**Y Wang**[1] **and J S Guo**

Key Laboratory of Textile Science and Technology, Ministry of Education, College of Textiles, Donghua University, 2999 North Renmin Road, Shanghai 201620, P. R. China

**Abstract.** A new type of hybrid material was prepared by grafting an ionic liquid monomer, 1-(p-vinylbenzyl)-3-methylimidazolium chloride, on the surface of the porous silica which was synthesized via sodium silicate hydrolysis. The as-synthesized products were characterized by scanning electron microscope, nitrogen physisorption experiment, thermogravimetric analysis and Fourier transform infrared spectra. A catalyst with Au was prepared using the hybrid material as carrier. The experimental results show that the catalyst exhibits a better catalytic effect of hydrogen peroxide on the degradation of methyl orange. The reason may be that the metal component of the catalyst facilitated the dissociation of hydrogen peroxide to produce abundant highly active free radicals which can rapidly ruin the structure of methyl orange molecules in water. Finally, a probable catalytic degradation mechanism based on diffusion was discussed.

## 1. Introduction

Methyl orange, an azo dye, which is extensively applied in various industries, is known to be carcinogenic and mutagenic. Thus, the degradation of methyl orange has attracted particular attention in the last decade. The degradation of methyl orange can be achieved through an intricate oxidation process with multiple auxiliary means. However, some oxidants such as hydrogen peroxide possess the ability to disrupt methyl orange molecules through their dissociation and yet the oxidant is usually stable in the presence of methyl orange. In order to degrade methyl orange thoroughly and quickly, a few auxiliary measures are necessary. Inorganic or organic components in some compounds have been proved to be efficient activators for hydrogen peroxide to generate a variety of free radicals and intermediates [1-5]. Xu et al found that bicarbonate anion can stimulate the dissociation of hydrogen peroxide to liberate active oxygen species which disrupt methyl orange molecules [6]. Ember et al studied the mechanism of Mn(II) activating hydrogen peroxide in the presence of bicarbonate anion and found that the active species formed in the reactions such as the Mn(IV)=O intermediate and hydroxyl radicals are the motivation of the degradation of methyl orange [7]. In addition, Fenton and Fenton-like methods are usually used in the degradation of methyl orange as important means [8-11].

Ionic liquids are typical green chemicals due to their special physicochemical properties. In this paper, we grafted an ionic liquid monomer onto the surface of the porous silica via surface-initiated polymerization, obtaining modified silica. A novel catalyst containing Au was prepared by means of

---

[1] Address for correspondence: Y Wang, Key Laboratory of Textile Science and Technology, Ministry of Education, College of Textiles, Donghua University, 2999 North Renmin Road, Shanghai 201620, P. R. China. E-mail: 1109001@mail.dhu.edu.cn.

the adsorption of the metal ions with the modified silica. This catalyst has prominent catalytic activity for the degradation of methyl orange in the presence of hydrogen peroxide.

## 2. Experimental

### 2.1. Materials
4-(chloromethyl) styrene (90%), 1-methylimidazole (99%), chloroauric acid (HAuCl$_4$, 48-50% based on Au), 2-bromoisobutyryl bromide (98%), γ-aminopropyl triethoxysilane (APS, 98%), triethylamine (TEA, 99%), 2, 2'-bipyridyl (BiPy, AR, 99%) and sodium silicate (47% based on SiO$_2$) were purchased from Aladdin. Ethyl acetate (AR, ≥99.5%), sulfuric acid (AR, 95-98%), acetone (AR, ≥99.5%), ethanol (AR, ≥95%), sodium borohydride (NaBH$_4$, ≥96.0%), hydrogen peroxide (H$_2$O$_2$, AR, ≥30%), N, N-Dimethylformamide (DMF, AR, ≥99.5%) and methyl orange (IND) were purchased from Sinopharm Chemical Reagent Co., Ltd. Toluene (AR, ≥99.5%) was purchased from Sinopharm Chemical Reagent Co., Ltd and dehydrated with 4A molecular sieve prior to use. Copper (I) chloride (CuCl, ≥99.99%) was purchased from Sigma-Aldrich. Other reagents were of analytical grades and used as received.

