

# Aqueous phototransformation of bisphenol S: the competitive radical-attack pathway to *p*-hydroxybenzenesulfonic acid

Xiaowen Wang, Jiahai Ma, Zhenpeng Wang, Rongrong Guo and Xuefeng Hu

## ABSTRACT

The kinetics, environmental influencing factors, products and reaction mechanism of aqueous phototransformation of bisphenol S (BPS), as an alternative to bisphenol A, which is of environmental concern, were investigated. *p*-Hydroxybenzenesulfonic acid, as the major transformation product was confirmed by gas chromatography – mass spectrometry, electrospray ionization, <sup>1</sup>H nuclear magnetic resonance and fluorescence spectrum analysis. A reaction pathway was proposed based on the reactive oxygen species related results by electron paramagnetic resonance and radical traps. The competition of the excited state of BPS between transferring electron to O<sub>2</sub> to •O<sub>2</sub> and directly oxidizing H<sub>2</sub>O to •OH was revealed.

**Key words** | bisphenol S, *p*-hydroxybenzenesulfonic acid, phototransformation, reactive oxygen species

**Xiaowen Wang**  
**Jiahai Ma** (corresponding author)  
**Rongrong Guo**  
School of Chemistry and Chemical Engineering,  
University of Chinese Academy of Sciences,  
Beijing 100049,  
China  
E-mail: [majia@ucas.ac.cn](mailto:majia@ucas.ac.cn)

**Xiaowen Wang**  
**Xuefeng Hu**  
Key Laboratory of Coastal Environmental  
Processes and Ecological Remediation,  
Yantai Institute of Coastal Zone Research,  
Chinese Academy of Sciences,  
Yantai Shandong 264003,  
China

**Zhenpeng Wang**  
Beijing Mass Spectrum Center,  
Institute of Chemistry,  
Chinese Academy of Sciences,  
Beijing 100190,  
China

## INTRODUCTION

Endocrine-disrupting chemicals, threatening natural water environments, have been studied widely spread over the past decades. Bisphenol A (BPA, 2,2-bis-(4-hydroxy-phenyl) propane or 4,4'-isopropylidenediphenol, Figure 1), is an important industrial chemical used for the production of epoxy resins and polycarbonate plastics, which are used in various food and drink packaging applications, baby bottles and dental sealants (Staples *et al.* 1998). As a representative endocrine disrupter, BPA causes not only a strong estrogenic endocrine-disrupting effect (Alexander *et al.* 1988), but also various diseases including cancer (Suarez *et al.* 2000). Concerns about the health risk of BPA are increasing, and restrictions/regulations have been put forward to limit BPA's application in consumer products, and some countries like Japan have banned BPA application completely.

BPA is being replaced with a number of alternatives, such as bisphenol S (BPS; 4,4'-sulphonyldiphenol), bisphenol B (2,2'-bis(4-hydroxyphenyl)butane) and bisphenol F (4,4'-dihydroxydiphenyl-methane) in industrial chemicals and

daily-life customer goods. A variety of treatment techniques for BPA in water have been examined using physical, biological, electrochemical and photochemical procedures. Nishiki and colleagues used β-cyclodextrin-linked chitosan beads to remove BPA (Nishiki *et al.* 2000). Lobos *et al.* (1992) isolated a gram-negative aerobic bacterium (strain MV1) that utilized BPA as the sole carbon source. Some researchers (Ohko *et al.* 2001; Fukahori *et al.* 2003) have reported the photocatalytic degradation of BPA in TiO<sub>2</sub> aqueous suspension, and various intermediate products such as phenol, *p*-hydroquinone, *p*-isopropenylphenol, *p*-hydroxybenzaldehyde, and 4-hydroxyphenyl-2-propanol were found. Due to the very similar molecular structure of bisphenol B, bisphenol F and BPA, it is reasonable that their phototransformation behavior is similar, too.

