**Catalytic Decomposition of H₂O₂ over a Au/Carbon Catalyst: A
Dual Intermediate Model for the Generation of Hydroxyl Radicals**

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Abstract

The generation of hydroxyl radical ($\text{HO}\cdot$) by H_2O_2 decomposition over solid catalysts (a Fenton-like reaction) will play an important role in the design of new processes for water treatment. More specifically, the understanding of H_2O_2 decomposition on Au nanoparticles (NPs) is crucial for the optimization of the structure of active sites and the evaluation of cytotoxicity of Au NPs. Here, the kinetic behavior of H_2O_2 decomposition over supported Au NPs was investigated in a buffer solution at $\text{pH} \approx 6.8$. Over a range of H_2O_2 concentration, the decay of H_2O_2 followed a pseudo- first order kinetics rate law with an apparent activation energy of 142 kJ/mol. The observed rate constant was linearly increased from $(3.0 \pm 1.0) \times 10^{-3}$ to $(66.7 \pm 2.3) \times 10^{-3} \text{ min}^{-1}$ with the increase in the Au NPs concentration. Further increase in the surface concentration of H_2O_2 may reduce the $\text{HO}\cdot$ generation efficiency. A dual intermediate model was proposed for the generation mechanism of $\text{HO}\cdot$.

Keywords: hydrogen peroxide; Au nanoparticles; hydroxyl radical; Fenton-like reaction; kinetics; dual intermediate model

1. Introduction

The increasing worldwide contamination of surface water and soil is a serious environmental problem [1]. In particular, the treatment of refractory (or non-biodegradable) organic compounds (ROC) with low concentrations (ppm level) in water is a great challenge because of its high operational cost and potential secondary pollution using conventional methods [2].

Fenton-catalytic process ($\text{Fe}^{2+} + \text{H}_2\text{O}_2$) has already proven to be a mature technique for ROC treatment, due to the rapid generation of hydroxyl radicals ($\text{HO}\cdot$), which can completely oxidize ROC into CO_2 and H_2O without light, heat or electricity [3-5]. However, there are still several formidable drawbacks, such as (i) the working pH range is too narrow (pH:2.5~3.5); (ii) the continuous supplement of Fe^{2+} during reaction is necessary for the loss of Fe^{2+} ; (iii) the accumulation of iron-containing sludge leads to the secondary pollution.

Therefore, in order to overcome those drawbacks, the advanced oxidation system with the combination of various iron-free Fenton-like solid catalysts, as a key technique in this process, has been developed to substitute for Fe^{2+} [6-8], such as Cu [9-11], Mn [12, 13], Co [14], Ce [15] and Au [16-18]. The output of sludge is expected to be remarkably reduced. Among all catalysts, supported Au nanocatalysts have demonstrated to be active for creating $\text{HO}\cdot$ by the Fenton-like process without abovementioned disadvantages [16-21]. However, the mechanism for the generation of $\text{HO}\cdot$ by H_2O_2 decomposition over Au catalysts is difficult to attain, since $\text{HO}\cdot$ is a short-life species and hard to instrumentally monitor.

As a versatile oxidant that is effective over the whole pH range with high oxidation potential (1.763 V at pH=0; 0.878 V at pH=14), hydrogen peroxide (H₂O₂) is widely distributed in natural aquatic systems at concentrations exceeding 100 nM [22]. It has proven to be responsible for the biogeochemistry of various transition metals and their complexes [23]. As a signal molecule *in vivo* system, H₂O₂ is an important oxidant for the oxidative metabolism process. Generally, H₂O₂ is relatively harmless as it reacts with biomolecules at reasonably low rates and specific enzymes (such as catalase) to facilitate its removal are usually present [24]. However, with the assistance of metals such as iron and copper, H₂O₂ may be closely related to the cytotoxicity to cells, proteins and living organisms due to the formation of strongly oxidizing reactive oxygen species (ROS) such as hydroxyl radical (HO·) *via* Fenton or Fenton-like processes [25, 26].

In natural aquatic environments, the decay process of H₂O₂ can be triggered by various metal ions (Mⁿ⁺) and HO· can be produced by one-electron reduction of H₂O₂ (eq.1), which serves as the initial step of the chain reaction [27, 28]. In the presence of organic compounds, the chain propagation reaction occurs between oxygen-containing radicals and hydrocarbons, while carbon-containing radicals are also involved in the reaction cycle [29-31]. The generation of HO· is influenced by several factors, such as pH value, [Mⁿ⁺]/[H₂O₂] ratio, dissolved oxygen, inorganic ion and organic substances [32-34].

Additionally, metal-containing solid also mediates the decay of H₂O₂ followed by the formation of HO·, despite the fact that the mechanisms for H₂O₂ decomposition and HO· generation over solid catalysts are still not well understood. Lu [35, 36] and

Andreozzi [37] et al. have proposed a reductive dissolution mechanism to explain the H_2O_2 decomposition over α -FeOOH, respectively. However, it has been demonstrated that the surface reactions were dominated by H_2O_2 decomposition and $HO\cdot$ generation over various solid state materials, including α -FeOOH, α -Fe₂O₃, γ -Fe₂O₃ and ferrihydrite [38-40]. On the basis of surface complexation process, H_2O_2 decomposition was assumed to proceed *via* a series of surface reactions [40-42], including the formation of surface complex (denoted as $[H_2O_2]_s$) (eq.2), a ground state electron-transfer from ligands to metals within the surface complexes (eq.3), the dissociation of ROS (eq.4) and so forth. The formation and decomposition of $[Fe-H_2O_2]_s$ were proposed to be the rate-limiting steps. $HO\cdot$ is yielded from the so-called radical pathway, and O_2 formed *via* a non-radical pathway directly leads to the waste of H_2O_2 in practical application.

