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### ABSTRACT

The generation of hydroxyl radicals (HO<sup>•</sup>) by H<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub> decomposition over supported Au NPs was investigated in a buffer solution at pH ~ 6.8. Over a range of H<sub>2</sub>O<sub>2</sub> concentrations, the decay of H<sub>2</sub>O<sub>2</sub> followed a pseudo-first-order kinetic 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  $(66.7 \pm 2.3) \times 10^{-3}$  min<sup>-1</sup> with the increase in the Au NPs concentration. Further increase in the surface concentration of H<sub>2</sub>O<sub>2</sub> may reduce the HO<sup>•</sup> generation efficiency. A dual intermediate model was proposed for the generation mechanism of HO<sup>•</sup>.

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# 1. Introduction

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

The Fenton catalytic process ( $Fe^{2+} + H_2O_2$ ) has already proven to be a mature technique for ROC treatment, due to the rapid generation of hydroxyl radicals (HO<sup>-</sup>), which can completely oxidize ROC into CO<sub>2</sub> and H<sub>2</sub>O without light, heat, or electricity [3–5]. However, there are still several formidable drawbacks: (i) the working pH range is too narrow (pH 2.5–3.5); (ii) continuous supplementation of Fe<sup>2+</sup> during reaction is necessary for the loss of Fe<sup>2+</sup>; (iii) the accumulation of iron-containing sludge leads to secondary pollution.

Therefore, to overcome those drawbacks, a advanced oxidation system with a combination of various iron-free Fenton-like solid catalysts as a key technique in this process has been developed to substitute for Fe<sup>2+</sup> [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 been demonstrated to be active for creating HO<sup>•</sup> by a Fenton-like process without the abovementioned disadvantages [16–21]. However, the mechanism for the generation of HO<sup>•</sup> by H<sub>2</sub>O<sub>2</sub> decomposition over Au catalysts is difficult to attain, since HO<sup>•</sup> is a short-lived species and hard to monitor instrumentally.

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 (H<sub>2</sub>O<sub>2</sub>) 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 in vivo systems, H<sub>2</sub>O<sub>2</sub> is an important oxidant for the oxidative metabolism process. Generally, H<sub>2</sub>O<sub>2</sub> is relatively harmless, as it reacts with biomolecules at reasonably low rates, and specific enzymes to facilitate its removal (such as catalase) are usually present [24]. However, with the assistance of metals such as iron and copper, H<sub>2</sub>O<sub>2</sub> may be closely related to cytotoxicity to cells, proteins, and living organisms due to the formation of strongly oxidizing reactive oxygen species (ROS) such as hydroxyl radicals (HO<sup>-</sup>) via Fenton or Fenton-like processes [25,26].



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In natural aquatic environments, the decay process of  $H_2O_2$  can be triggered by various metal ions ( $M^{n+}$ ) and HO<sup>•</sup> can be produced by one-electron reduction of  $H_2O_2$ ,

$$M^{n+} + H_2O_2 \xrightarrow{H^+} M^{(n+1)+} + HO^{-} + H_2O,$$
 (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,  $[M^{n+}]/[H_2O_2]$  ratio, dissolved oxygen, inorganic ions, and organic substances [32–34].

Additionally, metal-containing solids also mediate the decay of  $H_2O_2$ , followed by the formation of HO<sup>,</sup> despite the fact that the mechanisms for  $H_2O_2$  decomposition and HO<sup>,</sup> generation over solid catalysts are still not well understood. Lu [35,36] and Andreozzi et al. [37] have proposed a reductive dissolution mechanism to explain  $H_2O_2$  decomposition over  $\alpha$ -FeOOH. However, it has been demonstrated that the surface reactions were dominated by  $H_2O_2$  decomposition and HO<sup>,</sup> generation over various solid state materials, including  $\alpha$ -FeOOH,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, and ferrihydrite [38–40]. On the basis of the surface complexation process,  $H_2O_2$  decomposition was assumed to proceed via a series of surface reactions [40–42], including the formation of surface complexes (denoted as  $[H_2O_2]_s$ ),

$$\equiv Fe^{III} - OH + H_2O_2 \iff [Fe - H_2O_2]_s$$
<sup>(2)</sup>

a ground state electron-transfer from ligands to metals within the surface complexes,

$$[Fe-H_2O_2]_s \iff \equiv Fe^{II}O_2H' + H_2O, \tag{3}$$

and the dissociation of ROS,

$$\equiv Fe^{II}O_2H \iff \equiv Fe^{II} + HO_2 \tag{4}$$

The formation and decomposition of  $[Fe-H_2O_2]_s$  were proposed to be the rate-limiting steps. HO is yielded from the so-called radical pathway, and O<sub>2</sub> formed via a nonradical pathway directly leading to the waste of H<sub>2</sub>O<sub>2</sub> in practical application.