### 2.2. Characterization
Scanning electron microscope (SEM) measurements were carried out on a FEI (company) Quanta 200F SEM. Nuclear magnetic resonance (NMR) spectra were carried out on a Bruker AVANCE Ⅲ spectrometer. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker TENSOR27 spectrometer using KBr pellets. Thermogravimetric analysis(TGA) was performed on a NETZSCH STA449F3 thermogravimetric analyzer at a heating rate of 10℃/min under nitrogen atmosphere. Ultraviolet-Visible (UV-Vis) spectra were recorded on a SHIMADZU 2550 spectrometer. The nitrogen physisorption experiment was performed on a QUANTACHROME QUADRASORB SI gas sorption system in static measurement mode at 77 K. The Au loading of the catalyst was determined by an inductively coupled plasma (ICP) spectrometer (Prodigy, Leeman Corporation).

### 2.3. Preparation of ionic liquid monomer
Ionic liquid monomer, 1-(p-vinylbenzyl)-3-methylimidazolium chloride ([VBMI][Cl]), was prepared according to a previous literature [12]. Typically, a mixture of 4-(chloromethyl) styrene (4.58 g, 30 mmol) and 1-methylimidazole (2.05 g, 25 mmol) was stirred under N$_2$ at 42℃ for 24 h (figure 1). The reaction mixture was washed with ethyl acetate (3×45 mL) and then dried overnight under vacuum at ambient temperature. ^{1}H NMR (400 MHz, δ, ppm, DMSO-d$_6$): 3.92 (s,3H,-N-CH$_3$), 5.30 (d,1H, *J*=11.0 Hz, C*H*H=CH-), 5.58 (s,2H,Ph-CH$_2$-N-), 5.90 (d,1H, *J*=17.7 Hz, CH*H*=CH-), 6.72-6.79 (m,1H, CH$_2$=CH-), 7.42-8.02 (m,6H, -N-CH-CH-N- and Ph), 9.81 (s,1H, -N-CH-N-).
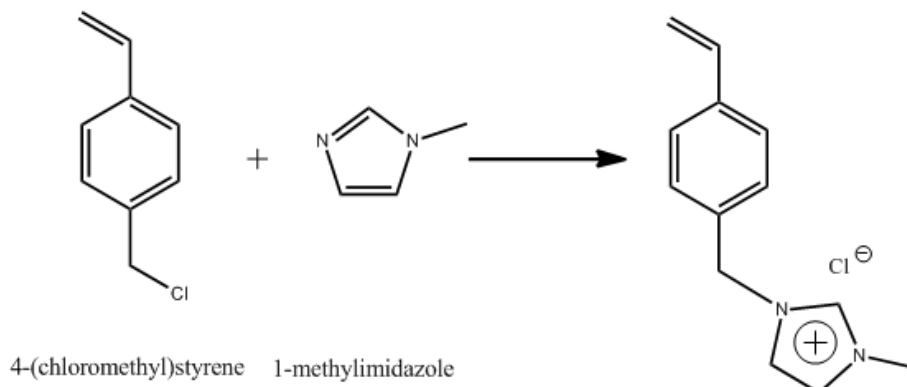


**Figure 1.** Preparation of ionic liquid monomer.

### 2.4. Preparation of porous silica

Porous silica was prepared via sodium silicate hydrolysis. In a typical process, to a solution of sodium silicate (5.0 g) in deionized water (50 mL) was added with stirring an aqueous solution of sulfuric acid (1.8 M, 20 mL). The reaction mixture was stirred at 75℃ for 5 h to form silica gel and then hydrothermally treated at pH=10 at 100 ℃ for 24 h. The crude product obtained was washed many times with deionized water and dried under vacuum conditions at 120℃ for 12 h.

