Mutual influence of cupric cations and several anions in anatase and rutile TiO₂ photocatalysis

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Abstract

Copper ions in aqueous solution are known to promote organic oxidation in semiconductor photocatalysis, but the counter anions seem to be important as well. In this work, the performance of Cu(ClO₄)₂ in presence of several anions in sodium forms (F[−], Cl[−], ClO₄[−], NO₃[−], and SO₄^{2−}) has been examined. Phenol oxidation in aqueous solution (pH 4) under UV light was used as model reaction and TiO₂ in the forms of anatase (AT) and rutile (RT) as photocatalysts. On the addition of 0.1–5 mM Cu²⁺, the reactions on AT and RT all increased. On the addition of 1 mM anions, reactions on AT increased by F[−] and SO₄^{2−}, but reactions on RT all decreased. In presence of 3 mM Cu²⁺, however, reactions on AT and RT all decreased by 1 mM anions except NO₃[−]. Such anion effects were also observed for H₂ production on AT and RT in presence of Cu²⁺ and 10% methanol. A possible mechanism for the positive and negative anion effects is discussed. This work indicates that the formation of a Cu(II)/Cu(I) complex with anions weakens the positive effect of copper ions on organic oxidation in TiO₂ photocatalysis.

Graphic abstract

Keywords TiO₂ · Photocatalysis · Copper · Anion · Phenol oxidation · Hydrogen production

1 Introduction

Semiconductor photocatalysis has been widely studied over the past four decades [1, 2]. This is because various redox reactions can occur at ambient temperature, only using light, O₂, and water as the input. In the system, it is a semiconductor that absorbs light, generates pairs of electrons and

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holes, and then reacts with substrates on the surface. For environmental remediation, anatase TiO_2 (AT) is the most studied photocatalyst, mainly due to its conduction band electrons (e_{cb}^-) reducing O_2 into O_2^- , and its valence band holes (h_{cb}^+) oxidizing various organics at the same time [3]. In a comparison with AT, rutile TiO_2 (RT) is poorly studied, mainly due to its electrons not enabling one-electron O_2 , even though RT produced at a high temperature has a potentially high photocatalytic activity [4, 5]. For any semiconductor photocatalysis, however, the photogenerated e_{cb}^- and h_{cb}^+ quickly recombine to heat or light, without net chemical reactions with the target. To improve the efficiency of charge separation, therefore, TiO_2 is usually modified with a co-catalyst, so as to speed up electron transfer to O_2 , and hole transfer to organics, and/or both [6]. For instance, Pt is not only an effective electron sink but also an excellent thermal catalyst for O_2 reduction. As a result, the efficiency of charge separation is improved, and the rate of counterpart organic oxidations is increased [7].

Inorganic ions are commonly present in the aquatic environment, and their influences on photocatalytic reactions have been studied and reviewed [8–11]. Some of those ions are beneficial to organic oxidation in TiO_2 photocatalysis, and hence they might be superior to noble metals as co-catalysts. Among transition metal ions, Cu^{2+} is the promising co-catalyst. The increased organic oxidation on TiO_2 by Cu^{2+} is due to Cu^{2+} reduction, improving the efficiency of charge separation [12–14]. Such a positive effect of Cu^{2+} has been observed for all TiO_2 (AT, RT, their mixture, and brookite) [13]. However, an optimum concentration of Cu^{2+} , at which a maximum reaction rate is achieved, varies from one report to another. It was 1–2 μM CuSO_4 for toluene and CH_3OH oxidation [15, 16], 0.25–0.5 mM CuCl_2 for phenol oxidation [13, 17], 1 mM $\text{Cu}(\text{NO}_3)_2$ for phenol and resorcinol oxidation [18, 19], and 0.12 wt% $\text{Cu}(\text{NO}_3)_2$ on RT for 4-chlorophenol oxidation [14]. Although different experimental conditions were used in those studies, the discrepancy may relate to different counter anions involved in those cupric salts, and/or due to different organic donors forming a complex with Cu^{2+} , and shifting more or less the redox potentials for the $\text{Cu}^{2+}/\text{Cu}^+$ and $\text{Cu}^{2+}/\text{Cu}^0$ couples in aqueous solution [20–22].

