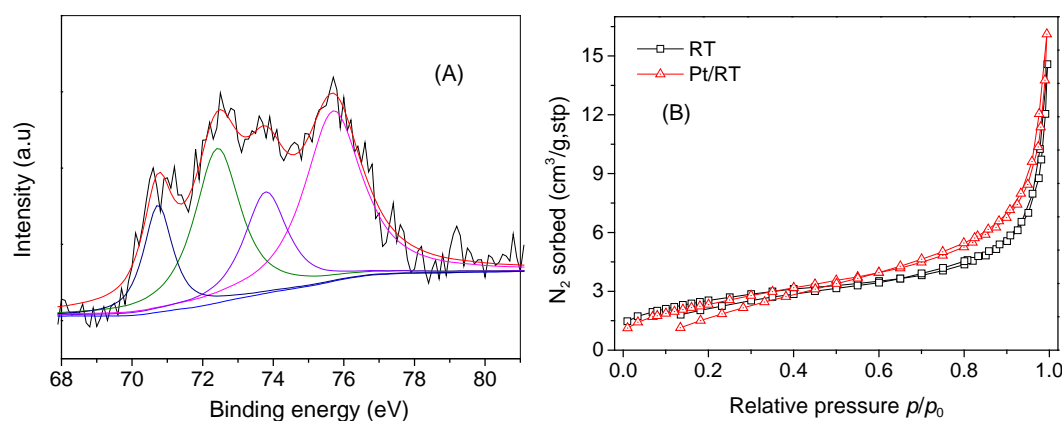


## Electronic Supplementary Information (ESI)

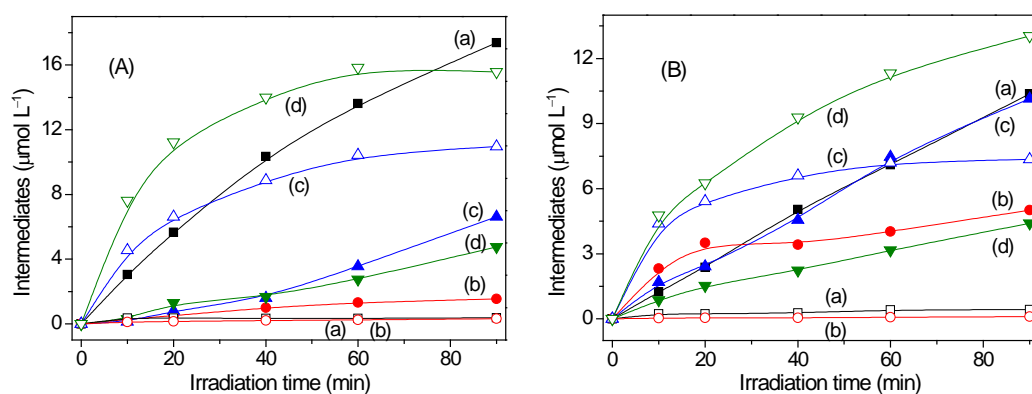
# Different effect of fluoride and phosphate anions on TiO<sub>2</sub> photocatalysis (rutile)

Jianjun Zhao, Shengwei Liu, Xiao Zhang, and Yiming Xu\*

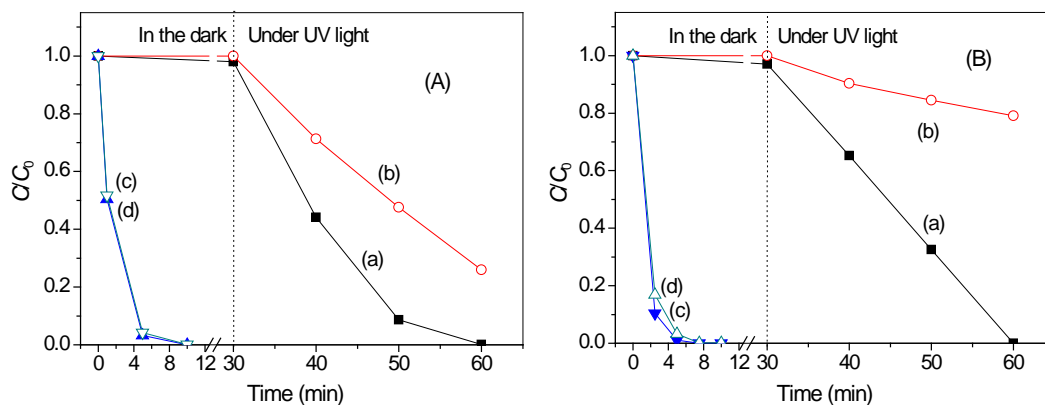
State Key Laboratory of Silicon Materials and Department of Chemistry, Zhejiang University,  
Hangzhou 310027, China.