### 2.5. Synthesis of initiator 2-bromo-2-methyl-N-(3-(triethoxysilyl) propyl) propanamide (BTPAm)

BTPAm was synthesized via the reaction of 2-bromoisobutyryl bromide and APS as described previously [13]. A solution of 2-bromoisobutyryl bromide (1.0 mL,8 mmol) in toluene (100 mL) was added dropwise to a cold solution of APS (1.8 mL,8 mmol) in dry toluene(100 mL) with TEA (1.2 mL, 8 mmol) at 0℃. The mixture was magnetically stirred for 3 h at 0℃ and then for another 10 h at ambient temperature (figure 2). The precipitate in the mixture was removed by filtration and the filtrate was evaporated under reduced pressure. $^1$H NMR (400 MHz, δ, ppm, CDCl$_3$): 4.58 (t, 2H, $J$=7.0 Hz, -Si-CH$_2$-), 5.16 (t, 9H, $J$=6.2 Hz, C$H_3$-CH$_2$-O-Si-), 5.57-5.59 (m, 2H, -Si-CH$_2$-C$H_2$-), 5.87 (s, 6H, CH$_3$-C-Br), 7.15 (m, 2H, -CH$_2$-NH-), 7.74-7.78 (m, 6H, CH$_3$-C$H_2$-O-Si-), 8.70 (s, 1H, -NH-).

### 2.6. Immobilization of the initiator onto the porous silica [14]

Porous silica (1.0 g) was added to a solution of BTPAm (0.1 mL) in anhydrous toluene (20 mL) and the mixture was stirred under N2 at room temperature for 24 h (figure 3). The solid was separated from the mixture by filtration and washed with toluene, acetone, and ethanol and then dried under vacuum conditions at room temperature for 12 h, affording BTPAm modified silica (silica-BTPAm).
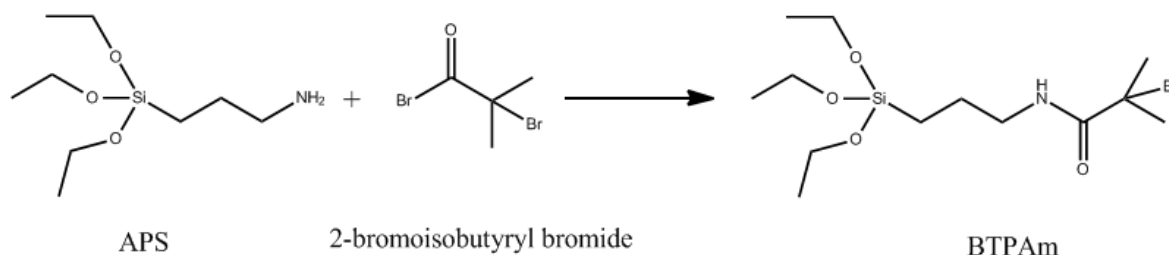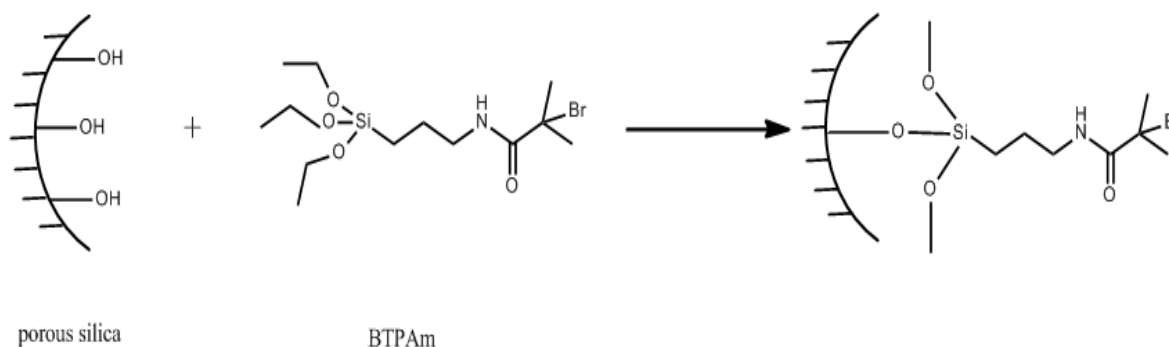