On the other hand, inorganic anions in an aqueous solution have a great influence on TiO_2 photocatalysis for organic degradation [10, 11, 23–28]. However, both an increased and decreased reaction have been reported, with a controversial mechanism. Probably, there is a competition between anions and organics for the surface sorptive sites and trapped holes of TiO_2 . Among the anions, F^- is the most studied, because it is beneficial to the photocatalytic degradation of either poorly or strongly adsorptive substrate [26, 28]. In those studies, AT or P25 (a mixture of 80% AT and 20% RT) was used as photocatalyst. But the anion effect on RT

photocatalysis is little known [29]. In the presence of both CuCl_2 and NaF , interestingly, the rate of phenol degradation on P25 was larger than those measured in the presence of CuCl_2 and NaF , respectively, due to a synergism between Cu^{2+} and F^- , further improving the efficiency of charge separation [17].

In this work, the performance of cupric ions in AT and RT photocatalysis has been examined in the presence of different anions (F^- , Cl^- , ClO_4^- , NO_3^- , and SO_4^{2-}). To minimize the effect of cations and anions, cupric perchlorate and sodium salts were used as source ions. Lewis and co-workers have reported that on a WO_3 anode, ClO_4^- is more stable than Cl^- and SO_4^{2-} against photo-oxidation [30]. To minimize the effect of organic adsorption and photolysis, phenol oxidation in an aqueous solution under a 320 nm light was chosen as a model reaction [3]. The experiment was carried out in presence of $\text{Cu}(\text{ClO}_4)_2$, sodium salts, and $\text{Cu}(\text{ClO}_4)_2$ plus sodium salts, respectively. To understand the role of those anions, several experiments were conducted, including the anion adsorption on solid, the electrochemical reduction of Cu^{2+} on a TiO_2 electrode, and the photocatalytic production of H_2 with methanol as a sacrificial reagent. Furthermore, a possible mechanism for the observed positive and negative anion effect is discussed.

2 Experimental section

Anatase TiO_2 (AT) was purchased from Sigma-Aldrich, and a mixture of anatase and rutile (P25) from Degussa. Other chemicals in the analytic grade were obtained from Sinopharm, including $\text{Cu}(\text{ClO}_4)_2$, NaClO_4 , NaF , NaCl , NaNO_3 , and Na_2SO_4 . Rutile TiO_2 (RT) was prepared from the hydrolysis of TiCl_4 in an iced HCl solution, followed by heating at 60 °C for 2 h, filtering, washing thoroughly with water, and drying at 80 °C [4]. Solid crystal structures were confirmed by X-ray diffraction analysis (Fig. S1A).

Photoreaction was conducted on an XPA apparatus, attached with a water-jacket (Xujiang electrochemical plant, China). Light source was a 300 W Hg lamp, equipped with a 320 nm cut-off filter. Unless otherwise mentioned, the experiment was carried out under fixed conditions (50 mL suspensions, 1.00 g/L catalyst, 0.43 mM phenol, and initial pH 4, and 25 °C). Prior to light illumination, a suspension containing necessary components was stirred in the dark for 30 min. At given time intervals, 2 mL of the suspension was withdrawn, filtered, and immediately analyzed by high-performance liquid chromatography on a Dionex UltiMate 3000 (column, C18; eluent, 50% vol. methanol aqueous solution acidified with 0.1% acetic acid; flow rate, 1.0 mL/min; detection wavelength, 280 nm). Anions were analyzed by IC (ion chromatography) on a Dionex ISC-90 (eluent, 3.5 mM Na_2CO_3 /1.0 mM NaHCO_3 ; flow rate, 1.16 mL/min).

Copper species was measured with a spectrophotometric method [31]. The pH value was measured on a PHSJ-3F pH meter (Leici, Shanghai). Light intensity reaching the reactor surface was measured with a UV-A radiometer (Beijing Shida Technology).