However, the chain reactions cannot occur over the oxides that are lack of variable oxidation states, such as Al_2O_3 , SiO_2 , Y_2O_3 and so forth [43-45]. Then, the decomposition process of H_2O_2 could be simplified into: (i) adsorption of H_2O_2 on the surface (eq.5), (ii) the homolysis of O-O bond and the desorption of radicals (eq.6), (iii) the recombination of free radicals (eq.7, 8), and (iv) the oxidation or reduction of surface cations (eq.9, 10).

More recently, the existence of radicals or surface-bond species from H_2O_2 decay was also demonstrated over various noble metals [46-48]. A charge-discharge model was proposed to explain H_2O_2 decomposition over Ag nanoparticles (NPs) [49, 50], a hydroxylating species instead of $\text{HO}\cdot$ was evidenced to be involved in the reaction cycle at $\text{pH} > 7$ (eq.11) [51, 52].

Up to now, only a few studies were contributed to H_2O_2 decomposition over the supported Au catalysts. The Tada's group proposed that this reaction was greatly determined by the properties of the support material, while the reaction rate linearly increased with the downshift of the d- band centers [53, 54]. On the contrary, the theoretical study based on different Au crystalline facets evidenced that the reaction was insensitive to structure. Nevertheless, those assertions were consistent with the experimental results over the peroxidase-like or catalase-like material catalysts [55]. Those disputations indicate the complexity of the reaction. In our previous work, we have found that Au NPs on styrene based activated carbon (SRAC) are highly active and durable for the degradation of BPA in a broad pH range (3.0–7.0) without extra energy compared to other Au-Fenton catalysts [16]. As a consecutive effort, we take Au/SRAC as a model to probe the surface reactions of Au nanocatalysts with H_2O_2 . In particular, the mechanisms of H_2O_2 decomposition and $\text{HO}\cdot$ generation over supported Au nanocatalysts were systematically studied. As a result, the rational design of heterogeneous Fenton

catalyst will be more facile. Furthermore, this study will also lead to a systematic understanding of the environmental implication and the *in vivo* cytotoxicity of naked and supported Au NPs.

2. Experimental

2.1 Catalyst preparation

The synthesis procedure of Au/SRAC (styrene based activated carbon) followed a reported method [16]. A polystyrene-based ion-exchange resin sphere (Rohm & Haas, USA) was used as the precursor of SRAC. It was then carbonated at 1073 K for 2h in a N₂ flow, followed by a steamy activation treatment (1073 K, 60 min). The carbon sphere was ground using an agate mortar, and sieved with 100 mesh. The deposition of Au NPs was carried out following a modified deposition-precipitation procedure, and Au(en)₂Cl₃ (en: 1,2-ethanediamine) was employed as the precursor [56]. The SRAC support was impregnated in the precursor solution (pH=3.0, 298 K) with the assistance of ultrasonic. The samples were washed with MilliQ (18.25 MΩ) water, dried at 313 K overnight, then sealed in a dark place. Before the kinetic measurement, the sample was reduced at 673 K for 30 min with a H₂ flow (10% vol in Ar, 20 ml/min). Several techniques were used for the characterization of Au/SRAC, such as N₂ Adsorption-desorption, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The detailed information was summarized in supporting information (SI). Au NPs catalysts supplied by World Gold Council, denoted as Au/X72s, Au/P25, Au/Fe-Al₂O₃ and Au/Fe₂O₃, were used as references.

2.2 Kinetics measurement

The interaction between Au/SRAC and H_2O_2 was tracked by measuring the concentration of H_2O_2 or $\text{HO}\cdot$ in the whole reaction. The experiments were conducted in an isothermal batch reactor stirring at a speed of 700 rpm. The rigid stirring assured the complete mixing of catalyst and H_2O_2 [57]. All solutions were prepared by MilliQ water (degassed by boiling) and chemicals with analytical reagent degree. The pH value was adjusted using NaOH (0.01 mol/L) and HNO_3 (0.01 mol/L) and monitored by a pH meter (Leici, China), which was kept within ± 0.1 pH unit. 3 (N-morpholino) propane-sulfonic acid (MOPS, Aladin Reagent, China) was used as the buffer to keep the pH of ~ 6.8 . After filtration with 0.22 μm Nafion[®] membranes, the samples were analyzed for pH, concentration of H_2O_2 , concentration of $\text{HO}\cdot$ and the residue of gold ion. The operations before analysis including sample collection, filtration or acidification (for $\text{HO}\cdot$ qualification only) will be finished within 30 s.

H_2O_2 concentration was analyzed colorimetrically using a UV-vis spectrophotometer (UX100, Phoenix, China) after complexation with a $\text{TiOSO}_4/\text{H}_2\text{SO}_4$ reagent [58]. The concentrations of $\text{HO}\cdot$ was measured by a molecular probe method [59]. Benzoic acid (BA) was selected as the probe, which had a determined reaction rate constant toward $\text{HO}\cdot$ ($4.2 \times 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$) in aqueous solution [60]. As mentioned by Zhou and Mopper [61], the BA solution should be acidified by diluted HCl (1.0 mol/L) to pH=3.0. Then BA and hydroxybenzoic acids (HBA) were quantified by high performance liquid chromatography (HPLC, Flex, Perkin Elmer, USA). A Spheri ODS-2 column with a length of 25 cm was equipped. The flow rate of mobile phase was set to 1 ml/min and the ratio of water (A) to acetonitrile (B) was gradually changed. Water was

kept 15% within the first 3 min and linearly increased to 100% in the following 12 min.