**Figure 2.** Synthesis of initiator BTPAm.



**Figure 3.** Immobilization of the initiator onto the porous silica.

### 2.7. Preparation of the porous silica grafted by poly ([VBMI][Cl]) via surface-initiated polymerization

Silica-BTPAm (2.0 g) was added to a round-bottom flask containing a solution of CuCl (9.9 mg, 0.1 mmol) and BiPy (31.2 mg, 0.2 mmol) in DMF (40 mL) and the mixture was degassed and then filled back with N$_2$. A degassed solution of [VBMI] [Cl] (2.5 g) in DMF (10 mL) was added to the flask. After the reaction mixture was stirred at 60℃ for 24 h (figure 4), the solid was separated from the reaction system by filtration and washed many times with DMF and water. Finally, the product was

dried under vacuum at 80℃ for 12 h, obtaining polymer-modified silica (Silica-PIL). It is shown that Silica-PIL can adsorb gold and palladium ions in water, but could not adsorb methyl orange in water.
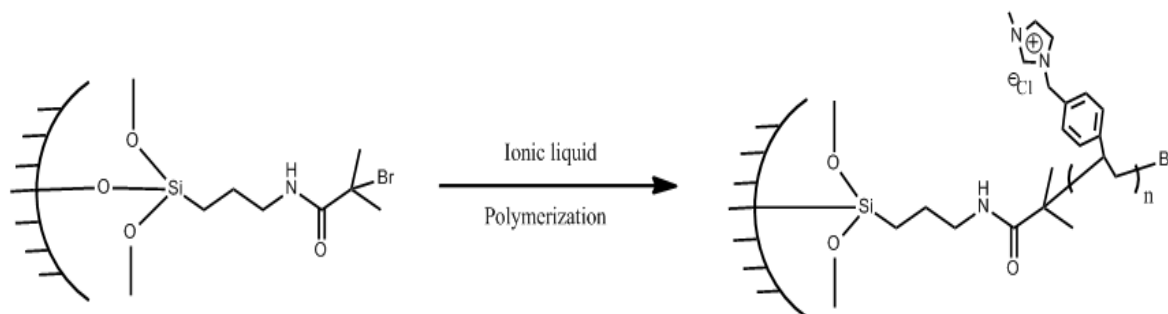


**Figure 4.** Preparation of porous silica grafted by poly ([VBMI][Cl]) via surface-initiated polymerization.

*2.8. Preparation of catalyst.*
Silica-PIL (0.1 g) was added into a vessel containing an aqueous solution of chloroauric acid (7 mM, 4.0 mL) and the mixture was sonicated in water bath and then stirred until the solution was discolored. The solid was separated from the mixture by filtration and dried under vacuum at 60℃ for 4 h. To a flask containing the above solid and deionized water(10 mL) was added with vigorous stirring a cold aqueous solution of sodium borohydride (0.1 M, 1.0 mL) at 0℃. The product was obtained by filtration and dried under vacuum at 40℃ for 4 h, affording the catalyst loaded with Au with a slightly ruby color (Silica-PIL-Au, Au: 4.52%, ICP).

*2.9. Oxidative degradation of methyl orange by hydrogen peroxide in the absence of the catalyst*
To a vessel containing an aqueous solution of methyl orange (100 mg/L, 3 mL) was added an aqueous solution of $H_2O_2$ (30%, 3 mL). The reaction mixture was kept at room temperature for 16 h without stirring.

*2.10. Oxidative degradation of methyl orange by hydrogen peroxide in the presence of Silica-PIL*
To a vessel containing the mixture of an aqueous solution of methyl orange(100 mg/L, 3 mL) and Silica-PIL(0.1 g) was added an aqueous solution of $H_2O_2$ (30%, 3 mL). The reaction mixture was kept at room temperature for 16 h without stirring.

*2.11. Oxidative degradation of methyl orange by hydrogen peroxide in the presence of the catalyst*
To a vessel containing the mixture of an aqueous solution of methyl orange(100 mg/L, 3 mL) and the above catalyst (0.1 g) was added an aqueous solution of $H_2O_2$ (30%, 3 mL). The reaction mixture was kept at room temperature for 16 h without stirring.