As BPS is regarded as the alternative of BPA, the demand and production of BPS in China and Japan are increasing continuously (Liu 2005). Because of its increasingly widespread application, the potential water contamination of and human exposure to BPS is very high. Further, BPS has a

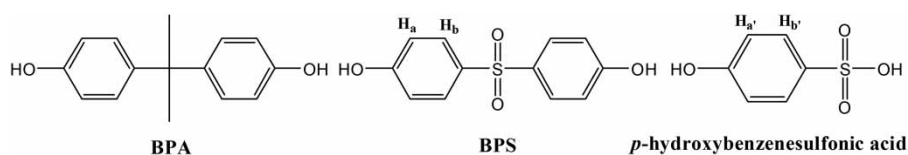


Figure 1 | Molecular structure of BPA, BPS and *p*-hydroxybenzenesulfonic acid.

different molecular structure to other bisphenol analogs, and thus the study of the environmental fate of BPS is urgently needed. The environmental and human body concentration of BPS has been measured in paper products and currency bills, sediments and urine (Liao *et al.* 2012a, b, c). However, studies on the environmental phototransformation of BPS are limited. The elementary degradation kinetics of BPS under UV ( $\lambda = 254$  nm) was studied by Cao *et al.* (2010, 2012); however, the products of phototransformation and detailed reaction pathway under the full solar spectrum remain unclear until now.

The objective of the present work is to study: (i) whether BPS could be easily transformed under photo-irradiation and, if so, whether the major transformation product is unharmed or not; and (ii) whether reactive oxygen species (ROS) are responsible for the transformation and, if so, which reactive species plays the dominating role. Thus, the present study focused on the phototransformation product and detailed reaction pathway of BPS. Better understanding of these reactions is needed for both the elucidation of the environmental fate of BPS and the successful application of suitable remediation technologies for BPS.

## EXPERIMENTAL

### Materials and chemicals

BPS, BPA, Aldrich humic acid, furfuryl alcohol and Rose Bengal were obtained from Alfa Aesar. *p*-Hydroxybenzenesulfonic acid was purchased from J&K Scientific Technology Co., Ltd. The spin trap reagent, 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO), was from Sigma. Benzoquinone and  $\text{FeCl}_3$  were of analytical grade. Deionized water was distilled and purified further in a Milli-Q system to a resistivity greater than  $18 \text{ M}\Omega\text{-cm}$ .

BPS dissolved much more easily in water with a tiny amount of ethanol than in pure water, and the corresponding absorption spectra had little difference (Figure S1, available online at <http://www.iwaponline.com/wst/070/257.pdf>), thus the former was used in the whole work except where noted. A  $4.0 \times 10^{-4}$  mol/L stock solution of

BPS was prepared by dissolving 25.0 mg BPS in 245 mL water with 5 mL ethanol and was kept at  $4^\circ\text{C}$ ; the test solution of different reagents was prepared by spiking water with an appropriate amount of the stock solution to obtain a final concentration of  $4.0 \times 10^{-5}$  mol/L, and the ethanol content was  $<0.2\%$ .

### Photochemical experiments

Photochemical experiments were conducted in a photochemical reaction chamber using a 350-W xenon lamp (Shanghai Irradiation Lamp Co., Ltd, China) as the irradiation source, and Figure S2 (available online at <http://www.iwaponline.com/wst/070/257.pdf>) shows the emission spectrum. The reaction solution volume was 50 mL, and the temperature was maintained at  $25 \pm 1^\circ\text{C}$ . At given reaction time intervals, approximate 3 mL samples were taken out and analyzed immediately. Each experiment was conducted at least twice with relative errors less than 5%. All experiments were carried out under aerated condition, except that the specially noted  $\text{O}_2$ -free experiments were done under ultrapure  $\text{N}_2$ .

### Instrument analysis

The absorption spectra of the BPS solution were recorded on a UV-2550 UV-visible spectrophotometer (Shimadzu, Japan), and the reaction kinetics for BPS transformation was determined by measuring its absorbance change at 258 nm with time.

Fluorescence spectra were measured in a quartz cuvette using a HORIBA FluoroMax-4 spectrofluorometer.

$^1\text{H}$  NMR (nuclear magnetic resonance) spectra were acquired using a 600 MHz Agilent DD2 spectrometer: collected for 16 repetitions, relax delay 5.000 s, pulse width 45.0 degrees, acquire time 1.704 s and width 9,615.4 Hz.

Electrospray ionization (ESI) mass spectra were obtained in negative-ion ionization mode on a mass spectrometer (micrQTOF Bruker, Germany), using a double ion funnel electrospray ion source. The mass spectrum acquisition rate was 20 per second.