The residue contents of Au in reaction solutions were also measured by ICP-MS.

The modeling of the kinetic data and the prediction of reaction network were undertaken with the assistance of DynaFit (4.05.087 version) [62].

3. Results and Discussion

3.1 Structure of Au/SRAC

Unless otherwise stated, Au(1.5wt%)/SRAC was used as a model catalyst in the present study. Its surface area is 980 m²/g, as estimated by BET (Fig. S1a). The carbon support was stacked by numerous spherical particles within a size range 30-100 nm (Fig. S1b). The aggregative particles linked with each other at random directions, which led to the formation of 3D meso- or macro-porous structure. The Au NPs were evenly dispersed on the support with an average size of 4.6 ± 0.8 nm (Fig. S1c and S1d).

3.2 Kinetics of H₂O₂ decomposition

The rate of H₂O₂ decomposition over Au/SRAC was determined by measuring the relationship of H₂O₂ concentration vs. time. The reaction is regarded as irreversible due to the final formation of gaseous oxygen. The mass balance in this reaction system can be summarized as eq. 12.

$$V_r \frac{d[H_2O_2]}{dt} + [H_2O_2] \frac{dV_r}{dt} = \dot{V}_{in}[H_2O_2]_{in} - \dot{V}_{out}[H_2O_2] - k_{obs}[H_2O_2]^m V_r \quad (12)$$

For a continuous stirred tank reactor (CSTR), assuming the V_r and ρ as constant, thus

$$\frac{d[H_2O_2]}{dt} = \frac{[H_2O_2]_{t=0} - [H_2O_2]_{t=\tau}}{\tau} - k_{obs}[H_2O_2]^m \quad (13)$$

192 The reaction rate of H_2O_2 decomposition can be expressed as eq. 14, where m is the order
193 of reaction.

$$194 \quad r_{\text{H}_2\text{O}_2} = -\frac{d[\text{H}_2\text{O}_2]}{dt} = k_{\text{obs}}[\text{H}_2\text{O}_2]^m \quad (14)$$

$$195 \quad -\frac{d[\text{H}_2\text{O}_2]_{t=\tau}}{dt} = k_{\text{obs}}[\text{H}_2\text{O}_2]_{t=\tau} \quad (15)$$

196
197 **Fig. 1** First-order fit curves of H_2O_2 decomposition at different initial concentrations of
198 H_2O_2 : 3.29 mM (■); 5.18 mM (●); 6.65mM (▲); 10.64 mM (▼); 17.53mM (◆); 35.21
199 mM (►), catalyst 250 mg/L, 298K, pH=6.8

200 As mentioned by previous works [32, 47, 63], H_2O_2 decomposition was generally
201 assumed as a first-order reaction. Therefore, the concentration of H_2O_2 on a log scale was
202 plotted as a function of the reaction time by eq.16 (Fig. 1). The fitting of the data was
203 obviously a linear regression, which yielded the correlation coefficients above 0.98. This
204 indicated that the decomposition of H_2O_2 over Au/SRAC followed a pseudo first- order
205 kinetic rate law (eq. 16).

$$\ln([H_2O_2]_{t=\tau}/[H_2O_2]_{t=0}) = -k_{obs}t \quad (16)$$

The k_{obs} represented the observed first-order rate constant, being independent of the initial concentration of H_2O_2 ($[H_2O_2]_0 \leq 6.65$ mM), corresponding to an average rate constant of $(44.2 \pm 2.0) \times 10^{-3} \text{ min}^{-1}$. The observed rate constant decreased with the increase in the initial concentration of H_2O_2 ($[H_2O_2]_0 > 6.65$ mM), which indicated that the number of active sites for H_2O_2 decomposition was limited and the reaction pathway began to differentiate with an increase in the H_2O_2 concentration. The kinetic modeling over the whole concentration range will be proposed in the last section.

We compared the observed rate constants of Au/SRAC ($[H_2O_2]_0 \leq 6.65$ mM) with those of other supported Au catalysts (Table 1). Based on the concentration of exposed Au atoms (eq.17), the turnover frequency (TOF) of H_2O_2 decomposition was calculated as eq. 18. The TOFs of supported Au catalysts varied from about $\sim 1.0 \text{ h}^{-1}$ to over one thousand per hour [19, 53, 54, 64]. It indicated that the number and the performance of the specific active sites responsible for the decay of H_2O_2 changed significantly with the variation of the structure and the support of these supported Au catalysts. Both the size effect and the interaction between Au NPs and the support greatly influenced the decomposition rate.

$$[Au, \text{exposed}] = \frac{m_{Au}}{M_{Au}} \times 6 \frac{V_m/a_m}{d} \quad (17)$$

$$TOF = \frac{r_{H_2O_2}}{[Au, \text{exposed}]} \quad (18)$$

226 **Table 1**

227 The summary of the first-order rate constants of H₂O₂ decomposition over different Au- Fenton catalysts

Catalyst	Loading amount (wt%)	Particle size (nm)	Rate or Rate constant (h ⁻¹)	TOF (h ⁻¹)	Catalyst Loading (mg/L)	T (K)	pH	Target Compound s	Ref.
Au/SRAC	1.5	4.6	2.7	1706	250	313	6.8	--	This work
Au/TiO ₂	0.2	3.5		181	1000	298	4.5	--	[53]
Au/SrTiO ₃	0.6	2.7		337	1000	298	6.0	--	[54]
Au/Fe ₂ O ₃ - Al ₂ O ₃	1.6	3.5		1	1 × 10 ⁴	313	~6.8	--	[64]
Au/CeO ₂	1.0	5		372	49.0		4.0	phenol	[19]
Au/Fe ₂ O ₃	1.5	4		27	32.8			(100 mg/L)	
Au/TiO ₂	1.5	15		240	32.8	298		--	