## 3. Results and discussion

*3.1. Morphology and physicochemical properties of porous silica*
Morphology of the porous silica was investigated by SEM observation and shown in figure 5. It can be observed that the surface of the sample is scraggly and found many alveolate holes. This special structure may adsorb copious catalytic substances under certain conditions and further provide many active sites for chemical reactions.

The specific surface area and pore volume of the porous silica were calculated from the nitrogen physisorption isotherm (figure 6) using Brunauer- Emmett-Teller (BET) method. The pore size of the porous silica was determined through the above SEM image. Some parameters on the properties of the porous silica are shown in table 1.

### 3.2. Thermal stability of Silica-PIL

TGA, an effective tool to investigate thermal stabilities of various materials, was carried out for Silica-PIL from 30 to 850℃ under nitrogen atmosphere (figure 7). For Silica-PIL, the weight loss around 100℃ is due to the desorption of the physic-adsorbed water. In the range of 200-700℃, a weight loss of 37.38% is mainly ascribed to the decomposition of the organic substances, such as polymeric ionic liquids grafted onto the surface of the sample.
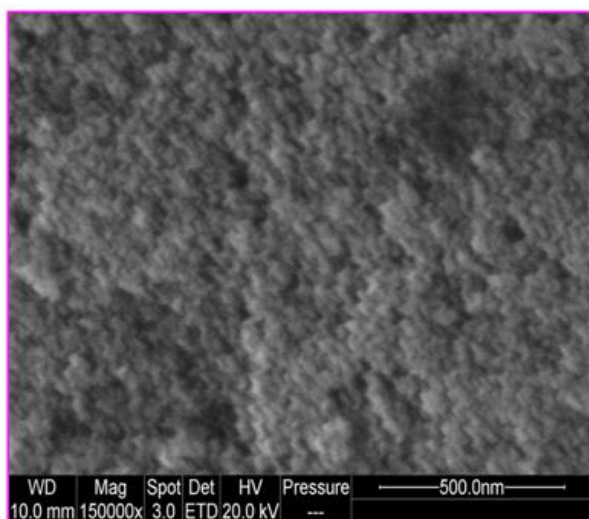


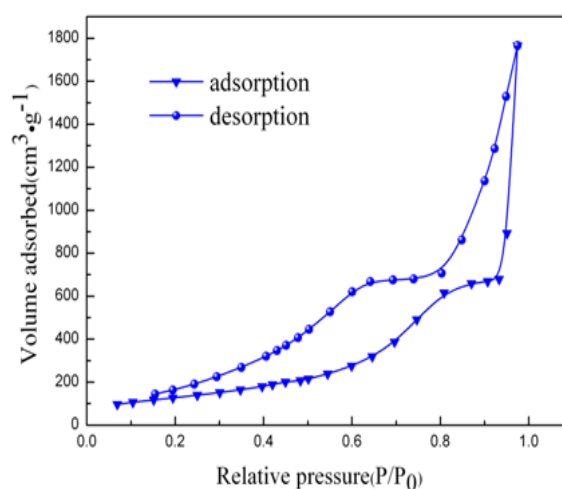**Figure 5.** Morphology of the porous silica.



