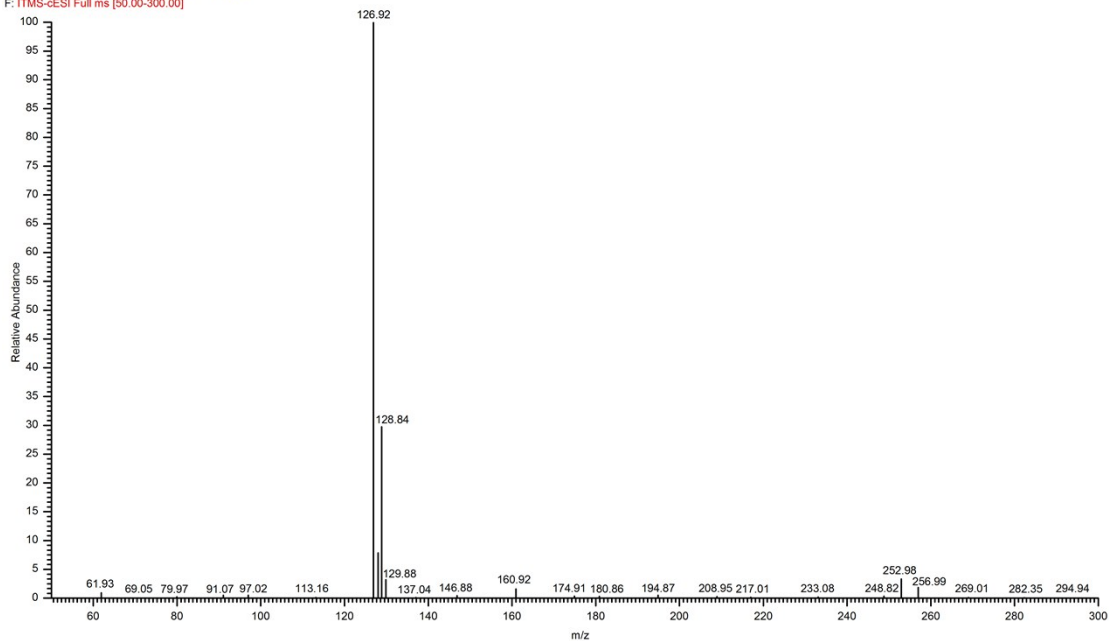


Catalytic degradation of 4-chlorophenol with La/TiO₂ in dielectric barrier discharge system

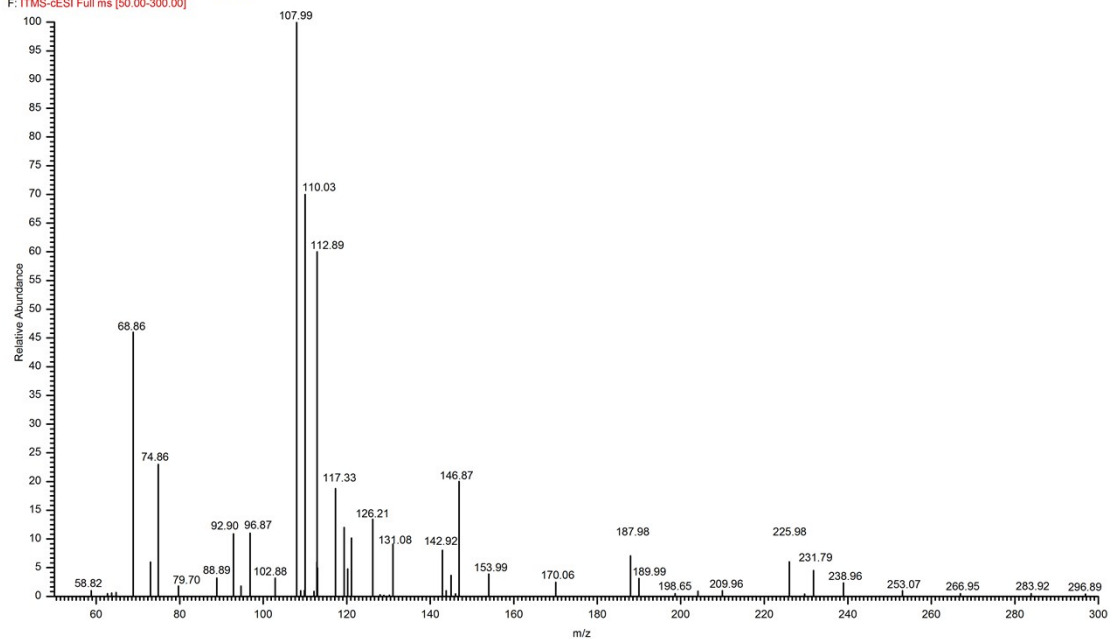
1. Mass spectrum analysis

CP-i #285-311 RT: 0.91-0.97 AV:27 NL:1.72E3
F: ITMS-cESI Full ms [50.00-300.00]



(a)

CP-f #241-257 RT: 0.85-0.90 AV:17 NL:2.96E2
F: ITMS-cESI Full ms [50.00-300.00]



(b)

Fig. 1 Mass spectrums of 4-chlorophenol before treatment (a) and after treatment (b)

The pathways for the degradation of 4-CP have been suggested based on MS identification of some intermediates of reaction, known intermediates of degradation as reported [1, 2, 3, 4, 5] and possible products of degradation. The mass spectrums of initial 4-CP sample and degradation are shown in the first and second figures. The major intermediates detected in this case were: benzoquinone (m/z 107.99), hydroquinone (m/z 110.03), maleic acid (m/z 112.89). Degradation is an oxidative process, and given a facile oxidation of hydroquinone to benzoquinone [6, 7]. Then the rings are broken to generate the corresponding carboxylic acid. Gradually, the carboxylic acids are mineralized to carbon dioxide and water.