Gas chromatography–mass spectrometry (GC-MS) experiments were performed on a GCMS-QP2010 (Shimadzu, Japan). A DB-5 fused-silica capillary column (30 m × 0.25 mm i.d., 0.25 μm thickness) was used for GC separation, and helium was used as the carrier gas at 1 mL/min. The oven temperature was initially 100 °C for 2 min, increased to 300 °C at 20 °C/min, and held at 300 °C for 20 min. The injector and source temperatures were set at 250 and 200 °C, respectively.

EPR (electron paramagnetic resonance) experiments were performed on a JES FA200 spectrometer (JEOL, Japan): microwave power 4.0 mW, time constant 0.03 s, sweep time 2.0 min, 1 accumulation and 4,096 data points. The amount of DMPO added was  $4 \times 10^{-3}$  mol/L. Samples were placed in a quartz capillary tube, and the same tube was used for all the measurements to minimize errors.

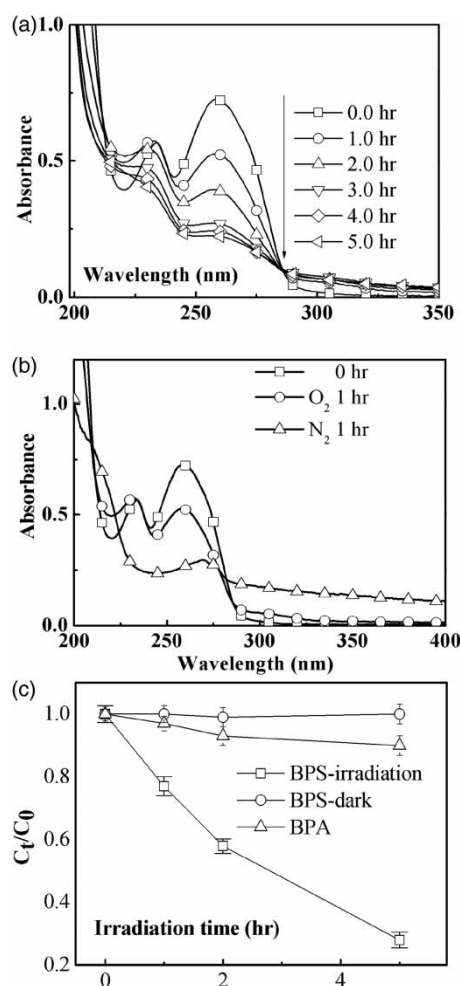
## RESULTS AND DISCUSSION

### Phototransformation of BPS

The initial absorption spectrum (before irradiation) of BPS had two peaks at 234 and 258 nm, and the second peak was the determination wavelength for its higher molar absorptivity. The initial peaks of BPS decreased as irradiation time increased, indicating that the concentration of BPS decreased as phototransformation proceeded (Figure 2(a)). Figure 2(b) shows the transformation of BPS under N<sub>2</sub> condition and air condition, respectively, suggesting that dissolved oxygen did play a role in the phototransformation process (see discussions below). Besides, Figure 2(c) shows that the phototransformation efficiency of BPS was higher than that of BPA, which indicated that BPS had shorter lifetime than BPA in aqueous environment.