**Figure 6.** Nitrogen physisorption isotherm for the porous silica.

**Table 1.** Parameters on the properties of the porous silica.

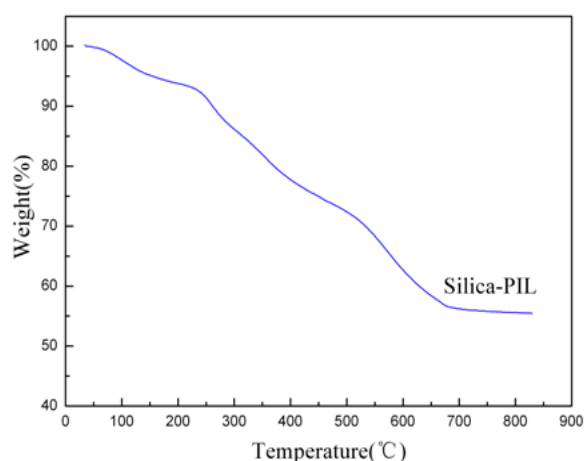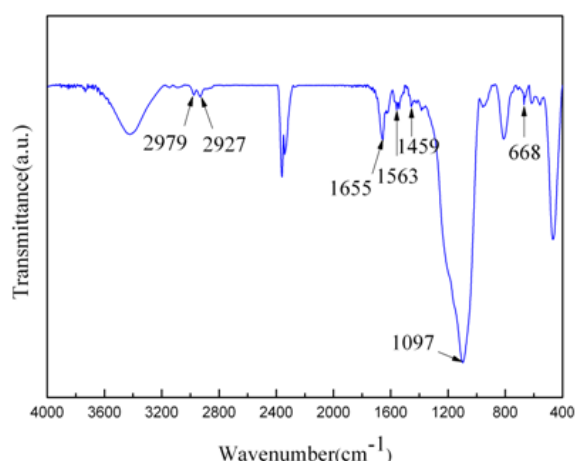|  | specific surface area ($m^2$ $g^{-1}$) | pore volume (mL $g^{-1}$) | pore size (nm) |
| --- | --- | --- | --- |
| porous silica | 479 | 2.73 | 20.0 |



**Figure 7.** TGA curve of Silica-PIL.



**Figure 8.** FT-IR spectrum of Silica-PIL.

### 3.3. The structural analysis of Silica-PIL

The structure of ionic liquid-polymer modified porous silica was investigated by means of FTIR spectrum (figure 8). The FTIR spectrum exhibits a strong band at 1097 cm$^{-1}$ due to Si-O-Si stretching vibration [15, 16]. The bands at 2979 and 2927 cm$^{-1}$ are attributed to C-H stretching vibration [17, 18]. The spectrum also shows other characteristic absorption bands at 1655 and 1563 cm$^{-1}$ for imidazole

ring vibration [19-21] and 1459 cm$^{-1}$ for benzene ring vibration [15, 16]. The band at 668 cm$^{-1}$ can be assigned to C-H bending vibration [15, 16].

*3.4. Evaluation of catalytic activities*
The color of the aqueous solution of methyl orange oxidated by hydrogen peroxide was changed from orange to yellow in the absence of the catalyst and kept this color even after 14 days (image (a) in figure 9). The result shows that the effect of the degradation of methyl orange only over hydrogen peroxide without any catalyst is poor and the thorough degradation of methyl orange in water could not be achieved under the condition. The probable reason is that hydrogen peroxide is stable in the presence of methyl orange [22] and could not produce abundant free radicals to decompose methyl orange. Similar result was obtained for Silica-PIL, suggesting that Silica-PIL has no the catalytic activity for methyl orange.

However, the aqueous solution of methyl orange oxidated by hydrogen peroxide catalyzed by Silica-PIL-Au was decolorized and became clarified after 16 h (image (b) in figure 9), which indicated that the thorough degradation of methyl orange was achieved.
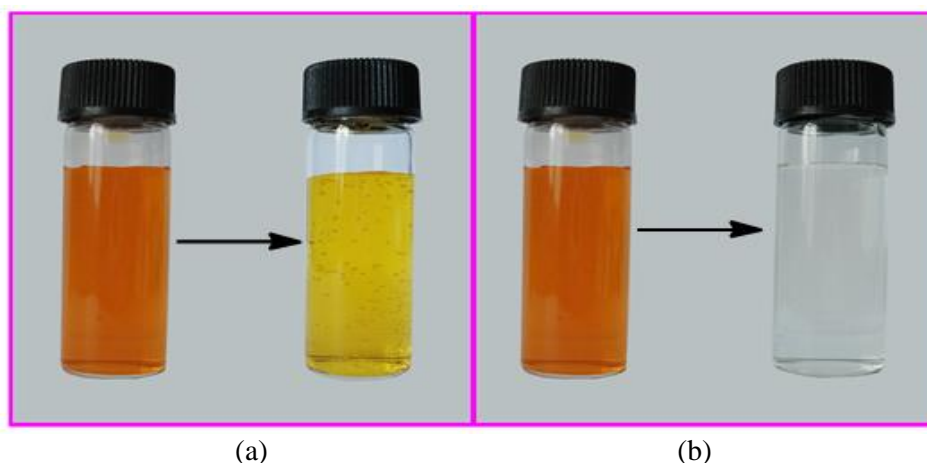