However, the chain reactions cannot occur over the oxides that lack variable oxidation states, such as  $Al_2O_3$ ,  $SiO_2$ , and  $Y_2O_3$  [43–45]. Thus, the decomposition process of  $H_2O_2$  could be simplified into (i) adsorption of  $H_2O_2$  on the surface,

$$H_2O_{2(aq)} \iff H_2O_{2(ads)},\tag{5}$$

(ii) homolysis of the O-O bond and desorption of radicals,

$$H_2O_{2(ads)} + M \rightarrow HO'_{(ads)} + HO' + M^{n+}, \tag{6}$$

(iii) recombination of free radicals,

$$\mathrm{HO}^{\cdot} + \mathrm{HO}^{\cdot} \to \mathrm{H}_{2}\mathrm{O}_{2}, \tag{7}$$

$$2HO_2 \rightarrow H_2O_2 + O_2,$$
 (8)

and (iv) the oxidation or reduction of surface cations,

$$M^{n+} + HO_2 \rightarrow M^{(n-1)+} + H^+ + O_2,$$
 (9)

$$M^{n_{+}} + HO' \to M^{(n+1)_{+}} + OH^{-}.$$
 (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 HO<sup>•</sup> was evidenced to be involved in the reaction cycle at pH > 7 [51,52]:

$$Ag-O(H)-OH + H_2O_2 \rightarrow Ag^+ + O_2^- + 2H_2O.$$
 (11)

Up to now, only a few studies have addressed H<sub>2</sub>O<sub>2</sub> decomposition over the supported Au catalysts. Tada's group proposed that this reaction was largely determined by the properties of the support material, while the reaction rate linearly increased with the downshift of the *d* band centers [53,54]. In contrast, 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 disputes 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 with 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 HO<sup>-</sup> generation over supported Au nanocatalysts were systematically studied. As a result, the rational design of heterogeneous Fenton catalysts will be more facile. Furthermore, this study will also lead to a systematic understanding of the environmental implications and the in vivo cytotoxicity of naked and supported Au NPs.

## 2. Experimental

### 2.1. Catalyst preparation

The synthesis 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 2 h under a N<sub>2</sub> 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)<sub>2</sub>Cl<sub>3</sub> (en: 1,2ethanediamine) was employed as the precursor [56]. The SRAC support was impregnated into the precursor solution (pH 3.0, 298 K) with the assistance of ultrasound. The samples were washed with MilliQ (18.25 M $\Omega$ ) water, dried overnight at 313 K, and then sealed in a dark place. Before the kinetic measurements, the sample was reduced at 673 K for 30 min with a H<sub>2</sub> flow (10 vol. % in Ar, 20 ml/min). Several techniques were used for the characterization of Au/SRAC, such as N<sub>2</sub> adsorption-desorption, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The detailed information is summarized in the 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. Kinetic measurement

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

H<sub>2</sub>O<sub>2</sub> concentration was analyzed colorimetrically using a UVvis spectrophotometer (UX100, Phoenix, China) after complexation with a  $TiOSO_4/H_2SO_4$  reagent [58]. The concentrations of HO<sup> $\cdot$ </sup> was measured by a molecular probe method [59]. Benzoic acid (BA) was selected as the probe, which had a determined reaction rate constant toward HO<sup>•</sup>  $(4.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})$  in aqueous solution [60]. As mentioned by Zhou and Mopper [61], the BA solution was 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 used. The flow rate of the mobile phase was set to 1 ml/min and the ratio of water (A) to acetonitrile (B) was gradually changed. Water was kept at 15% within the first 3 min and linearly increased to 100% in the following 12 min. The residue of Au in reaction solutions was also measured by ICP-MS.