### Product analysis

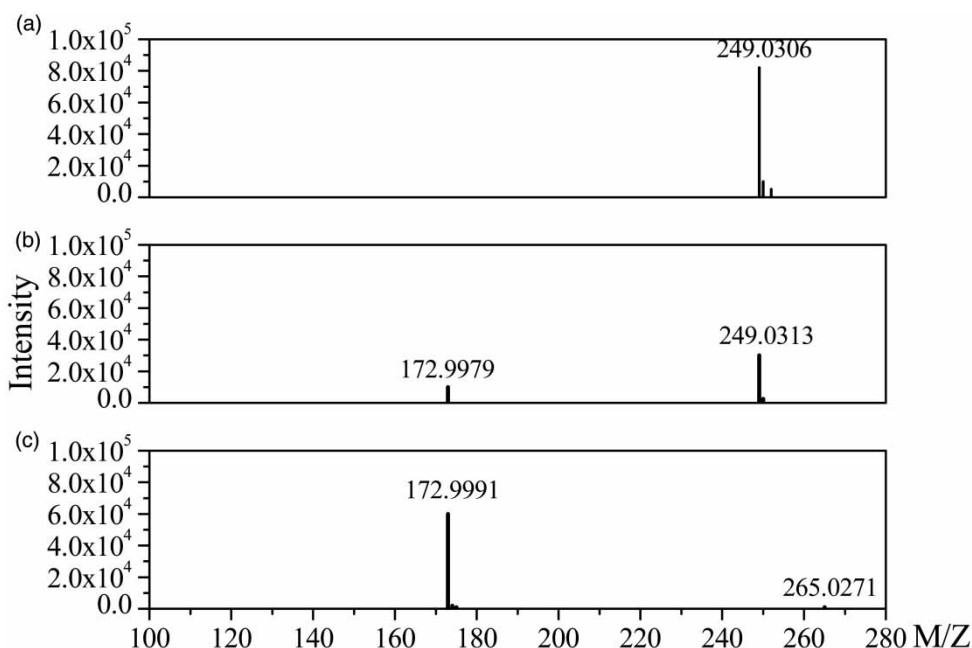
The phototransformation products of BPS were first examined by ESI-MS and GC-MS (Figure 3, Table 1, Figure S3, available online at <http://www.iwaponline.com/wst/070/257.pdf>); one main product was identified by the molecular ion and mass fragment peaks and by comparison with GC-MS library data. As shown in Figure 3, the ion peak intensity of *m/z* 249 decreased, while the ion peak intensity of *m/z* 172.3 increased with irradiation. Herein, the ion at *m/z* 249 was identified as the deprotonated molecule [(M-H)<sup>-</sup>] of BPS, and another ion at *m/z* 172.3 was identified as the deprotonated molecule [(M-H)<sup>-</sup>] of the phototransformation



**Figure 2** | Absorption spectra of the BPS ( $4.0 \times 10^{-5}$  mol/L) solution at (a) different irradiation time of 0–5 hr and (b) different aerated conditions of O<sub>2</sub> or N<sub>2</sub>. (c) Comparison of degradation rate between BPA and BPS in dark or under irradiation.

product of BPS. Further, GC-MS results (Table 1 and Figure S3) identified the product at the retention time 2.824 min as corresponding to *p*-hydroxybenzenesulfonic acid; and it was exactly consistent with ESI-MS peak at *m/z* 173. More important, the mass spectra results suggested that there were no other phototransformation intermediates besides *p*-hydroxybenzenesulfonic acid.

In order to further confirm whether the major product was *p*-hydroxybenzenesulfonic acid, phototransformation samples were compared with the standard sample by <sup>1</sup>H NMR and fluorescence spectra. The temporal <sup>1</sup>H NMR spectral patterns in the phototransformation of BPS in CD<sub>3</sub>OD solution are shown in Figure 4(a). The doublet peak of the 3- and 5-position protons (H<sub>b</sub>) of BPS appeared at 7.72, 7.74 ppm, and the doublet peak of the 2- and 6-position protons (H<sub>a</sub>) appeared at 6.88, 6.90 ppm. The



**Figure 3** | ESI-MS for BPS phototransformation after certain irradiation time: (a) 0 hr, (b) 1 hr and (c) 3 hr.

**Table 1** | GC-MS information about phototransformation products of BPS

Name	$t_i$ (hr)	$t_R$ (min)	M	m/z	Structure
BPS	0	14.716	250	39,65,93,110,141,250	
<i>p</i> -Hydroxybenzenesulfonic acid	3	2.824	174	26,39,50,66,74,94	
	5	2.826			

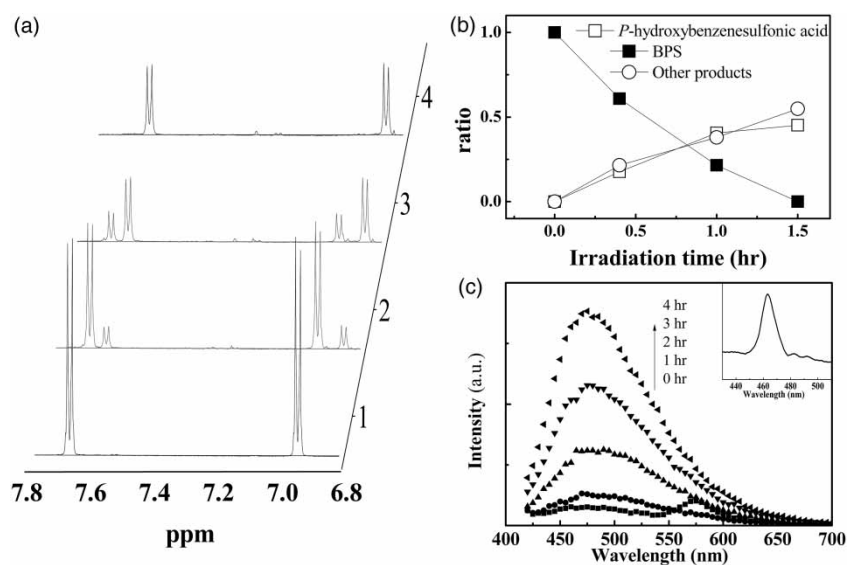
$t_i$  – irradiation time.  $t_R$  – retention time. M – molecular weight.