(a)                                      (b)

**Figure 9.** Comparison of the degradation of methyl orange without or with the catalyst.

UV-Vis spectra also demonstrated the complete degradation of methyl orange in water oxidated by hydrogen peroxide in the presence of the catalyst (figure 10). The band at wavelength of 463 nm due to the conjugated structure constructed via azo bond [23, 24] disappeared after the degradation, indicating that the azo structure of methyl orange molecule was damaged. Benzene ring of methyl orange molecule was also damaged after the degradation owning to the disappearance of the band at 273 nm assigned to $\pi$-$\pi^*$ transition of a benzene molecule [25].

Based on the experimental process and results, a probable mechanism is proposed. Obviously, Au immobilized on the catalysts is able to stimulate the decomposition of hydrogen peroxide to form abundant free radicals, such as hydroxyl radicals [10]. These free radicals can rapidly degrade the methyl orange molecules in water (figure 11). And the action continued through the diffusion of the methyl orange molecules in the reaction system toward the surface of the catalyst.

**4. Conclusions**
The synthesis of a novel ionic liquid-polymer modified porous silica was achieved via surface-initiated polymerization. The composite was used as a kind of catalyst after it was loaded with Au. The results showed that the degradation of methyl orange was significantly accelerated and thoroughly achieved under the action of the catalyst compared with that without the catalyst. The probable reason is that Au immobilized on the catalyst facilitates hydrogen peroxide decomposition to produce abundant free radicals which can rapidly damage the molecular structure of methyl orange. Our work has significant implications for preparation of novel catalysts and degradation mechanism of methyl orange.
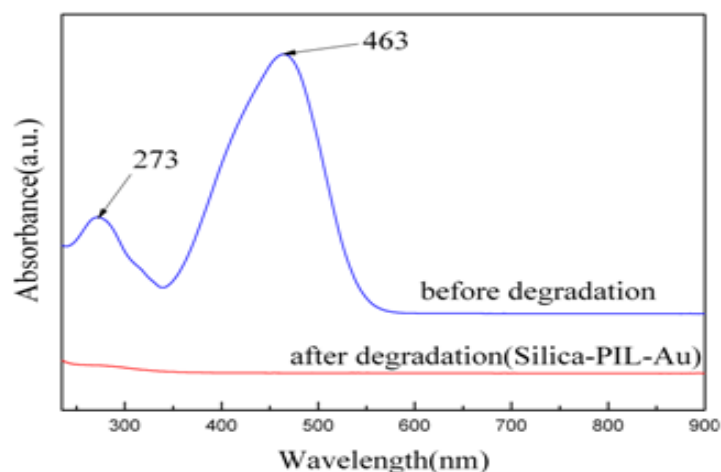
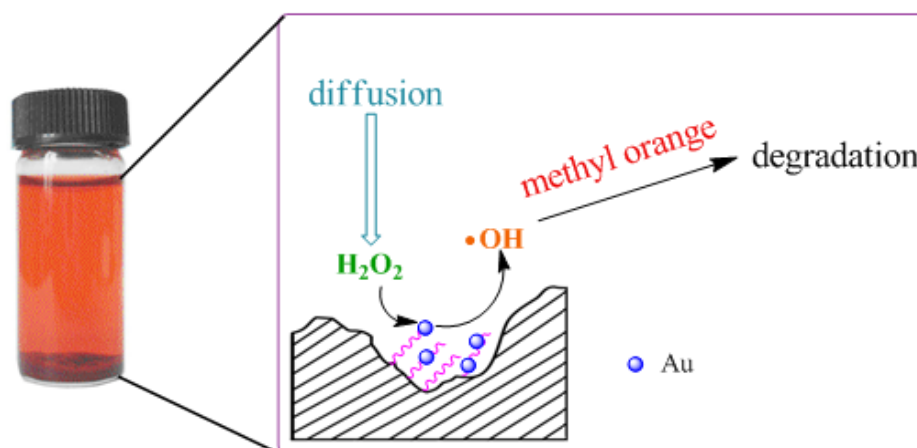**Figure 10.** UV-Vis spectra of methyl orange before/after the degradation.