Au/C	0.8	10		118	61.6				
Au/HO-npD	1.0	<1		47	49.2				
Au/TiO ₂	0.8	3.1		2.5×10^4	2500	353	3.5		
Au(3)/C	0.1	5.1		16.7×10^4				phenol	
Au(5)/C	0.5	4.9		4.1×10^4				(4500	[65]
Au(7)/C	0.5	6.8		2.3×10^4				mg/L)	
Au(10)/C	0.5	9.1		1.9×10^4					

228 TON mol H₂O₂/mol Au exposed

229

3.2.1 The effect of Au/SRAC concentration

At pH~6.8, catalysts of 5, 10, 15, 25 and 50 mg were added into H₂O₂ (35.21 mM) solutions of 100 ml. Thus, the molar ratio of H₂O₂ to Au/SRAC was in the range 0.35~3.52. As a function of reaction time, the conversion of H₂O₂ was plotted in a log scale (Fig. 2). The observed rate constant was $(3.0 \pm 1.0) \times 10^{-3} \text{ min}^{-1}$ with the catalyst of 50 mg/L, and increased to $(66.7 \pm 2.3) \times 10^{-3} \text{ min}^{-1}$ over 500 mg/L catalyst. The rate constant was directly proportional to the catalyst concentration. Therefore, we try to fit the rate constants as a function of catalyst concentration (Fig. 3). Then, the rate expression can be expressed by eq.19.

$$-\frac{d[\text{H}_2\text{O}_2]}{dt} = -k[\text{catal.}][\text{H}_2\text{O}_2]_{t=\tau} \quad (19)$$

Fig. 2 First-order fit curves of H₂O₂ decomposition at different concentrations of the Au/SRAC catalyst: 50 mg/L (■); 100 mg/L (●); 150 mg/L (▲); 250 mg/L (▼); 500 mg/L (◆), initial concentration of H₂O₂ 35.21mM, 298 K, pH=6.8

The fitting of a second-order reaction rate law was generally proceeded. The directly proportional relationship between the observed rate constant and the catalyst concentration may indicate a surface-intermediate reaction mechanism [40]. By this strategy, we obtained the second-order rate constant with respect to the concentration of catalyst and H_2O_2 as $0.14 \text{ L} \cdot \text{min}^{-1} \cdot \text{g}^{-1}$. As summarized in Table 2, the second order rate constant for H_2O_2 decomposition on Au/SRAC with respect to the concentration of catalyst and H_2O_2 falls into the same range as those on bulk iron-solid catalysts, and it is a magnitude lower than those on supported Fe-Fenton catalysts and homogenous Fenton catalysts. As reported by Garcia et al. [19], Au-based Fenton system has high potential on the generation efficiency of $\text{HO}^\cdot$, as high as 79%. Unfortunately, the relative low reaction rate may hamper its practical application. As listed in Table 2, we observed a comparable reaction rate based on the identical weight of the catalyst. However, the correlation coefficients is as low as 0.91. It implies the decomposition of H_2O_2 over Au nano-catalyst as an intricate and ingenious process.

Fig. 3 Fitting curve of rate constant as the function of catalyst concentration

Table 2

The comparison of second-order rate constant of H₂O₂ decomposition on Au/SRAC with those on other catalysts

Catalyst	Rate constant (M ⁻¹ ·S ⁻¹)	Ref.
Ferrous ion	0.044	[66]
Ferric ion	0.01~0.09	[67]
Fe ₂ O ₃ /Al ₂ O ₃	0.03	[68]
Goethite	0.0016	[69]
Ag NPs	0.0031	[70]
Au/SRAC	0.0024	this study

3.2.2 The effect of reaction temperature

The dependency of rate constant on the reaction temperature usually follows the Arrhenius equation (eq.20), where E_a is the activation energy for the reaction, A is the pre-exponential factor and R is the gas constant. The linear regression of the conversion in a log scale vs. the reaction time exhibited that the reaction was in good agreement with the first-order behavior in the temperature range 298~353K. E_a can be calculated by the correlation of ln*k*_{obs} vs. 1/T. With the rise of temperature, the rate constant increased from (9.2±0.7) × 10⁻³ min⁻¹ (298 K) to (16.6±0.7) × 10⁻³ min⁻¹ (353 K), while the E_a of 142 kJ/mol was obtained (Fig. 4). As compared to the homolysis energy of O-O bond in H₂O₂, 208 kJ/mol, the decrease in E_a indicated the catalytic effect of Au/SRAC on its metal-

liquid interface. However, the relative high E_a for Au/SRAC in comparison with other metal oxide systems (generally 30~60 kJ/mol) [40, 43, 45, 71, 72] indicated a different reaction pathway of H_2O_2 decomposition over this catalyst.

$$k_{obs} = Ae^{-E_a/RT} \quad (20)$$

Fig. 4 First-order fit curves of H_2O_2 decomposition at different reaction temperatures: 298 K (■); 303 K (●); 313 K (▲); 328 K (▼); 343 K (◆); catalyst 250 mg/L, initial H_2O_2 concentration 6.65mM, pH=6.8

3.2.3 The effect of diffusion

To study the diffusion effect on this reaction, we calculated the Thiele modulus by eq. 21

$$\phi = [k_{obs}/(D/L^2)]^{0.5} \quad (21)$$

Where D is the diffusion coefficient (cm^2/s), and L is the thickness of the stagnant liquid film or the pore length (cm). Typically, the diffusion coefficient is $ca. 1.0 \times 10^{-5} cm^2/s$,

while the thickness of the stagnant liquid film can be estimated ca. 1.0×10^{-3} cm [73]. Therefore, the Thiele modulus, ϕ of H_2O_2 decomposition over this Au/SRAC catalyst was in the range $2.84 \times 10^{-3} \sim 7.36 \times 10^{-3}$. So, the process was much slower than the diffusion with $\phi > 5$. Moreover, the calculated activation energy (142 kJ/mol) was also significantly higher than that of a diffusion-controlling reaction (10~13 kJ) [74]. Therefore, the diffusion effect of this system is negligible, and the system is reaction-controlling.