ratio of each signal peak area, against TMS (trimethylsilylated derivatization) reference, was 1 (6.88, 6.90 ppm) : 1 (7.72, 7.74 ppm). Finally, both peaks disappeared after 1.5 hr of irradiation. Simultaneously, two new doublet peaks (6.78, 6.80 and 7.66, 7.68 ppm) attributed to *p*-hydroxybenzenesulfonic acid (i.e.  $H_{a'}$  and  $H_{b'}$ ) appeared. The quantitative transformation of BPS and generation of products are shown in Figure 4(b). *p*-Hydroxybenzenesulfonic acid was the only product which could be observed in the  $^1H$  NMR, and its generating ratio was 41% after 1.5 hr of irradiation, while BPS signals completely disappeared at that time. The non-balance of element S from NMR results suggested that one or more products, which could not be observed by  $^1H$  NMR, were produced, and the products probably were not organic sulfur species any more, and

could be volatile  $SO_2$  and  $SO_3$ . Also, Figure 4(c) shows that the relative fluorescence intensity increased as irradiation time increased, and the emission peak kept at around 470 nm, which meant new product(s) had been produced during the phototransformation; the inset in Figure 4(c) is the fluorescence of *p*-hydroxybenzenesulfonic acid with emission maximum at 463 nm, and it confirmed that *p*-hydroxybenzenesulfonic acid was probably the major phototransformation product again.

### Phototransformation mechanism

Dissolved oxygen in water could participate in BPS phototransformation by producing oxidative ROS such as  $^1O_2$  (Chen *et al.* 2008) and  $\cdot O_2^-$  (Draper & Crosby 1983), which



**Figure 4** | The <sup>1</sup>H NMR (a) and corresponding quantitative analysis (b) and fluorescence spectra (c) of the BPS ( $4.0 \times 10^{-5}$  mol/L) solution under irradiation. For (a) at different irradiation time, 1: 0 hr; 2: 0.4 hr; 3: 1 hr; 4: 1.5 hr. The inset in (c) is the fluorescence spectrum of *p*-hydroxybenzenesulfonic acid ( $4.0 \times 10^{-4}$  mol/L).

may greatly affect the degradation of BPS. As shown in Figure 2(b), the transformation of BPS differed markedly between N<sub>2</sub> condition and air condition, confirming that dissolved oxygen did contribute to the phototransformation process (see discussion below).

Further, the phototransformation of BPS in the presence of several radical initiators or traps such as humic acid (HA), Fe(III), Rose Bengal, methanol, furyl alcohol and *p*-benzoquinone was examined, as shown in Table 2.

HA molecules absorb light and generate excited triplet (<sup>3</sup>HA\*), and ROS could be generated from the reaction between <sup>3</sup>HA\* and oxygen (Richard *et al.* 1997; Zepp *et al.* 1985; Zhan *et al.* 2005), and could attack BPS efficiently. From Table 2, the effects of HA on accelerating the phototransformation of BPS, suggested the important role of ROS.

**Table 2** | BPS phototransformation efficiency with different ROS-target additives

Target	Additive ( $10^{-3}$ mol/L)	Degradation% <sub>t=a,b</sub>
Control	None	23 <sup>a</sup> 72 <sup>b</sup>
Generate ROS	HA/2 (mg/L)	80 <sup>b</sup>
Generate •OH	Fe(III)/1	91 <sup>b</sup>
Generate <sup>1</sup> O <sub>2</sub>	Rose Bengal/0.4	32 <sup>a</sup>
Trap •OH	Methanol/1	6 <sup>a</sup>
Trap <sup>1</sup> O <sub>2</sub> (main) + •OH	Furfuryl alcohol/1	10 <sup>a</sup>
Trap O <sub>2</sub> <sup>-</sup>	Benzoquinone/0.1	46 <sup>a</sup>
	Benzoquinone/100	61 <sup>a</sup>

<sup>a</sup>Irradiation 1 hr.