**Figure 11.** Schematic diagram of a possible mechanism of the catalyzed oxidative degradation of the methyl orange in the reaction system.

**References**
[1]    Thi D N, Ngoc H P, Manh H D and Kim T N 2011 *J. Hazard. Mater.* **185** 653-61
[2]    Panda N, Sahoo H and Mohapatra S 2011 *J. Hazard. Mater.* **185** 359-65
[3]    Xu H Y, Prasad M, Qi S Y and Li Y 2010 *Sci. China. Technol. Sc.* **53** 3014-19
[4]    Ran J W, Li X Y, Zhao Q D, Qu Z P, Li H, Shi Y and Chen G H 2010 *Inorg. Chem. Commun.* **13** 526-8
[5]    Devi L G, Kumar S G, Reddy K M and Munikrishnappa C 2009 *J. Hazard. Mater.* **164** 459-67
[6]    Xu A H, Li X X, Xiong H and Yin G C 2011 *Chemosphere* **82** 1190-95
[7]    Ember E, Gazzaz H A, Rothbart S, Puchta R and van Eldik R 2010 *Appl. Catal. B-Environ.* **95** 179-91
[8]    Ali M E M, Gad-Allah T A, Elmolla E S and Badawy M I 2014 *Desalin. Water. Treat.* **52** 4538-46
[9]    Pham A N, Xing G W, Miller C J and Waite T D 2013 *J. Catal.* **301** 54-64
[10]   Lin T Y and Wu C H 2005 *J. Catal.* **232** 117-26
[11]   Shah V, Verma P, Stopka P, Gabriel J, Baldrian P and Nerud F 2003 *Appl. Catal. B-Environ.* **46** 287-92
[12]   He X Y, Yang W and Pei X W 2008 *Macromolecules* **41** 4615-21
[13]   Sun Y B, Ding X B, Zheng Z H, Cheng X, Hu X H and Peng Y X 2007 *Eur. Polym. J.* **43** 762-72

[14]    Schepelina O and Zharov I 2008 *Langmuir* **24** 14188-94
[15]    Hu F X, Neoh K G, Cen L and Kang E T 2006 *Biomacromolecules* **7** 809-16
[16]    Li C M, Yang J, Wang P Y, Liu J and Yang Q H 2009 *Micropor. Mesopor. Mat.* **123** 228-33
[17]    Nasef M M, Saidi H, Dessouki A M and El-Nesr E M 2000 *Polym Int* **49** 399-406
[18]    Castillejos E, Debouttiere P J, Roiban L, Solhy A, Martinez V, Kihn,Y, Ersen O, Philippot K, Chaudret B and Serp P 2009 *Angew. Chem. Int. Edit.* **48** 2529-33
[19]    Dan Y M, Yu H G, Long Q, Hou A, Liu Y and Qu S S 2004 *Thermochim. Acta.* **419** 169-72
[20]    Wu J P, Wang M J and Stark J P W 2006 *J. Quant. Spectrosc. Ra.* **102** 228-35
[21]    Nanbu N, Sasaki Y and Kitamura F 2003 *Electrochem. Commun.* **5** 383-7
[22]    Cheng L, Wei M Y, Huang L H, Pan F, Xia D S, Li X X and Xu A H 2014 *Ind. Eng. Chem. Res.* **53** 3478-85
[23]    Chen Y P, Liu S Y, Yu H Q, Yin H and Li Q R 2008 *Chemosphere* **72** 532-6
[24]    Zhang A P and Fang Y 2006 *Chem. Phys.* **331** 55-60
[25]    Takeuchi M, Hidaka M and Anpo M 2014 *Res. Chem. Intermediat.* **40** 2315-25