The modeling of the kinetic data and the prediction of the 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(1.5 wt.%)/SRAC was used as a model catalyst in the present study. Its surface area is 980 m<sup>2</sup>/g, as estimated by BET (Fig. S1a). The carbon support was stacked as numerous spherical particles within a size range of 30–100 nm (Fig. S1b). The aggregative particles linked with each other in random directions, which led to the formation of a 3D meso- or macroporous structure. The Au NPs were evenly dispersed on the support with an average size of  $4.6 \pm 0.8$  nm (Fig. S1c and d).

## 3.2. Kinetics of H<sub>2</sub>O<sub>2</sub> decomposition

The rate of  $H_2O_2$  decomposition over Au/SRAC was determined by measuring the  $H_2O_2$  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

$$V_{\rm r} \frac{d[{\rm H}_2{\rm O}_2]}{dt} + [{\rm H}_2{\rm O}_2] \frac{dV_{\rm r}}{dt} = \dot{V}_{\rm in} [{\rm H}_2{\rm O}_2]_{\rm in} - \dot{V}_{\rm out} [{\rm H}_2{\rm O}_2] - k_{\rm obs} [{\rm H}_2{\rm O}_2]^m V_{\rm r}$$
(12)

For a continuous stirred tank reactor (CSTR), assuming  $V_{\rm r}$  is constant,

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

The reaction rate of H<sub>2</sub>O<sub>2</sub> decomposition can be expressed as

$$\frac{d[H_2O_2]}{dt} = \frac{[H_2O_2]_{t=0} - [H_2O_2]_{t=\tau}}{\tau} - k_{obs}[H_2O_2]^m$$
(14)

$$-\frac{d[H_2O_2]_{t=\tau}}{dt} = k_{obs}[H_2O_2]_{t=\tau}$$
(15)

where m is the order of the reaction.

As mentioned in previous works [32,47,63],  $H_2O_2$  decomposition was generally assumed to be a first-order reaction. Therefore, the concentration of  $H_2O_2$  on a log scale was plotted as a function of the reaction time by

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

The fitting of the data was obviously a linear regression, which yielded correlation coefficients above 0.98. This indicated that the decomposition of  $H_2O_2$  over Au/SRAC followed a pseudo-first-order kinetic rate law (see Fig. 1). The  $k_{obs}$  represents the observed first-order rate constant, which is independent of the initial concentration of  $H_2O_2$  ( $[H_2O_2]_0 \le 6.65 \text{ mM}$ ), 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  $H_2O_2$  ( $[H_2O_2]_0 > 6.65 \text{ mM}$ ), 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 ( $[H_2O_2]_0 - \le 6.65 \text{ mM}$ ) with those of other supported Au catalysts (Table 1). Based on the concentration of exposed Au atoms,

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

the turnover frequency (TOF) of  $\mathrm{H_2O_2}$  decomposition was calculated as

$$\text{TOF} = \frac{r_{\text{H2O2}}}{[\text{Au}, \text{exposed}]}.$$
(18)

The TOFs of supported Au catalysts varied from  ${\sim}1.0~h^{-1}$  to over one thousand per hour [19,53,54,64]. This indicated that the number and the performance of the specific active sites responsible for the decay of H<sub>2</sub>O<sub>2</sub> 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.

#### 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  $H_2O_2$  (35.21 mM) solutions of 100 ml. Thus, the molar ratio of  $H_2O_2$  to Au/SRAC was in the range 0.35–3.52. As a function of reaction time, the conversion of  $H_2O_2$  was plotted on 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

**Fig. 1.** First-order fit curves of  $H_2O_2$  decomposition at different initial concentrations of  $H_2O_2$ : 3.29 mM ( $\blacksquare$ ); 5.18 mM ( $\blacklozenge$ ); 6.65 mM ( $\blacktriangle$ ); 10.64 mM ( $\blacktriangledown$ ); 17.53 mM ( $\blacklozenge$ ); 35.21 mM ( $\triangleright$ ). Catalyst 250 mg/L, 298 K, pH 6.8.