3.3 Plausible mechanism

3.3.1 Generation of hydroxyl radicals

The efficiency of $\text{HO}\cdot$ generation was already defined as described by eq.22 [26, 75, 76]. The decay rates for H_2O_2 and BA were measured simultaneously. The generation efficiency of $\text{HO}\cdot$ was strongly dependent on the ratio of H_2O_2 /catalyst after dosing probe molecules. The $\text{HO}\cdot$ efficiency of 31.7% (Table 3) was estimated when the initial H_2O_2 concentration was lower than 6.65 mM, and it decreased with an increase in the initial concentration of H_2O_2 .

$$\delta = \frac{\Delta[\text{probe}]}{\Delta[\text{H}_2\text{O}_2]} \times 100\% \quad (22)$$

Table 3HO $\cdot$ generation efficiency over Au/SRAC

H ₂ O ₂ (mM)	Catal. (mg·L ⁻¹)	δ (%)
3.29	250	30.22
5.18	250	33.24
6.65	250	31.65
10.64	250	27.90
17.53	250	22.89
35.21	250	17.45

3.3.2 Mechanistic modeling

DMPO-trapped EPR spectra [16] have demonstrated that HO $\cdot$ was indeed generated during the degradation of BPA. This robust oxidant has long been demonstrated to benefit the degradation of numerous persistent compounds in aqueous phase. Therefore, the high yield of HO $\cdot$ by H₂O₂ decomposition consequently leads to the economic advantages of the involved Fenton process.

As assumed by Bond [77], the decomposition of H₂O₂ over metal catalysts in aqueous solution involved an electron transfer from metal to adsorbate and a chain reaction on the surface of metal. The negative charged Au NPs facilitate the adsorption and reaction of H₂O₂. The edge sites of Au NPs would likely decrease the energy barrier for surface-OH desorption, which could enhance the generation of HO $\cdot$ radicals [78, 79]. It should be noted that here we only focus on the mechanistic understanding of the generation process of HO $\cdot$ and the decomposition process of H₂O₂. The structure-

performance relationship of the present H₂O₂-Au/SRAC system was beyond the study of this work.

The reaction pathway of H₂O₂ decomposition changed significantly with the variation of H₂O₂ concentration. We assumed that the intermediates could further react with H₂O₂, leading to a series of more complicated surface reactions and a subsequent reduction on the overall consuming rate of H₂O₂. As indicated by our previous work [16], HO· radicals were created and OOH·/O₂· radicals were involved in the regeneration of active sites. Thus, the proposed reaction mechanism was summarized as Reactions 1-5, which indicated the surface reactions between the catalyst and H₂O₂. The further oxidation of OOH· leads to the generation of O₂ through Reactions 4-5.

According to the reaction mechanism, the rate of H₂O₂ decomposition can be presented by eq.23.

$$-\frac{d[\text{H}_2\text{O}_2]}{dt} = k_1[\text{Au}^{\delta-}][\text{H}_2\text{O}_2] + k_2[\text{H}_2\text{O}_2][\text{S}] + k_4[\text{H}_2\text{O}_2][\text{S}\cdot] \quad (23)$$

The surface species directly formed as depicted as Reaction 2, where (Au^{δ-}-H₂O₂)_s is simplified as S (Intermediate 1 in Scheme 1). Its generation rate is:

$$-\frac{d[\text{S}]}{dt} = k_2[\text{S}][\text{H}_2\text{O}_2] + k_3[\text{S}] - k_1[\text{Au}^{\delta-}][\text{H}_2\text{O}_2] \quad (24)$$

However, the further reaction between S and H₂O₂ resulted in the generation of (Au^{δ-}-HO)_s, denoting as S[·] (Intermediate 2 in Scheme 1). Therefore, the accumulation rate of S[·] is calculated as eq. 25.

$$-\frac{d[S^{\cdot}]}{dt} = k_2[S][H_2O_2] - k_{2a}[S^{\cdot}] - k_4[S^{\cdot}][H_2O_2] \quad (25)$$

Assuming that the intermediate S and S[·] were in steady states, and the accumulation rates of them approached to zero. Thus, the concentrations of S and S[·] can be obtained from eqs. 26-27, respectively.

$$[S^{\cdot}] = \frac{k_2[S][H_2O_2]}{k_{2a} + k_4[H_2O_2]} \quad (26)$$

$$[S] = \frac{k_1[Au^{\delta-}][H_2O_2]}{k_2[H_2O_2] + k_3} \quad (27)$$

After the substitution of eq.26 and eq. 27 into eq. 23, the following equation (eq. 27) representing H₂O₂ decomposition rate is yielded.

$$\begin{aligned} r = -\frac{d[H_2O_2]}{dt} &= \left\{ k_1 + \frac{k_1 k_2 [H_2O_2]}{k_2 [H_2O_2] + k_3} + \frac{k_1 k_2 k_4 [H_2O_2]^2}{(k_2 [H_2O_2] + k_3)(k_{2a} + k_4 [H_2O_2])} \right\} [Au^{\delta-}][H_2O_2] \\ &= \left\{ k_1 + \frac{k_1 k_2 [H_2O_2]}{k_2 [H_2O_2] + k_3} + \frac{k_1 k_2 k_4 [H_2O_2]^2}{(k_2 [H_2O_2] + k_3)(k_{2a} + k_4 [H_2O_2])} \right\} [Catal.][H_2O_2] \end{aligned} \quad (28)$$