<sup>b</sup>Irradiation 5 hr.

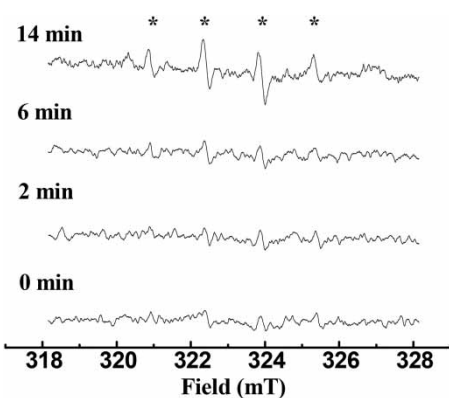
Addition of Fe(III) also accelerated the transformation of BPS. It is well known that UV light could directly lead to •OH formation and regeneration of Fe<sup>2+</sup> from the photolysis of the Fe(OH)<sup>2+</sup> in solution as follows (Ma *et al.* 2005):



The •OH quantum yield for Equation (1) is 0.14 at 313 nm and 0.017 at 360 nm (Zuo & Hoigne 1992). The •OH radical has a high oxidizing potential for the degradation of organic pollutants in water, and thus it suggested that the •OH plays an important role in oxidation and promotes the phototransformation of BPS.

Further, compared with control reaction, the degradation of BPS was not remarkably accelerated in the presence of Rose Bengal, which was used for efficiently generating <sup>1</sup>O<sub>2</sub>, and thus it suggested that <sup>1</sup>O<sub>2</sub> did not contribute much to the phototransformation of BPS.

Simultaneously, excess amounts of methanol, *p*-benzoquinone and furyl alcohol were added as effective scavengers for •OH, •O<sub>2</sub><sup>-</sup> and <sup>1</sup>O<sub>2</sub> (Sun & Pignatello 1992; Li *et al.* 2012), respectively. Table 2 shows that BPS degradation rates were suppressed in the presence of excess methanol and furyl alcohol, which confirmed that •OH could greatly affect BPS phototransformation; also, the small deviation between the two scavengers also confirmed that <sup>1</sup>O<sub>2</sub> really contributed slightly in the process. *p*-Benzoquinone was used as •O<sub>2</sub><sup>-</sup> trap and it was found that the

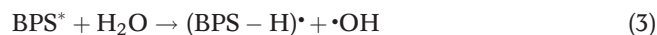


**Figure 5** | EPR spectra of the DMPO-HO• adducts in the irradiated BPS solution.

phototransformation process was significantly accelerated for both concentrations ( $10^{-4}$  and  $10^{-1}$  M). More important, when the amount of benzoquinone was increased dramatically, the BPS degradation efficiency had no corresponding increase, and thus it confirmed that the observed increased rate of BPS degradation was indeed due to trapping of  $\cdot\text{O}_2^-$  and not due to the benzoquinone-sensitized reaction (Ma *et al.* 2006). There was a readily possible explanation for this: first,  $\cdot\text{BPS}^+$  would be accumulated because  $\cdot\text{O}_2^-$  was trapped (reaction (2)); second,  $\cdot\text{BPS}^+$  was more easily degraded than BPS under  $\cdot\text{OH}$  attack. More important, the clearly accelerated phototransformation process with  $\cdot\text{O}_2^-$  trap not only proved that  $\cdot\text{O}_2^-$  played a role but also suggested that there may be a competition between  $\cdot\text{O}_2^-$  and  $\cdot\text{OH}$  in the phototransformation process.