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2. Reactive species analysis

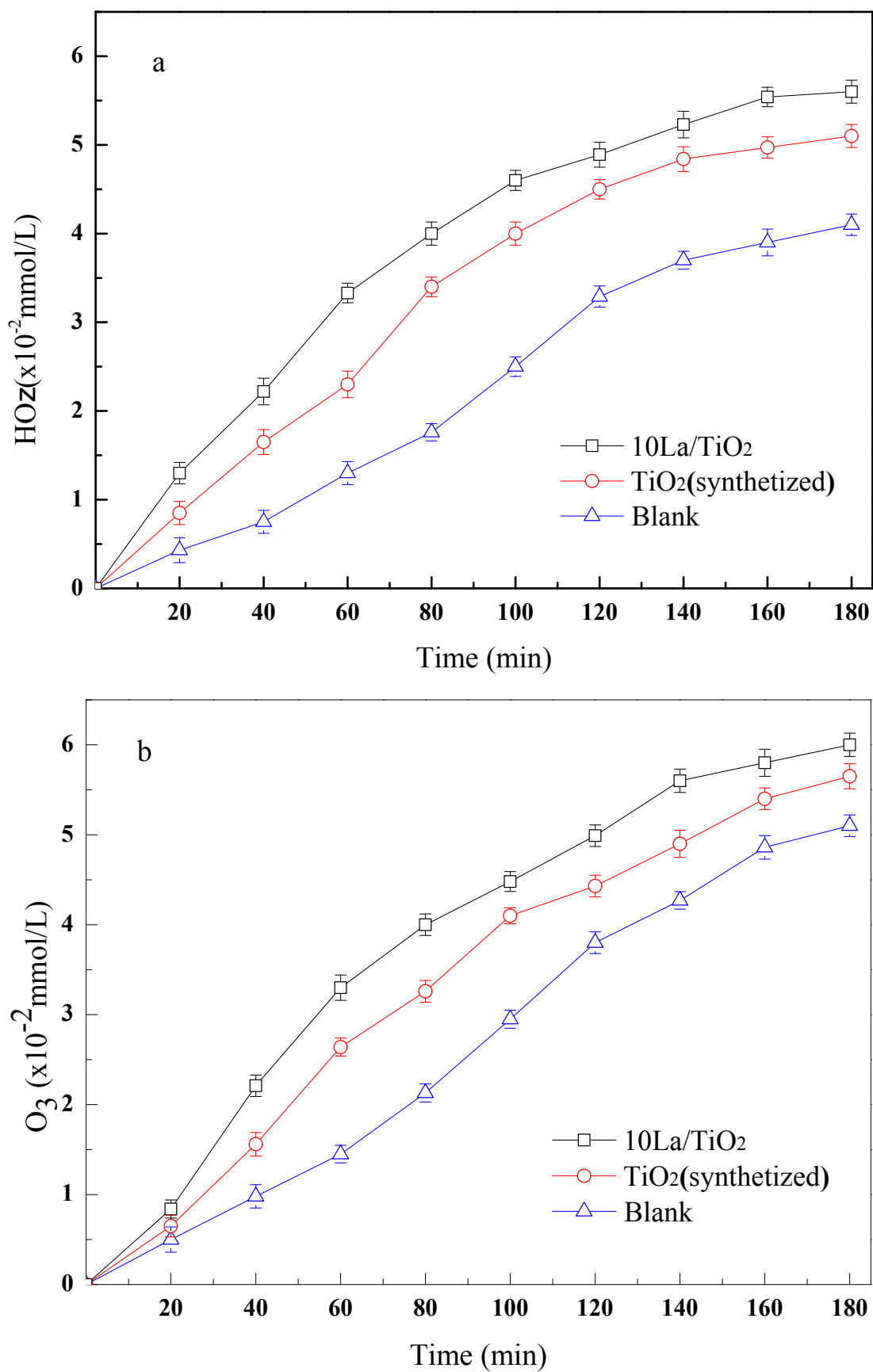


Fig. 2 HO[•] (a) and O₃ concentration of optimum La doping, synthesized TiO₂ and blank (b)

HO• was determined through chemical method using salicylic acid as the probe [1].

And ozone was measured by UV absorption at 254 nm using UV-vis spectrophotometer (TU-1810). In our DBD system, HO• can be formed when water is ionized by electric current and irradiated with high energy ultraviolet light. As Fig. 2a shown, catalyst can promote the production of HO•. And catalyst with doping La can strengthen this process. The formation HO• as follow [2-6]:



The concentration of ozone with catalyst is always higher than that without catalyst as shown in Fig. 2b. This result might be attributed to highly energized electrons (e^-), holes (h^+_{vb}) in the valence band and electrons (e^-_{cb}) in the conductance band on the surface of catalyst, oxygen in gas or aqueous phase may be converted to more active species (i.e. $O^\bullet_{(aq)}$, $O^{\bullet-}_{2(aq)}$) [7]. The reaction equation [8, 9]:



And direct electron transfer and adsorption reactions are induced on the surface of TiO₂ under ultraviolet light and visible light [10, 11].

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