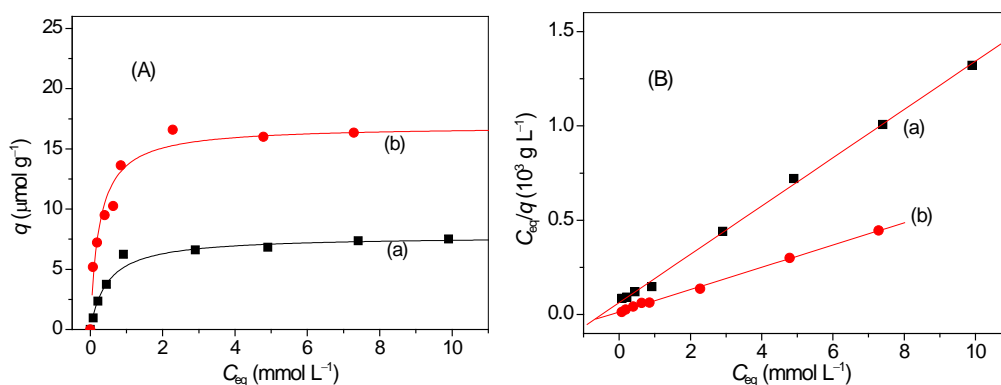
**Fig. S1** (A) XPS spectra of Pt 2f for Pt/RT. (B) N<sub>2</sub> adsorption–desorption isotherms on RT and Pt/RT.



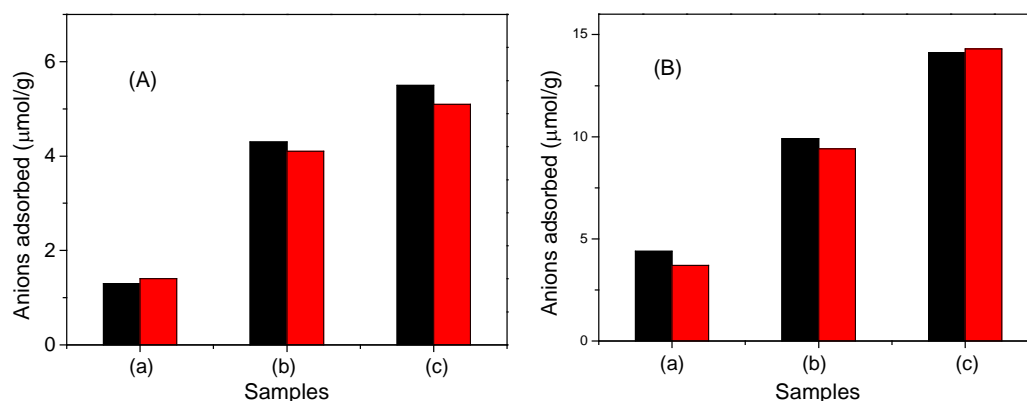
**Fig. S2** Anion effect of (A) fluoride, and (B) phosphate, on the formation of hydroquinone (HQ, solid symbols) and benzoquinone (BQ, open symbols) in aqueous solution, measured from phenol degradation over (a) RT, (b) RT + anion, (c) Pt/RT, and (d) Pt/RT + anion.