H₂ production was carried out in a flask, from which four UV-LEDs (3 W, 365 nm) were located 1 cm away. A suspension (50 mL) containing necessary components (1.00 g/L catalyst, 10 vol.% methanol aqueous solution, 0.25 mM copper perchlorate, and 1.0 mM sodium salt) was purged with N₂ for 30 min, and then sealed, followed by light illumination. At given intervals, 0.25 mL gas in flask was withdrawn, and analyzed by gas chromatography on an Agilent Technologies 7820A (thermal conductivity detector).

3 Results and discussion

Anion effect In this study, sodium salts were used as anion sources. Figure 1A shows the time profiles for phenol oxidation on AT and RT. As the irradiation time (t) increased, phenol concentration (C/C_0) decreased. All curves in the early period of time well fit the rate equation of $\ln C/C_0 = k_{\text{obs}} t$, where k_{obs} represents the apparent rate constants (k_{obs}) for phenol oxidation (Fig. S2A). The resulting k_{obs} for AT and RT were 0.53, and 0.066 h⁻¹, respectively. In the presence of 1 mM NaF, the corresponding k_{obs} changed to 1.55, and 0.036 h⁻¹, respectively. This is indicative of NaF being positive to AT, but negative to RT, respectively [28, 29, 32]. Then control experiments with 1.0 g/L AT, 0.43 mM phenol, and 1 mM NF were conducted (Fig. S2B). First, in the dark, phenol adsorption on solid was negligible (0.4%). But the amounts of F⁻ adsorbed on AT on addition of phenol decreased a little (52.8 vs. 49.8 μmol/g). Clearly, phenol

does poorly adsorb onto TiO₂ (3 μmol/g) from an aqueous solution. Second, under UV light, phenol photolysis was absent. Third, under a 420 nm light in presence of TiO₂, phenol also degraded, due to a surface complex of phenol with Ti(IV), absorbing visible light, undergoing the ligand-to-metal charge transfer, and hence initiating phenol oxidation and O₂ reduction on TiO₂ [33]. However, the reaction rate (0.033 h⁻¹), obtained under visible light (1.6 mW/cm²), was one order of magnitude smaller than that (0.53 h⁻¹), measured under UV light (0.88 mW/cm²). Therefore, the observed decrease of phenol concentration with time under UV light is surely due to a reaction initiated by TiO₂ photocatalysis.

The experiment was then conducted with 1 mM NaClO₄, NaNO₃, NaCl, and Na₂SO₄, and the results are shown in Fig. 1B. For phenol oxidation on AT, NaF was largely positive, Na₂SO₄ was slightly positive [27, 28], and other salts had a negligible effect [13]. For phenol oxidation on RT, however, these salts were all negative, which is little known in literature [29, 32]. Under fixed conditions (catalyst loading, light intensity, and others), the rate of organics degradation is first-order in organics, and a larger k_{obs} means a higher concentration of reactive species (RS) produced [34]. Moreover, the reaction rate is proportional to the solid crystallinity and the substrate surface concentration on solid, respectively [35]. The former is due to the increased charge migration onto the surface, while the latter is because the reaction between RS and substrate (O₂, and organics) occurs on the solid surface. In a comparison with RT, AT has a smaller surface area, a higher crystallinity, and a more energetic electron for O₂ reduction, and hence it shows a larger k_{obs} for phenol oxidation. Then in the presence of anions, the increased and decreased k_{obs} correspond to an enhanced and reduced production of RS, respectively. Since phenol

Fig. 1 A Phenol degradation on (a) AT and (b) RT, measured in the absence (open symbols) and presence of 1.0 mM NaF (solid symbols). B Apparent rate constants of phenol degradation (k_{obs}), obtained in presence of different sodium salts (1 mM)

adsorption on TiO_2 is little ($3 \mu\text{mol/g}$), the reduced production of RS is mostly due to the surface anions inhibiting O_2 adsorption and reduction on TiO_2 , as inferred from O_2 reduction on a RT electrode [29]. This is more critical to RT than to AT, as rutile has a more positive conduction band edge potential in aqueous solution, and a smaller adsorption heat toward O_2 in solid–gas phase, as compared to anatase [36, 37]. However, the amount of O_2 adsorbed on solid in solution is not easily determined [38]. This issue of O_2 adsorption will be further discussed below.