By using Dyna Fit, the model fitting according to the reaction set (Reaction 1-5, Table 4) is able to explain the H₂O₂ decay process in the initial concentration range 6.65~35.21 mM. The reaction rate was proportional (but not linear) to the initial concentration of H₂O₂ (Fig. 5). The formation of (Au-H₂O₂)_s surface species acted as the precursor for HO[·] generation. When the active sites are fully covered by H₂O₂, HO[·] cannot desorb from the surface of catalysts, but form surface species, (Au-OH)_s. The

surface OH is more electrophilic toward Au NPs than adsorbed H_2O_2 molecule [80]. Thus, $(\text{Au-OH})_s$ was more electron deficient than $(\text{Au-H}_2\text{O}_2)_s$ as well as Au NPs. This active site of electron deficient will lead to the oxidation of H_2O_2 and the formation of $\cdot\text{OOH}$ as a consequence. In general, the formation of active complex (Intermediate 1 and 2 in Scheme 1) with a steady-state will lead to the production of different radicals and gaseous oxygen.

Fig. 5 Model verification for H_2O_2 decomposition at different loading of catalyst: 50 mg/L (■); 100 mg/L (●); 150 mg/L (▲); 250 mg/L (▼); 500 mg/L (◆), initial concentration of H_2O_2 35.21mM, 298 K, pH=6.8

Table 4

Rate constants of the elemental surface reactions

Reaction No.	Equation	Reaction rate constant ($M^{-1} \cdot \text{min}^{-1}$)
1	$\text{Au}^{\delta-} + \text{H}_2\text{O}_2 \xrightarrow{k_1} (\text{Au}^{\delta-} - \text{H}_2\text{O}_2)_s$	$(19.5 \pm 0.7) \times 10^{-3}$
2	$(\text{Au}^{\delta-} - \text{H}_2\text{O}_2)_s + \text{H}_2\text{O}_2 \xrightarrow{k_2} (\text{Au}^0 - \text{HO})_s + \text{H}_2\text{O} + \text{OOH} \cdot$	$(0.3 \pm 0.1) \times 10^{-3}$
3	$(\text{Au}^{\delta-} - \text{H}_2\text{O}_2)_s \xrightarrow{k_3} \text{Au}^0 + \text{OH}^- + \text{OH} \cdot$	$(1.7 \pm 0.1) \times 10^2$
4	$(\text{Au}^0 - \text{HO})_s + \text{H}_2\text{O}_2 \xrightarrow{k_4} \text{Au}^{\delta-} + \text{OOH} \cdot + \text{H}_2\text{O}$	84.9 ± 4.5
5	$\text{Au}^0 + \text{OOH} \cdot \xrightarrow{k_5} \text{Au}^{\delta-} + \text{O}_2 + \text{H}^+$	$(2.7 \pm 0.1) \times 10^3$

The dual-intermediate mechanism proposed for this process was schematically expressed as Scheme 1. It should be noted that the generation of ROS by one-electron transfer in turn inhibited H_2O_2 decomposition in the whole concentration range. With an increase in the initial concentration of H_2O_2 , the dominant surface species evolved from $(\text{Au}-\text{H}_2\text{O}_2)_s$ to $(\text{Au}-\text{OH})_s$. As a result of the formation of $(\text{Au}-\text{OH})_s$ species, the H_2O_2 decay process followed a competitive inhibition behavior. The distribution or equilibrium of different surface species determined the reaction between radical (one-electron transfer) and non-radical (two-electron transfer) pathway. In natural aquatic environments, therefore, the H_2O_2 dependence of formation of dual intermediates $((\text{Au}-\text{H}_2\text{O}_2)_s$ and $(\text{Au}-\text{OH})_s$) arising from Au NPs reacting with H_2O_2 suggests that Au NPs may be more toxic

in lower H_2O_2 environments as excess H_2O_2 may render the reaction shift from radical (one-electron transfer) to non-radical (two electron transfer) pathway.

Scheme 1. The proposed reaction mechanism

4. Conclusions

Au/SRAC catalysts were proven to be effective Fenton-like catalysts for the generation of $\text{HO}\cdot$. The kinetics study indicated that the decomposition of H_2O_2 over Au NPs followed a pseudo- first order kinetics rate law with an apparent activation energy of 142 kJ/mol. With an increase in the catalyst concentration from 50 mg/L to 500 mg/L, the rate constant of the catalytic H_2O_2 decomposition was linearly increased from $(3.0\pm 1.0)\times 10^{-3}$ to $(66.7\pm 2.3)\times 10^{-3} \text{ min}^{-1}$. A dual-intermediate mechanism was proposed on the basis of the structure of Au/SRAC and the kinetic study. $(\text{Au}-\text{H}_2\text{O}_2)_s$ and $(\text{Au}-\text{OH})_s$, which lead to the generation of different radicals and gaseous oxygen, are key intermediates of the H_2O_2 decomposition process. The dominant surface species evolved

from (Au-H₂O₂)s to (Au-OH)s with the increase in the H₂O₂ concentration. Consequently, excess H₂O₂ may render the reaction shift from radical to non-radical mechanism, thus reducing the HO· generation efficiency.