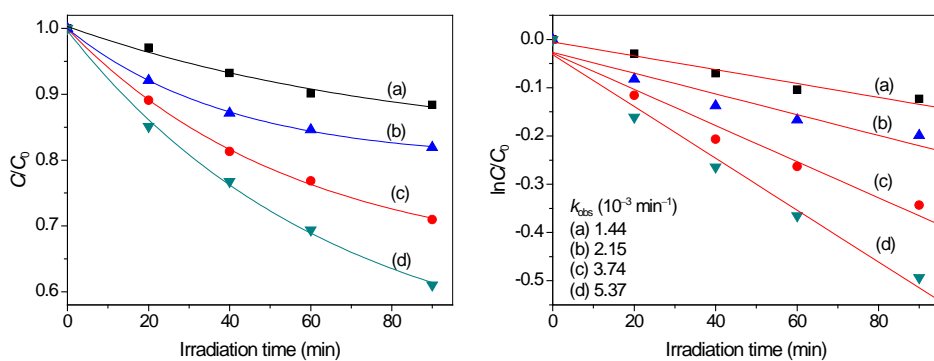
**Fig. S3** Effect of (A) fluoride, and (B) phosphate, on 10 mM H<sub>2</sub>O<sub>2</sub> adsorption and decomposition in absence of phenol, with (a) RT, (b) RT + 1.0 mM anion, (c) Pt/RT, and (d) Pt/RT + 1.0 mM anion.



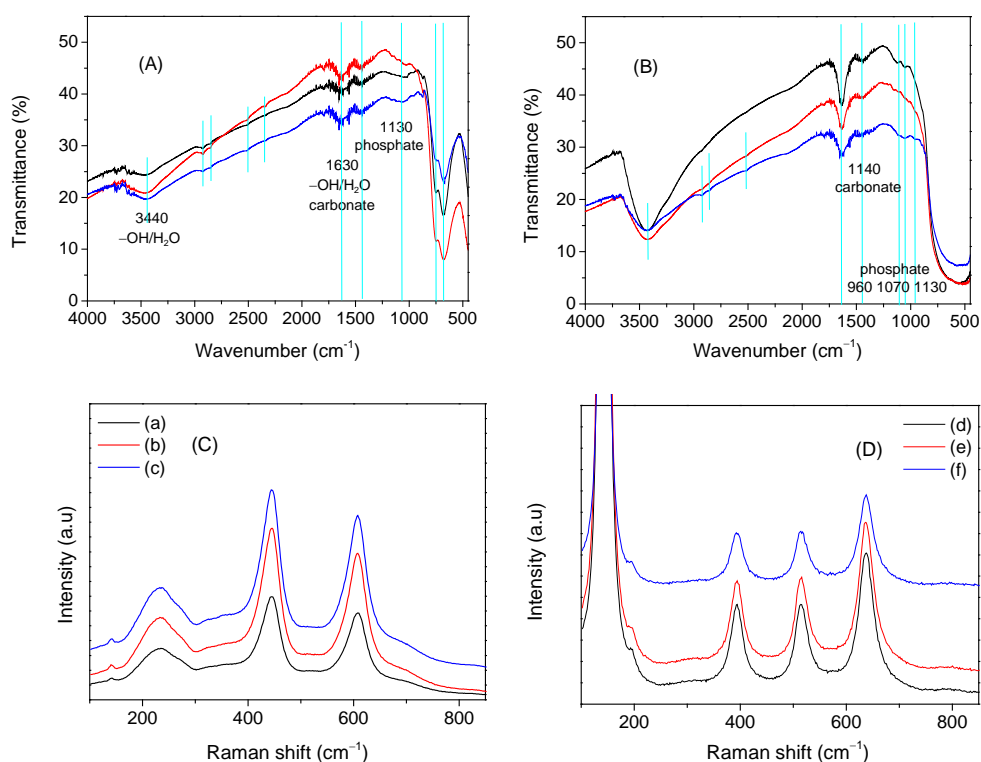
**Fig. S4** (A) Adsorption isotherms on Pt/RT of (a) fluoride, and (b) phosphate in aqueous solution, measured without phenol. (B) Fitting with Langmuir adsorption equation,  $q/q_m = KC_{eq}/(1 + KC_{eq})$ , where  $q_m$  is the maximum amount of adsorption,  $K$  is adsorption constant,  $C_{eq}$  is the equilibrium concentration in aqueous phase, and  $q$  is the amount of adsorption at  $C_{eq}$ .



