Supporting information

Directed Synthesis of Hierarchical Nano-Structured TiO_2 Catalysts and their Morphology-Dependent Photocatalysis for Phenol Degradation

Lu Liu*, Huajie Liu, Ya-Ping Zhao*, Yuqiu Wang, Yueqin Duan, Guandao Gao, Ming Ge, Wei Chen*

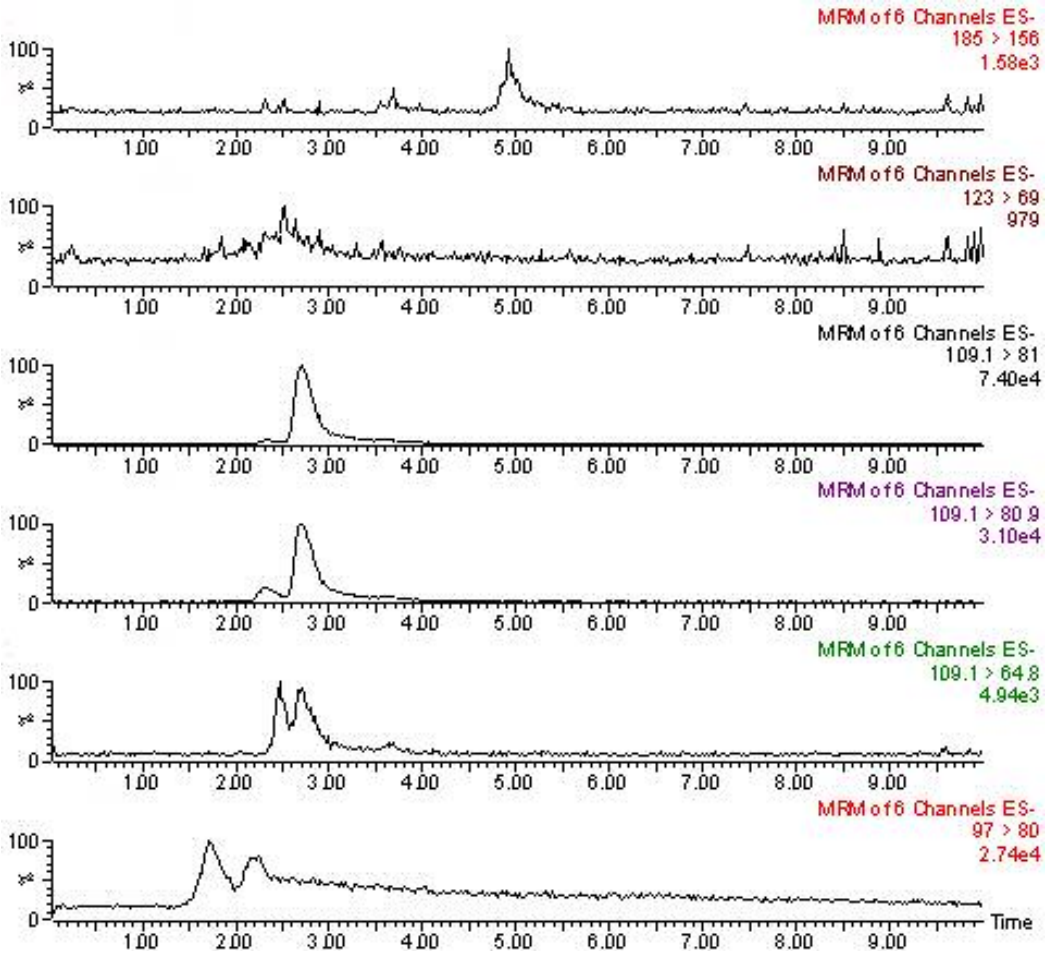

Figure. I.a. Samples TiO_2 $3D_{1D}$ microspheres for HPLC/MS/MS analysis were taken at 180min, MRM chromatogram of intermediates of phenol degradation: RT1.72min-maleic anhydride, RT2.53min-benzoquinone, RT4.93min-4,4'-dihydroxybiphenyl, RT2.30min-p-dihydroxybenzene, RT2.49-m-dihydroxybenzene, RT2.70-o-dihydroxybenzene.