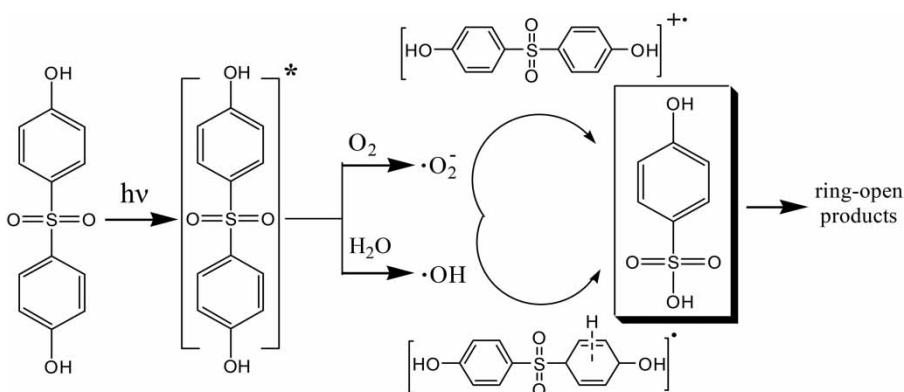
Photoexcitation of anthraquinone and its single- or double-substituted sulfonate derivatives leads to efficient production of a semiquinone radical and  $\cdot\text{OH}$  by apparent one-photon photooxidation of water (Ononye *et al.* 1986; Ma *et al.* 2011). Here, it was suggested that BPS could

perform the same reaction as the quinones do. Therefore, on the basis of the above experiment data, we propose the two competitive reaction pathways as follows:



BPS absorbed light, then generated  $\text{BPS}^*$  would react with  $\text{O}_2$  and  $\text{H}_2\text{O}$  in the solution, producing  $\cdot\text{O}_2^-$  and  $\cdot\text{OH}$ . The phototransformation of BPS involves competitive attacking of substrate by  $\cdot\text{O}_2^-$  due to electron transfer from the excited state of BPS ( $\text{BPS}^*$ ) to dissolved  $\text{O}_2$  and by  $\cdot\text{OH}$  from  $\text{BPS}^*$  directly oxidizing  $\text{H}_2\text{O}$ , and the latter contributed more than the former. Indeed, the EPR spin-trap results evidenced the signals of DMPO-HO• in the irradiated BPS solution. As illustrated in Figure 5, four characteristic peaks of DMPO-HO• were obviously observed after irradiation, and the signal intensity increased with irradiation time; however, no such signals were detected in the dark. Direct addition of hydrogen peroxide had no acceleration effect on the phototransformation of BPS; thus it excluded that the observed DMPO-HO• signals came from other pathways, such as the photolysis of hydrogen peroxide which might be formed from superoxide radicals. The fact that  $\cdot\text{OH}$  was produced provided solid evidence that photo-excited BPS could oxidize  $\text{H}_2\text{O}$  to produce  $\cdot\text{OH}$ . Further, the  $\text{O}_2$ -free results also supported this mechanism, i.e. in the absence of  $^1\text{O}_2$  and  $\cdot\text{O}_2^-$ , the phototransformation of BPS proceeded much faster, strongly suggesting the reaction pathway of BPS's direct oxidation of  $\text{H}_2\text{O}$  to produce  $\cdot\text{OH}$ .

Therefore, on the basis of the above experiment data, the pathway of phototransformation of BPS could be



**Figure 6** | The proposed phototransformation pathway of BPS.

illustrated in Figure 6. Under the aerated condition, the BPS phototransformation mechanism involved competitive attacking of substrate by  $\cdot\text{O}_2^-$ , due to electron transfer from BPS\* to  $\text{O}_2$ , and  $\cdot\text{OH}$  from BPS\* directly oxidizing  $\text{H}_2\text{O}$ , leading to *p*-hydroxybenzenesulfonic acid; since  $\cdot\text{OH}$  has much stronger oxidizing potential than  $\cdot\text{O}_2^-$  (Ma et al. 2006),  $\cdot\text{OH}$  should contribute more than  $\cdot\text{O}_2^-$  in the phototransformation. And under  $\text{O}_2$ -free condition, due to the lack of competition from the  $\cdot\text{O}_2^-$  route,  $\cdot\text{OH}$  as the only radical played the dominating role, and thus the phototransformation became much more efficient.

## CONCLUSION

Based on the above results and discussions, in contrast to BPA, the aqueous phototransformation of BPS could readily proceed. Various radical traps and further EPR results confirmed  $\cdot\text{OH}$  and  $\cdot\text{O}_2^-$  competitively playing a role in the phototransformation of BPS under aerated condition, and the main product was unharmed *p*-hydroxybenzenesulfonic acid identified by ESI-MS, NMR and fluorescence. Under  $\text{O}_2$ -free condition,  $\cdot\text{OH}$  was exclusively formed and played the dominating role, and thus the phototransformation became much more efficient. Better understanding of these reactions is very important not only for studying the environmental fate of BPS but also for the successful treatment of practical wastewaters containing BPS component.

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