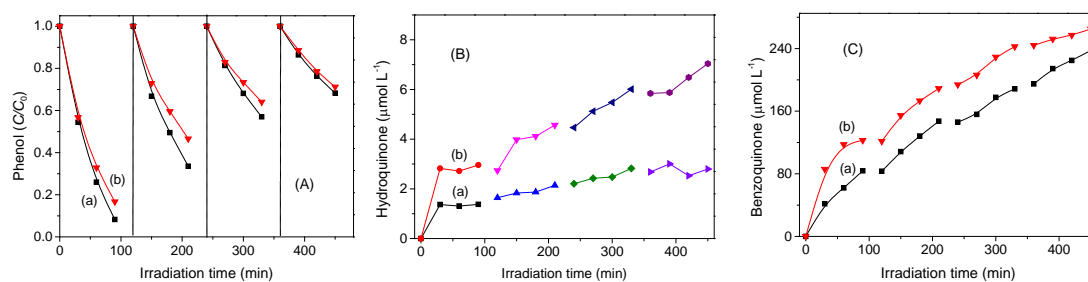
**Fig. S5** Amounts of (A) fluoride, and (B) phosphate, adsorbed on Pt/RT in aqueous solution, at initial concentration of (a) 0.1, (b) 1.0, and (c) 5 mM, measured in the dark (black symbols) and under UV light for 1 h (red symbols). Analysis was made as quick as possible.



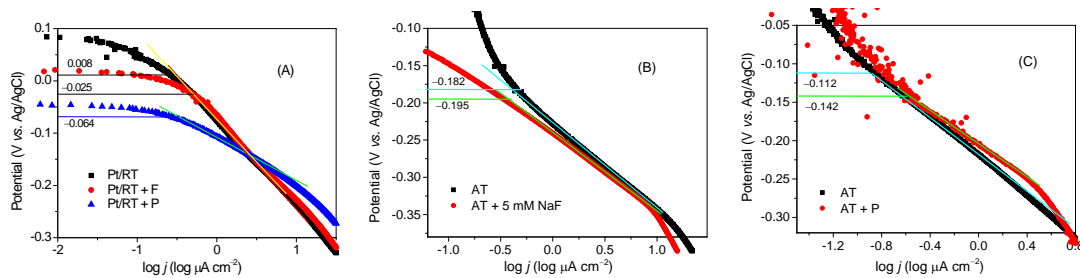
**Fig. S6** Phenol degradation in aqueous solution on (a) RT, (b) AT, (c) Pt/RT, and Pt/AT. Experiment was carried under similar condition (1 g/L TiO<sub>2</sub>, 0.43 mM phenol, initial pH 5.2, and UV light).



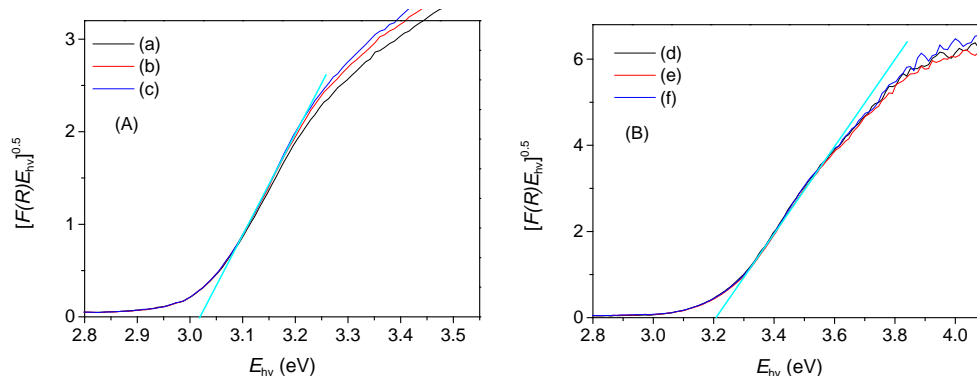
**Fig. S7** (A, B) FTIR, and (C, D) Raman spectra (a) RT, (b) NaF/RT, (c) Na<sub>3</sub>PO<sub>4</sub>/RT, (d) AT, (e) NaF/AT, and (f) Na<sub>3</sub>PO<sub>4</sub>/AT. The anion sample was prepared by dark equilibrium of the suspension (1 g/L TiO<sub>2</sub> and 50 mM anions) overnight, followed by filtration and drying in a vacuum at 80 °C.