 $\begin{array}{l} \textbf{Table 1} \\ \text{Summary of the first-order rate constants of $H_2O_2$ decomposition over different Au Fenton catalysts.} \end{array}$ 

Catalyst	Loading amount (wt.%)	Particle size (nm)	Rate or rate constant $(h^{-1})$	TOF $(h^{-1})$	Catalyst loading (mg/L)	T (K)	pН	Target compounds	Ref.
Au/SRAC	1.5	4.6	2.7	1706	250	313	6.8	-	This work
Au/TiO <sub>2</sub>	0.2	3.5		181	1000	298	4.5	-	[53]
Au/SrTiO <sub>3</sub>	0.6	2.7		337	1000	298	6.0	-	[54]
Au/Fe <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub>	1.6	3.5		1	$1  imes 10^4$	313	${\sim}6.8$	-	[64]
Au/CeO <sub>2</sub>	1.0	5		372	49.0		4.0	Phenol (100 mg/L)	[19]
Au/Fe <sub>2</sub> O <sub>3</sub>	1.5	4		27	32.8			-	
Au/TiO <sub>2</sub>	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 <sub>2</sub>	0.8	3.1		$2.5  imes 10^4$	2500	353	3.5	Phenol (4500 mg/L)	[65]
Au(3)/C	0.1	5.1		$16.7  imes 10^4$					
Au(5)/C	0.5	4.9		$4.1  imes 10^4$					
Au(7)/C	0.5	6.8		$2.3 imes10^4$					
Au(10)/C	0.5	9.1		$1.9\times10^4$					



**Fig. 2.** First-order fit curves of  $H_2O_2$  decomposition at different concentrations of the Au/SRAC catalyst: 50 mg/L ( $\blacksquare$ ); 100 mg/L ( $\bullet$ ); 150 mg/L ( $\blacktriangle$ ); 250 mg/L ( $\blacktriangledown$ ); 500 mg/L ( $\blacklozenge$ ). Initial concentration of  $H_2O_2$  35.21 mM, 298 K, pH 6.8.



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

as a function of catalyst concentration (Fig. 3). Then the rate expression can be expressed by

$$-\frac{d[H_2O_2]}{dt} = -k[\text{catal.}][H_2O_2]_{t=\tau}$$
(19)

The fitting of a second-order reaction rate law was generally pursued. 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 L min<sup>-1</sup> g<sup>-1</sup>. As summarized in Table 2, the second-order rate constant for H<sub>2</sub>O<sub>2</sub> decomposition on Au/SRAC with respect to the concentration of catalyst and H<sub>2</sub>O<sub>2</sub> falls into the same range as those on bulk iron solid catalysts, and it is an order of magnitude lower than those on supported Fe Fenton catalysts and homogenous Fenton catalysts. As reported by Garcia et al. [19], a Au-based Fenton system has high potential for generation efficiency of HO, as high as 79%. Unfortunately, the relatively 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 coefficient is as low as 0.91. This implies the decomposition of H<sub>2</sub>O<sub>2</sub> over Au nanocatalyst as an intricate and ingenious process.

### 3.2.2. The effect of reaction temperature

Table 2

The dependence of the rate constant on the reaction temperature usually follows the Arrhenius equation,

$$k_{\rm obs} = A e^{-E_{\rm a}/RT} \tag{20}$$

where  $E_a$  is the activation energy for the reaction, *A* is the preexponential factor, and *R* is the gas constant. The linear regression of the conversion on a log scale vs. the reaction time exhibited that the reaction was in good agreement with the first-order behavior in the temperature range 298–353 K.  $E_a$  can be calculated by the correlation of ln  $k_{obs}$  vs. 1/T. With the rise of temperature, the rate constant increased from  $(9.2 \pm 0.7) \times 10^{-3} \min^{-1}$  (298 K) to  $(16.6 \pm 0.7) \times 10^{-3} \min^{-1}$  (353 K), while the  $E_a$  of 142 kJ/mol was obtained (Fig. 4). As compared to the homolysis energy of the O–O bond in H<sub>2</sub>O<sub>2</sub>, 208 kJ/mol, the decrease in  $E_a$  indicated the catalytic effect of Au/SRAC on its metal–liquid interface. However, the relatively high  $E_a$  for Au/SRAC in comparison with other metal oxide

Comparison of the second-order rate	e constant	of H <sub>2</sub> O <sub>2</sub>	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 <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	0.03	[68]
Goethite	0.0016	[69]
Ag NPs	0.0031	[70]
Au/SRAC	0.0024	This study

systems (generally 30–60 kJ/mol) [40,43,45,71,72] indicated a different reaction pathway of H<sub>2</sub>O<sub>2</sub> decomposition over this catalyst.