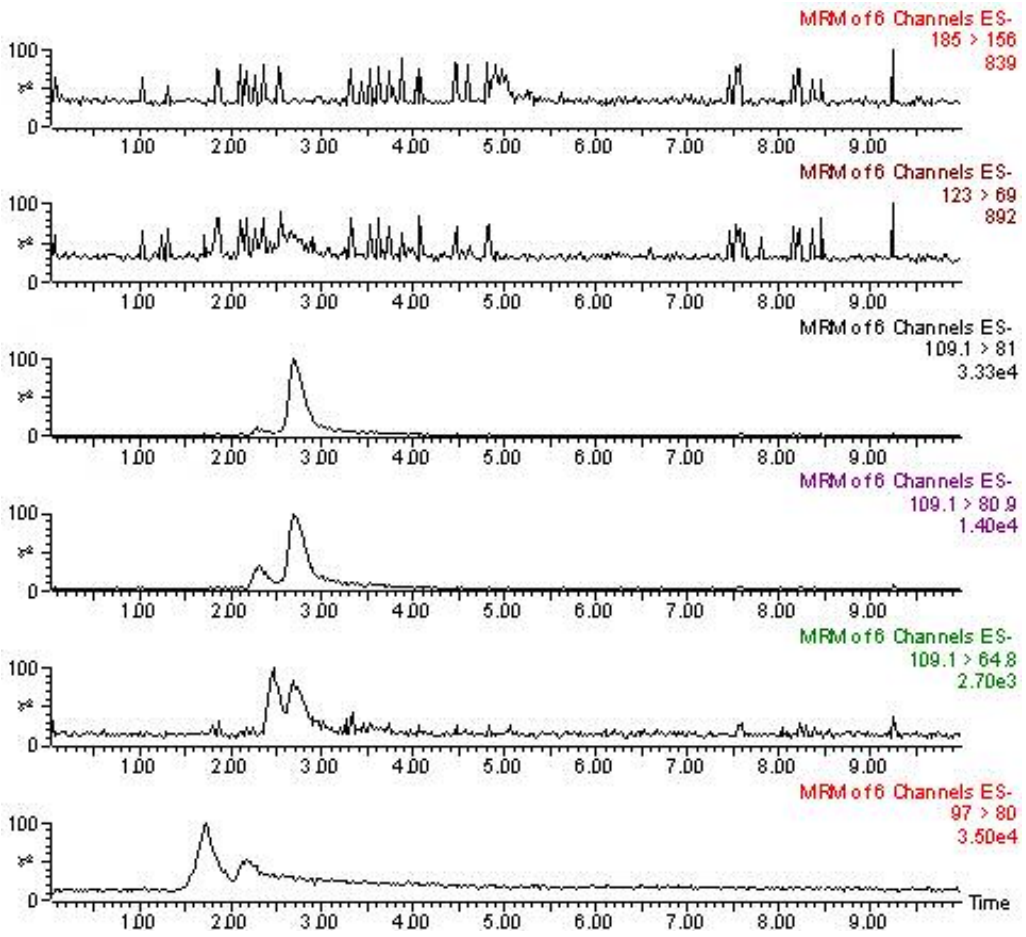

Figure. I.b. Samples TiO_2 1D nanorods for HPLC/MS/MS analysis were taken at 180min,MRM chromatogram of intermediates of phenol degradation: RT1.72min-maleic anhydride, RT2.53min-benzoquinone, RT4.93min-4,4'-dihydroxybiphenyl, RT2.30min-p-dihydroxybenzene, RT2.49-m-dihydroxybenzene, RT2.70-o-dihydroxybenzene.