In aqueous solution, metal salts influence the particle aggregation of TiO_2 , changing more or less the photocatalytic reaction [39]. Then several experiments with RT in aqueous solution were performed. Within 60 min, the particles settled down, especially in the presence of NaF and Na_2SO_4 (Fig. S2). Then the amounts of F^- , Cl^- , SO_4^{2-} , and NO_3^- adsorbed on RT were measured, which were 153.4, 74.5, 72.7, and $8.1 \mu\text{mol/g}$, respectively. The amount of F^- adsorbed on RT larger than that on AT (153.4 vs. $52.8 \mu\text{mol/g}$) matches the solid surface area (175.5 vs. $73.8 \text{ m}^2/\text{g}$). Moreover, the anion-adsorbed RT samples were dried, and characterized (Fig. S1 and Table S1). All modified samples had similar bandgap energies, but their surface area decreased by a factor of 1.2–1.4, as compared to RT. In the infrared spectra, the vibrations due to ClO_4^- and NO_3^- were observed. Obviously, these anions in an aqueous solution have a different interaction with TiO_2 . An increased size of TiO_2 aggregates and a larger amount of anion adsorption mean a reduced amount of O_2 adsorption, disfavoring the photocatalytic reaction.

Several groups have proposed that Cl^- , SO_4^{2-} , and NO_3^- are oxidized into the anion radicals by the photoholes of P25 or AT [10, 23, 24, 40, 41]. In thermodynamics, these processes are feasible. In aqueous solution at pH 0, the valence band edge potentials for anatase and rutile are 3.08 V vs. NHE [36], more positive than those potentials for the $\text{Cl}^\bullet/\text{Cl}^-$, $\text{SO}_4^{\bullet-}/\text{SO}_4^{2-}$, $\text{NO}_3/\text{NO}_3^-$, and $\text{ClO}_4/\text{ClO}_4^-$ couples (2.43 – 2.75 V vs. NHE) [42]. The anion radicals then oxidize phenol into phenol $^\bullet$ (1.44 V, NHE) [43], together with the anion regeneration. Because anions are adsorbed on TiO_2 more preferentially than phenol, more holes are consumed, and hence more phenol are oxidized. Meanwhile, the counter electrons survive longer, and more O_2 are reduced. As a result, the efficiency of charge separation is improved. The increased oxidation of phenol by SO_4^{2-} has been observed for AT (Fig. 1B), and for P25 [27]. But a negligible effect of Cl^- , NO_3^- , and ClO_4^- to AT were observed here. Probably, other reactions also occur, including Cl^- oxidation to Cl_2 [30], NO_3^- reduction to N_2 [44], and ClO_4^- reduction to Cl^- [45], all of which compete with the anion oxidation. The negative effect of those anions to RT is due to the inhibited adsorption of O_2 , as discussed above. In thermodynamics, the hole oxidation of $\text{OH}^-/\text{H}_2\text{O}$ into $\text{OH}^\bullet$ (2.81 V, NHE)

is also feasible. One of the evidences is a DMPO-OH adduct detected by electron paramagnetic resonance spectroscopy, where DMPO is 5,5-dimethyl-1-pyrroline N-oxide. However, the adduct may result from a hole attack to DMPO, followed by hydrolysis. Based on experimental data, Salvador has pointed out that the photoholes of TiO_2 cannot oxidize the adsorbed $\text{OH}^-/\text{H}_2\text{O}$ into $\text{OH}^\bullet$ on the oxide. Instead, they oxidize bridging $\text{OH}^-/\text{O}^{2-}$ into bridging $\text{OH}^\bullet/\text{O}^\bullet$, followed by water attack to release O_2 [46, 47]. On the other hand, many anions are efficient $\text{OH}^\bullet$ scavengers. In the presence of SO_4^{2-} , CO_3^{2-} , and PO_4^{3-} , however, phenol oxidation on AT is increased, not decreased [27, 29, 48], denying the presence of $\text{OH}^\bullet$ as well. In terms of F^- effect, the hole oxidation of F^- into $\text{F}^\bullet$ (3.6 V, NHE) is unfeasible. Since F^- adsorbs onto TiO_2 via replacement of the linear OH^- groups [49], we have proposed that the adjacent F^- species stabilize the bridging $\text{OH}^\bullet/\text{O}^\bullet$ via a hydrogen bond, inhibiting recombination with electrons, and hence improving the efficiency of charge separation [29]. As a result, phenol oxidation on AT or P25 is greatly increased [25, 27–29, 32]. Phenol oxidation on RT promoted by F^- can be achieved when Ag^+ ions are used to replace O_2 as electron scavengers, or Pt as electron sink and co-catalyst for O_2 reduction [29, 32].