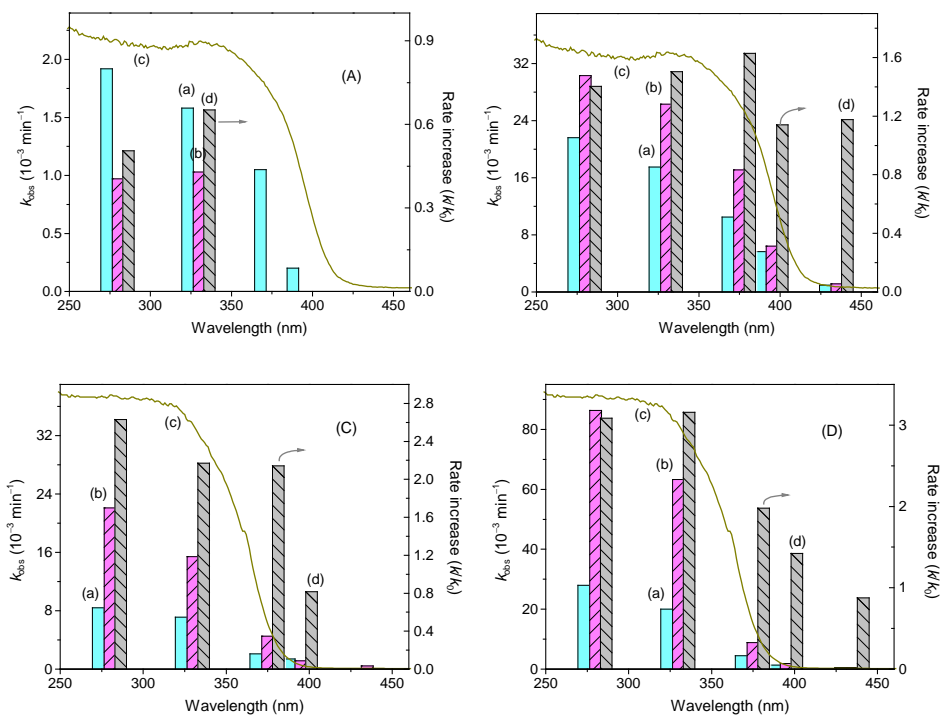
**Fig S8.** (A) Recycling test of phenol degradation on Pt/RT with (a) 5 mM NaF and (b) Na<sub>3</sub>PO<sub>4</sub>. The corresponding formation of (B) hydroquinone, and (C) benzoquinone. After each run, only drops of fresh phenol solution was supplemented, to restore its initial concentration around 0.43 mM.



**Fig. S9.** Reduction of O<sub>2</sub> on a film electrode in 0.5 M NaClO<sub>4</sub> pH 5.2. (A) Pt/RT, with or without 1 mM anions. (B) AT, with or without 5 mM NaF. (C) AT with or without 5 mM Na<sub>3</sub>PO<sub>4</sub>.



**Fig. S10** Tauc plots for indirect transition, where  $R$  is reflectance,  $F_R$  is  $(1 - R)^2/(2R)$ , and  $E_{hv}$  is light energy. (Samples were (a) RT, (b) NaF/RT, (c) Na<sub>3</sub>PO<sub>4</sub>/RT, (d) AT, (e) NaF/AT, and (f) Na<sub>3</sub>PO<sub>4</sub>/AT.



**Fig. S11** Apparent rate constants of phenol degradation on (A) RT, (B) Pt/RT, (C) AT, and (D) Pt/AT, (a) in absence, and (b) in presence of 5 mM NaF, measured on a 500 We Xenon lamp with a cut-off filter at 280, 330, 375, 395, and 435 nm. Curve (c) is the absorption spectra of rutile for (A),

B), and anatase for (C, D). The bars (d) is  $k/k_0$ , the ratio of  $k_{\text{obs}}$  with anions to  $k_{\text{obs}}$  without anions.