Annotation I: Intermediates of phenol was identified in the negative ion mode in the m/z 40-200 for HPLC/LC/MS/MS(Quattro MicroTM Api, Waters, USA) equipped with an electrospray ionization source (ESI). HPLC series (waters 2695, USA) is equipped with a reversed-phase C18 column (Xterra, USA) of 150×2.1mm and 5μm particle diameter. Column temperature was maintained at 25°C. The mobile phase used for eluting phenol from the HPLC columns consisted of acetonitrile and water (40:60v/v) at a flow-rate of 0.2 mL/min.

Negative ions were acquired in multiple reaction monitoring (MRM) mode with a dwell time of 200 ms. For the negative model, the temperature of the heated capillary and source were 350 °C and 90°C, respectively. The source voltage was set

to 4.0 kV. Analysis of the intermediates of phenol was performed using LC-ESI-MS/MS with multiple reaction monitoring (MRM). The optimal conditions for MS/MS analysis of the compounds and the precursor, [M-H]-, and product ions monitored in MRM mode are summarized in Table.I.

Table.I. Optimal ESI-MS/MS Conditions for Analysis of intermediates of phenol

analyte	Precursor ion, $[M-H]^-$(m/z)	Product ion (m/ z)	Cone voltage (V)	Collision energy (eV)
4,4'-dihydroxybiphenyl	185	156	30	33
benzoquinone	123	39	30	28
p-dihydroxybenzene	109	81	30	16
m-dihydroxybenzene	109	65	30	12
o- dihydroxybenzene	109	81	30	12
maleic anhydride	97	80	30	17

The result of intermediates of phenol degradation obtained at Figure.I.a and Figure. I.b.

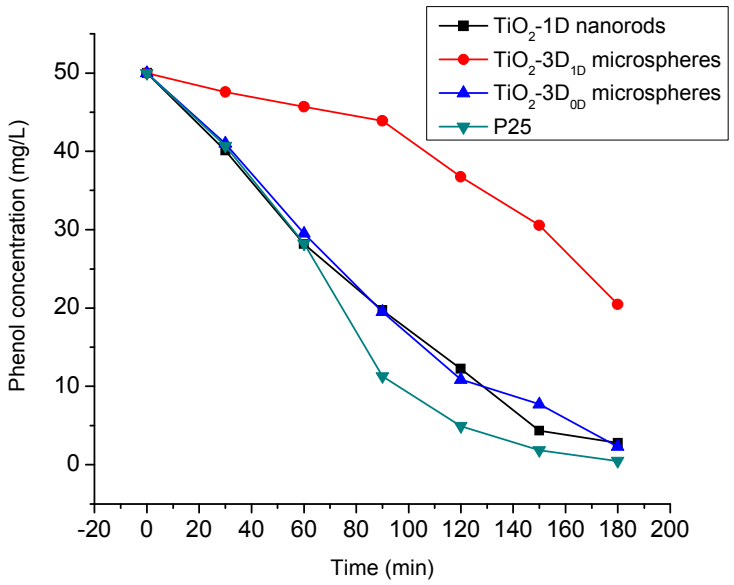

Figure.II. Phenol concentration decreased as irradiation time, using TiO_2 $3D_{0D}$ microspheres, TiO_2 1D nanorods, TiO_2 $3D_{1D}$ microspheres, and Degussa P25.

Annotation II：

Experimental results obtained in the present study showed that when Degussa P25 was used as the photocatalyst, white emulsion was formed in solution after treatment for 180 minutes; this emulsion makes it difficult to separate the photocatalyst, a difficult issue that has to be handled in treatment processes. The synthetic TiO_2 $3D_{0D}$ microspheres, however, can precipitate from wastewater much more easily after treatment because the diameters of these microspheres are approximately 5000-10000 times as large as those of Degussa P25 (with diameters from 21 to 24 nm). Therefore, the synthetic TiO_2 $3D_{0D}$ microspheres are much easier to separate than the Degussa P25 nanoparticles. This is a significant advantage of the synthetic TiO_2 $3D_{0D}$ microspheres over Degussa P25.