Effect of Cu^{2+} ions In this study, $\text{Cu}(\text{ClO}_4)_2$ was used as a Cu^{2+} source. Figure 2A shows the results of phenol oxidation on AT, RT, and P25. In all cases, the reaction rates obtained in the presence of 0.1 – 5 mM Cu^{2+} were notably larger than those measured in the absence of Cu^{2+} . Meanwhile, Cu^{2+} concentration remained nearly unchanged with time (Fig. 2B). In addition, the amount of Cu^{2+} adsorbed on TiO_2 in the dark was little, while phenol oxidation in a homogenous aqueous solution of Cu^{2+} under UV light was not observed. These observations confirm that Cu^{2+} has a catalytic effect on phenol oxidation over illuminated TiO_2 in the forms of anatase, rutile, and their mixture. In an aqueous solution at pH 0, the conduction band edge potentials for anatase and rutile are -0.12 and 0.10 V vs. NHE, [36] respectively. These potentials are all more negative than that potential for the $\text{Cu}^{2+}/\text{Cu}^+$ or Cu^{2+}/Cu couple (0.15 or 0.34 V, NHE). Therefore, the reduction of Cu^{2+} into Cu^+ and Cu^0 by the photoelectrons of TiO_2 are all feasible. Then Cu^+ or Cu^0 is quickly oxidized by O_2 , so that Cu^{2+} ions remain unchanged.

As $[\text{Cu}^{2+}]$ increased, the reaction rates obtained for RT and P25 increased toward a limit, respectively. This is reasonable, because the number of charge carriers on TiO_2 photogenerated under fixed conditions is limited. In literature, however, a maximum reaction rate was observed for cupric salts at different concentrations [13–19]. Possibly, the counter anions for Cu^{2+} are also involved in TiO_2 photocatalysis. Note that the rate of Cu^{2+} reduction on a TiO_2 film was little influenced by ionic strength (0.1 – 0.5 M) in aqueous solution [21]. Different from RT and P25, AT showed a maximum

Fig. 2 **A** Rate constants (k_{obs}) for phenol oxidation on (a) AT, (b) RT, and (c) P25, measured in the presence of 0–5 mM $\text{Cu}(\text{ClO}_4)_2$. **B** The corresponding change of Cu^{2+} concentration with time (1 mM Cu^{2+})

reaction rate. In this case, the kinetic fitting to phenol degradation was satisfactory only in the early period of time (Fig. S3). Probably, both light illumination and Cu^{2+} influence the de-aggregation of AT particles, so that small particles harvest more photons, with an increased reaction rate.

Co-effect of Cu^{2+} and anions Figure 3A shows the results of phenol oxidation on RT in the presence of 3 mM $\text{Cu}(\text{ClO}_4)_2$, where k_0 and k represent the rate constants of phenol oxidation measured in the absence and presence of sodium salts, respectively. Except NO_3^- , all anions (ClO_4^- , Cl^- , F^- , and SO_4^{2-}) showed a negative effect, the degree of which increased with the anion concentration. At 1 mM,

the anion negative effect was $\text{Cl}^- > \text{F}^- > \text{SO}_4^{2-} > \text{ClO}_4^-$. This trend for the anion negative effect remains nearly unchanged for phenol oxidation on AT (Fig. 3B). Probably, these anions form a complex with Cu^{2+} or Cu^+ , altering the reactivity of either cations or anions.