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References

- [1] R.P. Schwarzenbach, B.I. Escher, K. Fenner, T.B. Hofstetter, C.A. Johnson, U. von Gunten, B. Wehrli, *Science* 313 (2006) 1072.
- [2] E.V. Rokhina, J. Virkutyte, *Crit. Rev. Environ. Sci. Technol.* 41 (2010) 125.
- [3] E. Neyens, J. Baeyens, *J. Hazard. Mater.* 98 (2003) 33.
- [4] D. Mantzavinos, D. Kassinos, S.A. Parsons, *Water Research* 43 (2009) 3901.
- [5] R. Andreozzi, V. Caprio, A. Insola, R. Marotta, *Catal. Today* 53 (1999) 51.
- [6] M. Hartmann, S. Kullmann, H. Keller, *J. Mater. Chem.* 20 (2010) 9002.
- [7] A. Dhakshinamoorthy, S. Navalon, M. Alvaro, H. Garcia, *ChemSusChem* 5 (2012) 46.
- [8] E.G. Garrido-Ramírez, B.K.G. Theng, M.L. Mora, *Appl. Clay. Sci.* 47 (2010) 182.
- [9] A.N. Pham, G. Xing, C.J. Miller, T.D. Waite, *J. Catal.* 301 (2013) 54.
- [10] F.-S. Xiao, J. Sun, X. Meng, R. Yu, H. Yuan, J. Xu, T. Song, D. Jiang, R. Xu, *J. Catal.* 199 (2001) 273.
- [11] V. Subbaramaiah, V.C. Srivastava, I.D. Mall, *AIChE J.* 59 (2013) 2577.
- [12] Y.-F. Han, F. Chen, K. Ramesh, Z. Zhong, E. Widjaja, L. Chen, *Appl. Catal. B: Environ.* 76 (2007) 227.
- [13] T. Sriskandakumar, N. Opembe, C.-H. Chen, A. Morey, C. King'onde, S.L. Suib, *J. Phys. Chem. A* 113 (2009) 1523.
- [14] T. Valdés-Solís, P. Valle-Vigón, M. Sevilla, A.B. Fuertes, *J. Catal.* 251 (2007) 239.
- [15] E.G. Heckert, S. Seal, W.T. Self, *Environ. Sci. Technol.* 42 (2008) 5014.
- [16] X. Yang, P.-F. Tian, C. Zhang, Y.-q. Deng, J. Xu, J. Gong, Y.-F. Han, *Appl. Catal. B: Environ.* 134-135 (2013) 145.

- 440 [17] S. Navalon, M. de Miguel, R. Martin, M. Alvaro, H. Garcia, J. Am. Chem. Soc. 133
441 (2011) 2218.
- 442 [18] Y.-F. Han, N. Phonthammachai, K. Ramesh, Z. Zhong, T. White, Environ. Sci.
443 Technol. 42 (2008) 908.
- 444 [19] S. Navalon, R. Martin, M. Alvaro, H. Garcia, Angew. Chem. Int. Ed. 49 (2010) 8403.
- 445 [20] R. Martín, S. Navalon, M. Alvaro, H. Garcia, Appl. Catal. B: Environ. 103 (2011)
446 246.
- 447 [21] S. Navalon, R. Martin, M. Alvaro, H. Garcia, ChemSusChem 4 (2011) 650.
- 448 [22] W.J. Cooper, R.G. Zika, Science 220 (1983) 711.
- 449 [23] E.V. Shtamm, A.P. Purnmal, Y.I. Skurlatov, Russ. Chem. Rev. 60 (1991) 2373.
- 450 [24] J.A. Simpson, K.H. Cheeseman, S.E. Smith, R.T. Dean, Biochem. J. 254 (1988) 519.
- 451 [25] H. Bataineh, O. Pestovsky, A. Bakac, Chem. Sci. 3 (2012) 1594.
- 452 [26] A.L.-T. Pham, F.M. Doyle, D.L. Sedlak, Water Research 46 (2012) 6454.
- 453 [27] J. Weiss, The Free Radical Mechanism in the Reactions of Hydrogen peroxide,
454 Advances in Catalysis, Academic Press, 1952, p. 343.
- 455 [28] F. Haber, J. Weiss, P. Roy. Soc. A-Math. Phy. 147 (1934) 332.
- 456 [29] R. Chen, J.J. Pignatello, Environ. Sci. Technol. 31 (1997) 2399.
- 457 [30] J.H. Merz, W.A. Waters, Discuss. Faraday Soc. 2 (1947) 179.
- 458 [31] C. Walling, Accounts. Chem. Res. 8 (1975) 125.
- 459 [32] J. De Laat, H. Gallard, Environ. Sci. Technol. 33 (1999) 2726.
- 460 [33] C.K. Duesterberg, W.J. Cooper, T.D. Waite, Environ. Sci. Technol. 39 (2005) 5052.
- 461 [34] C.K. Duesterberg, S.E. Mylon, T.D. Waite, Environ. Sci. Technol. 42 (2008) 8522.
- 462 [35] M.-C. Lu, Chemosphere 40 (2000) 125.

463 [36] M.-C. Lu, J.-N. Chen, H.-H. Huang, *Chemosphere* 46 (2002) 131.

464 [37] R. Andreozzi, A. D'Apuzzo, R. Marotta, *Water Research* 36 (2002) 4691.

465 [38] W.P. Kwan, B.M. Voelker, *Environ. Sci. Technol.* 37 (2003) 1150.

466 [39] M.A. Voinov, J.O.S. Pagán, E. Morrison, T.I. Smirnova, A.I. Smirnov, *J. Am. Chem.*
467 *Soc.* 133 (2010) 35.

468 [40] S.-S. Lin, M.D. Gurol, *Environ. Sci. Technol.* 32 (1998) 1417.