### 3.2.3. The effect of diffusion

To study the effect of diffusion on this reaction, we calculated the Thiele modulus,

$$\varphi = [k_{\rm obs}/(D/L^2)]^{0.5} \tag{21}$$

where *D* is the diffusion coefficient (cm<sup>2</sup>/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<sup>2</sup>/s, while the thickness of the stagnant liquid film can be estimated as ca.  $1.0 \times 10^{-3}$  cm [73]. Therefore, the Thiele modulus  $\varphi$  of H<sub>2</sub>O<sub>2</sub> decomposition over this Au/SRAC catalyst was in the range  $2.84 \times 10^{-3}$ – $7.36 \times 10^{-3}$ . So the process was much slower than the diffusion with  $\varphi > 5$ . 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 HO<sup>•</sup> generation was already defined as described by [26,75,76].

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

The decay rates for  $H_2O_2$  and BA were measured simultaneously. The generation efficiency of HO<sup>•</sup> was strongly dependent on the  $H_2$ - $O_2$ /catalyst ratio after dosing with probe molecules. The HO<sup>•</sup> 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  $H_2O_2$ .

## 3.3.2. Mechanistic modeling

DMPO-trapped EPR spectra [16] have demonstrated that HO<sup>•</sup> was indeed generated during the degradation of BPA. This robust oxidant has long been demonstrated to benefit the degradation of numerous persistent compounds in the aqueous phase.



**Fig. 4.** First-order fit curves of  $H_2O_2$  decomposition at different reaction temperatures: 298 K ( $\blacksquare$ ); 303 K ( $\bullet$ ); 313 K ( $\blacktriangle$ ); 328 K ( $\checkmark$ ); 343 K ( $\bullet$ ). Catalyst 250 mg/L, initial  $H_2O_2$  concentration 6.65 mM, pH 6.8.

ľa	bl	e	3	

0.	generation	efficiency	over	Au/SRAC.	
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$H_2O_2$ (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

Therefore, the high yield of HO<sup> $\cdot$ </sup> by H<sub>2</sub>O<sub>2</sub> decomposition leads to the economic advantages of the involved Fenton process.

As assumed by Bond [77], the decomposition of  $H_2O_2$  over metal catalysts in aqueous solution involves an electron transfer from metal to adsorbate and a chain reaction on the surface of the metal. The negatively charged Au NPs facilitate the adsorption and reaction of  $H_2O_2$ . The edge sites of Au NPs would likely decrease the energy barrier for surface-OH desorption, which could enhance the generation of HO<sup>•</sup> radicals [78,79]. It should be noted that here we only focus on the mechanistic understanding of the generation of HO<sup>•</sup> and the decomposition of  $H_2O_2$ . The structure–performance relationship of the present  $H_2O_2$ –Au/SRAC system is beyond the scope of this work.

The reaction pathway of  $H_2O_2$  decomposition changed significantly with  $H_2O_2$  concentration. We assumed that the intermediates could further react with  $H_2O_2$ , leading to a series of more complicated surface reactions and a subsequent reduction in the overall consumption rate of  $H_2O_2$ . As indicated by our previous work [16], HO<sup>•</sup> radicals were created and OOH<sup>•</sup>/O<sub>2</sub><sup>-</sup> radicals were involved in the regeneration of active sites. Thus, the proposed reaction mechanism is summarized as Reactions (1)–(5), which indicate the surface reactions between the catalyst and  $H_2O_2$ . The further oxidation of OOH<sup>•</sup> leads to the generation of  $O_2$  through Reactions (4) and (5):

$$Au^{\delta^{-}} + H_2O_2 \xrightarrow{k_1} (Au^{\delta^{-}} - H_2O_2)_s$$
 (Reaction1)