Interestingly, in presence of 0.25 mM $\text{Cu}(\text{ClO}_4)_2$, the rates of phenol oxidation on AT and RT all increased, on the addition of 1 mM NaF. In both cases, moreover, the reaction rate obtained in presence of Cu^{2+} plus F^- was larger than the rates measured in presence of Cu^{2+} and F^- , respectively (Fig. 4A). This means that at a low concentration, Cu^{2+} has a positive synergism with F^- , further improving the efficiency

Fig. 3 Effect of anions on phenol degradation in presence of 3 mM $\text{Cu}(\text{ClO}_4)_2$, measured **A** for RT on addition of (a) NaClO_4 , (b) NaNO_3 , (c) Na_2SO_4 , (d) NaCl , and (e) NaF , and **B** for RT and AT on

addition of 1 mM anions. The symbols k_0 and k are the apparent rate constants obtained without and with anion addition, respectively

Fig. 4 **A** Rate constants (k_{obs}) for phenol oxidation on AT and RT, measured in the absence and presence of 0.25 mM $\text{Cu}(\text{ClO}_4)_2$ or 1.0 mM NaF. **B** Rate of H_2 production on AT and RT in a

N_2 -presaturated solution containing 10% methanol and 1 mM $\text{Cu}(\text{ClO}_4)_2$, measured before and after addition of 1 mM sodium salts

of charge separation, as compared to individual ions. Such the observation was early reported by Tang and co-workers, for phenol oxidation on P25 in presence of 0.4 mM CuCl_2 and 1–9 mM NaF [17]. In principle, the Cu^{2+} -mediated electron transfer and the F^- -mediated hole transfer promote each other, greatly increasing reaction rates. In all cases, however, the reaction rate, obtained in presence of Cu^{2+} plus F^- , was not larger, or only slightly larger than the sum of the rates measured in presence of individual Cu^{2+} and F^- . The discrepancy is indicative of other factors also influencing the performance of Cu^{2+} and F^- .

Then the production of H_2 on AT and RT in the presence of 1 mM $\text{Cu}(\text{ClO}_4)_2$ and different sodium salts was conducted, and the results are shown in Fig. 4B. In this case, methanol was used as a hole scavenger and it was oxidized into CO_2 and HCHO [16], while Cu^{2+} was reduced to metallic Cu, followed by proton reduction [22]. Under UV light, the amount of H_2 evolved in the gas phase linearly increased with time (Fig. S4). On addition of 1 mM anions, the rate of H_2 production increased by NaNO_3 , decreased by NaF and Na_2SO_4 , but little changed by NaClO_4 and NaCl, respectively. This trend for the anion effect, obtained for proton reduction under N_2 in presence of 1 mM Cu^{2+} , is not entirely the same as that measured for phenol oxidation under air in presence of 3 mM Cu^{2+} (Fig. 3B). This is due to different Cu species involved in two different reactions.

Then the question becomes how to understand the positive and negative effect of 1 mM NaF on phenol oxidation in presence of 0.25 and 3 mM $\text{Cu}(\text{ClO}_4)_2$, respectively. In an aqueous solution, there is a reaction ($\text{Cu}^{2+} + 4\text{F}^- = \text{CuF}_4^{2-}$), whose equilibrium shifts toward CuF_4^{2-} , as Cu^{2+} concentration is increased. In the case of H_2 production, the reduction of Cu^{2+} to Cu^0 by the electrons of TiO_2 is inhibited, slowing

down H_2 production on Cu^0 . Since F^- is much more active for the hole transfer (Fig. 1B), its concentration decreases due to CuF_4^{2-} formation has a profound influence on methanol oxidation and hence on H_2 production (Fig. 4B), as compared to other anions. In the case of phenol oxidation, Cu^{2+} is reduced to Cu^+ , followed by O_2 reduction [12, 13]. Since CuF_2^- is more stable than CuF_4^{2-} , the oxidation of Cu^+ to Cu^{2+} by O_2 is inhibited, and the concentration of free F^- is decreased, consequently slowing down phenol oxidation. At a low concentration, CuF_4^{2-} and CuF_2^- are not formed in a dominant portion. As a result, the synergism between Cu^{2+} and F^- further increasing phenol oxidation was observed, even though the increased reaction rate is not as much as that expected.