469 [41] S. Chou, C. Huang, Y.-H. Huang, *Environ. Sci. Technol.* 35 (2001) 1247.

470 [42] B. Wang, J.-J. Yin, X. Zhou, I. Kurash, Z. Chai, Y. Zhao, W. Feng, *J. Phys. Chem. C*
471 117 (2012) 383.

472 [43] A. Hiroki, J.A. LaVerne, *J. Phys. Chem. B* 109 (2005) 3364.

473 [44] C.M. Lousada, A.J. Johansson, T. Brinck, M. Jonsson, *J. Phys. Chem. C* 116 (2012)
474 9533.

475 [45] C.u.M. Lousada, M. Jonsson, *J. Phys. Chem. C* 114 (2010) 11202.

476 [46] Y. Ono, T. Matsumura, N. Kitajima, S. Fukuzumi, *J. Phys. Chem.* 81 (1977) 1307.

477 [47] N. Kitajima, S. Fukuzumi, Y. Ono, *J. Phys. Chem.* 82 (1978) 1505.

478 [48] Y. Wang, P.B. Balbuena, *J. Chem. Theory Comput.* 1 (2005) 935.

479 [49] D. He, S. Garg, T.D. Waite, *Langmuir* 28 (2012) 10266.

480 [50] D. He, C.J. Miller, D.T. Waite, *J. Catal.* 317 (2014) 198.

481 [51] D. He, A.M. Jones, S. Garg, A.N. Pham, T.D. Waite, *J. Phys. Chem. C* 115 (2011)
482 5461.

483 [52] Z. Chen, J.-J. Yin, Y.-T. Zhou, Y. Zhang, L. Song, M. Song, S. Hu, N. Gu, *ACS*
484 *Nano* 6 (2012) 4001.

485 [53] T. Kiyonaga, Q. Jin, H. Kobayashi, H. Tada, *ChemPhysChem* 10 (2009) 2935.

486 [54] S.-i. Naya, M. Teranishi, K. Kimura, H. Tada, *Chem. Commun.* 47 (2011) 3230.
 487 [55] J. Li, W. Liu, X. Wu, X. Gao, *Biomaterials* 48 (2015) 37.
 488 [56] B.P. Block, J.C. Bailar, *J. Am. Chem. Soc.* 73 (1951) 4722.
 489 [57] O. Levenspiel, *Chemical reaction engineering*, Wiley New York etc., 1972.
 490 [58] I.R. Cohen, T.C. Purcell, A.P. Altshuller, *Environ. Sci. Technol.* 1 (1967) 247.
 491 [59] M.E. Lindsey, M.A. Tarr, *Chemosphere* 41 (2000) 409.
 492 [60] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, *J. Phys. Chem. Ref. Data*
 493 17 (1988) 513.
 494 [61] X. Zhou, K. Mopper, *Mar. Chem.* 30 (1990) 71.
 495 [62] P. Kuzmic, *Anal. Biochem.* 237 (1996) 260.
 496 [63] W.P. Kwan, B.M. Voelker, *Environ. Sci. Technol.* 36 (2002) 1467.
 497 [64] N.R.E. Radwan, E.A. El-Sharkawy, A.M. Youssef, *Appl. Catal. A: General* 281
 498 (2005) 93.
 499 [65] A. Quintanilla, S. García-Rodríguez, C.M. Domínguez, S. Blasco, J.A. Casas, J.J.
 500 Rodríguez, *Appl. Catal. B: Environ.* 111–112 (2012) 81.
 501 [66] L.R. Martin, M.P. Easton, J.W. Foster, M.W. Hill, *Atmos. Environ.* 23 (1989) 563.
 502 [67] W.G. Barb, J.H. Baxendale, P. George, K.R. Hargrave, *Trans. Faraday Soc.* 47
 503 (1951) 591.
 504 [68] J. Abbot, D.G. Brown, *Int. J. Chem. Kinet.* 22 (1990) 963.
 505 [69] R.L. Valentine, H.A. Wang, *J. Environ. Eng.* 124 (1998) 31.
 506 [70] A.M. Jones, S. Garg, D. He, A.N. Pham, T.D. Waite, *Environ. Sci. Technol.* 45
 507 (2011) 1428.

508 [71] C.M. Lousada, A.J. Johansson, T. Brinck, M. Jonsson, *Phys. Chem. Chem. Phys.* 15
 509 (2013) 5539.
 510 [72] W.-F. Huang, P. Raghunath, M.C. Lin, *J. Comput. Chem.* 32 (2011) 1065.
 511 [73] O. Levenspiel, *Chemical Reaction Engineering*, 3rd Edition, John Wiley & Sons.
 512 Inc., 1999.
 513 [74] W. Stumm, J.J. Morgan, *Aquatic chemistry: chemical equilibria and rates in natural*
 514 *waters*, 3 rd Edition, John Wiley & Sons, Inc, 1996.
 515 [75] L. Xu, J. Wang, *Appl. Catal. B: Environ.* 123 (2012) 117.
 516 [76] W. Luo, L. Zhu, N. Wang, H. Tang, M. Cao, Y. She, *Environ. Sci. Technol.* 44
 517 (2010) 1786.
 518 [77] G.C. Bond, *Catalysis by metals*, Academic Press, New York, 1962.
 519 [78] B.N. Zope, D.D. Hibbitts, M. Neurock, R.J. Davis, *Science* 330 (2010) 74.
 520 [79] C. Shang, Z.-P. Liu, *J. Am. Chem. Soc.* 133 (2011) 9938.
 521 [80] M. Suh, P.S. Bagus, S. Pak, M.P. Rosynek, J.H. Lunsford, *J. Phys. Chem. B* 104
 522 (2000) 2736.
 523
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