$$(\operatorname{Au}^{\delta-}-\operatorname{H}_2\operatorname{O}_2)_{s}+\operatorname{H}_2\operatorname{O}_2\xrightarrow{\kappa_2}(\operatorname{Au}^0-\operatorname{HO})_{s}+\operatorname{H}_2\operatorname{O}+\operatorname{HOO^{\bullet}} (\operatorname{Reaction} 2)$$

$$\operatorname{Au}^{\delta^{-}}-\operatorname{H}_{2}O_{2})_{s} \xrightarrow{\kappa_{3}} \operatorname{Au}^{0} + \operatorname{OH}^{-} + \operatorname{HO}^{-}$$
 (Reaction3)

$$(Au^{0}-HO)_{s} + H_{2}O_{2} \xrightarrow{\kappa_{4}} Au^{\delta-} + HOO^{\cdot} + H_{2}O \qquad (Reaction4)$$

$$\operatorname{Au}^{0} + \operatorname{HOO}^{\cdot} \xrightarrow{k_{5}} \operatorname{Au}^{\delta-} + \operatorname{O}_{2} + \operatorname{H}^{+}.$$
 (Reaction5)

According to the reaction mechanism, the rate of  $H_2O_2$  decomposition is presented by

$$-\frac{d[H_2O_2]}{dt} = k_1[Au^{\delta}][H_2O_2] + k_2[H_2O_2][S] + k_4[H_2O_2][S^{\circ}].$$
(23)

The surface species directly formed as depicted by Reaction (2), where  $(Au^{\delta-}-H_2O_2)_s$  is simplified as S (Intermediate 1 in Scheme 1). Its generation rate is

$$-\frac{d[S]}{dt} = k_2[S][H_2O_2] + k_3[S] - k_1[Au^{\delta_-}][H_2O_2].$$
(24)

However, the further reaction between S and  $H_2O_2$  results in the generation of  $(Au^{\delta}-HO)_s$ , denoted as S<sup>•</sup> (Intermediate 2 in Scheme 1). Therefore, the accumulation rate of S<sup>•</sup> is calculated as

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

Assuming that the intermediate S and S<sup> $\cdot$ </sup> were in steady states, their accumulation rates approach zero. Thus, the concentrations of S and S<sup> $\cdot$ </sup> can be obtained from

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



Scheme 1. The proposed reaction mechanism.

$$[S] = \frac{k_1 [Au^{\delta-}] [H_2 O_2]}{k_2 [H_2 O_2] + k_3}.$$
(27)

After the substitution of Eqs. (26) and (27) into Eq. (23), the following equation representing the H<sub>2</sub>O<sub>2</sub> decomposition rate is yielded:

$$\begin{aligned} r &= -\frac{d[H_2O_2]}{dt} \\ &= \left\{ k_1 + \frac{k_1k_2[H_2O_2]}{k_2[H_2O_2] + k_3} + \frac{k_1k_2k_4[H_2O_2]^2}{(k_2[H_2O_2] + k_3)(k_{2a} + k_4[H_2O_2])} \right\} [Au^{\delta -}] \\ &\times [H_2O_2] \\ &= \left\{ k_1 + \frac{k_1k_2[H_2O_2]}{k_2[H_2O_2] + k_3} + \frac{k_1k_2k_4[H_2O_2]^2}{(k_2[H_2O_2] + k_3)(k_{2a} + k_4[H_2O_2])} \right\} [Catal.] \\ &\times [H_2O_2]. \end{aligned}$$

$$(28)$$

Using Dyna Fit, the model fitting according to the reaction set (Reactions (1)–(5), Table 4) is able to explain the  $H_2O_2$  decay process in the initial concentration range 6.65–35.21 mM. The reaction rate is proportional (but not linearly) to the initial concentration of  $H_2O_2$  (Fig. 5). The formation of  $(Au-H_2O_2)_s$  surface species acted as the precursor for HO generation. When the active sites are fully covered by  $H_2O_2$ , HO cannot desorb from the surface of the catalysts, but forms surface species,  $(Au-OH)_s$ . The surface OH is more electrophilic toward Au NPs than the adsorbed  $H_2O_2$  molecule [80]. Thus,  $(Au-OH)_s$  is more electron-deficient than  $(Au-H_2O_2)_s$  as well as Au NPs. This active site of electron deficiency will lead to the oxidation of  $H_2O_2$  and the formation of 'OOH as a consequence. In general, the formation of active complexes (Intermediates 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 loadings of catalyst: 50 mg/L ( $\blacksquare$ ); 100 mg/L ( $\bullet$ ); 150 mg/L ( $\blacktriangle$ ); 250 mg/L ( $\blacktriangledown$ ); 500 mg/L ( $\bullet$ ). Initial concentration of  $H_2O_2$  35.21 mM, 298 K, pH 6.8.

The dual intermediate mechanism proposed for this process is schematically expressed as Scheme 1. It should be noted that the generation of ROS by one-electron transfer in turn inhibits H<sub>2</sub>O<sub>2</sub> decomposition in the whole concentration range. With an increase in the initial concentration of H<sub>2</sub>O<sub>2</sub>, the dominant surface species evolves from  $(Au-H_2O_2)_s$  to  $(Au-OH)_s$ . As a result of the formation of (Au-OH)<sub>s</sub> species, the H<sub>2</sub>O<sub>2</sub> decay process follows competitive inhibition behavior. The distribution or equilibrium of different surface species determines the reaction between radical (oneelectron transfer) and nonradical (two-electron transfer) pathways. In natural aquatic environments, therefore, the H<sub>2</sub>O<sub>2</sub> dependence of the formation of dual intermediates ((Au-H<sub>2</sub>O<sub>2</sub>)<sub>s</sub> and (Au-OH)<sub>s</sub>) arising from Au NPs reacting with H<sub>2</sub>O<sub>2</sub> suggests that Au NPs may be more toxic in lower-H<sub>2</sub>O<sub>2</sub> environments, as excess H<sub>2</sub>O<sub>2</sub> may cause a reaction shift from the radical (oneelectron transfer) to the nonradical (two-electron transfer) pathway.

### 4. Conclusions

Au/SRAC catalysts were proven to be effective Fenton-like catalysts for the generation of HO. The kinetic study indicated that the decomposition of  $H_2O_2$  over Au NPs followed a pseudo-first-order kinetic 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  $(66.7 \pm 2.3) \times 10^{-3}$  min<sup>-1</sup>. A dual-intermediate mechanism was proposed on the basis of the structure of Au/SRAC and the kinetic study.  $(Au-H_2O_2)_s$  and  $(Au-OH)_s$ , which lead to the generation of different radicals and gaseous oxygen, are key intermediates of

Rate constants of the elemental surface reactions.

Table 4

Reaction no.	Equation	Reaction rate constant $(M^{-1} min^{-1})$
1	$Au^{\delta-} + H_2O_2 \stackrel{k_1}{\rightarrow} (Au^{\delta-} - H_2O_2).$	$(19.5 \pm 0.7) \times 10^{-3}$
2	$(Au^{\delta-}-H_2O_2)_{,+} + H_2O_2 \stackrel{k_2}{\to} (Au^0-HO)_{,+} + H_2O + OOH^*$	$(0.3 \pm 0.1)  imes 10^{-3}$
3	$(\mathrm{Au}^{\delta-} - \mathrm{H}_2\mathrm{O}_2)_{\mathrm{s}} \stackrel{\mathrm{h}_3}{\to} \mathrm{Au}^0 + \mathrm{OH}^- + \mathrm{OH}^-$	$(1.7\pm0.1)\times10^2$
4	$(Au^0 - HO)_{\circ} + H_2O_2 \xrightarrow{k_4} Au^{\delta-} + OOH + H_2O$	84.9 ± 4.5
5	$Au^{0} + OOH \stackrel{k_{5}}{\longrightarrow} Au^{\delta-} + O_{2} + H^{+}$	$(2.7\pm0.1)\times10^3$

the  $H_2O_2$  decomposition process. The dominant surface species evolved from  $(Au-H_2O_2)_s$  to  $(Au-OH)_s$  with the increase in  $H_2O_2$ concentration. Consequently, excess  $H_2O_2$  may bring about a reaction shift from a radical to a nonradical mechanism, thus reducing the HO<sup>-</sup> generation efficiency.

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### **Appendix A. Supplementary material**

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2015.12.029.

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