To confirm the complex formation, the electrochemical reduction of Cu^{2+} on a TiO_2 film electrode was conducted. The experiment was carried out under air in a 0.5 M NaClO_4 solution containing 1 mM $\text{Cu}(\text{ClO}_4)_2$, and the results are shown in Fig. 5. As the potential was linearly swept from 0.5 V to -0.5 V vs. Ag/AgCl, a reduction peak at -4 mV was observed. On the addition of 1 mM NaF, NaCl, Na_2SO_4 , the peaks shifted to -20 , -20 , and -34 mV, respectively, while the corresponding currents decreased from $138 \mu\text{A}/\text{cm}^2$ to 135, 104, and $101 \mu\text{A}/\text{cm}^2$, respectively. Meanwhile, there appeared a shoulder peak around -390 mV for NaF, and a sharp peak at -340 mV for NaCl and Na_2SO_4 , respectively. The second peak is due to Cu^+ reduction to metallic Cu [50]. These observations confirm that Cu^+ species are stabilized by SO_4^{2-} , Cl^- , and F^- , respectively. As a result, the re-oxidation of Cu^+ to Cu^{2+} by O_2 is inhibited by those anions.

On addition of NO_3^- , however, only one peak at -34 mV with a reduced current was observed. This is indicative of

Fig. 5 Dark current–voltages curves for an AT film electrode in 0.5 M NaClO₄ (pH 4), measured under air in presence of 1 mM Cu(ClO₄)₂, and 1 mM different sodium salts. The dotted line represents O₂ reduction without the addition of Cu²⁺ and anions

NO₃[−] not easily forming a complex with Cu⁺. As a result, the re-oxidation of Cu⁺ by O₂ is little influenced, and the rate of phenol oxidation was not decreased (Fig. 3B). Then the increased rate of phenol oxidation by NO₃[−] in presence of 3 mM Cu²⁺ is attributed to NO₃ radicals. Similarly, the increased rate of H₂ production by NO₃[−] in presence of 1 mM Cu²⁺ is also due to the prior hole oxidation of NO₃[−] into NO₃ radicals, which then oxidizes methanol, and speeds up Cu²⁺ reduction to Cu for proton reduction into H₂. Such a positive contribution from NO₃ radicals to the photocatalytic reactions has been observed for AT and RT, respectively.

4 Conclusion

We have shown that F[−], Cl[−], ClO₄[−], NO₃[−], and SO₄^{2−} in aqueous solution have more or less influences on the performance of Cu²⁺ in TiO₂ photocatalysis. On one hand, these anions have different adsorption on TiO₂, inhibiting O₂ adsorption and reduction, and hence slowing down phenol oxidation. This is inferred from phenol oxidation on rutile, the rate of which decreases by all anions, but increases on the addition of F[−] when the slow reduction of O₂ is overcome by using Pt as co-catalyst. On the other hand, these anions except F[−] are oxidized by the photoholes of either anatase or rutile. The resulting anion radicals then oxidize organics (phenol and methanol), with the regeneration of the corresponding anions. This is inferred from the combined analysis of experimental and thermodynamic data. The positive effect of F[−] is due to the stabilized bridging ‘OH/O[−]’ radicals, improving the efficiency of charge separation for phenol oxidation. Since the electrons and holes of TiO₂

are generated and consumed in pairs, the Cu²⁺-mediated electron transfer to O₂ promotes the anion-mediated hole transfer to phenol, and vice versa. As a result, the mixed solution of 1 mM F[−] and 0.25 mM Cu²⁺ is more efficient than individual solutions in speeding up phenol oxidation either on anatase or on rutile. At a high Cu²⁺ concentration, however, the mixed solution of 1 mM F[−] and 3 mM Cu²⁺ is less efficient than 3 mM Cu²⁺ solution. With the aid of electrochemistry, the reduced activity of Cu²⁺ by F[−] is due to the formation of a Cu⁺ complex, which poorly reacts with O₂ to regenerate Cu²⁺, decreases the concentration of free F[−], and hence slows down the hole oxidation of phenol. Such a negative Cu⁺ complex is also formed with Cl[−] and SO₄^{2−}, respectively. In fact, a Cl[−] and SO₄^{2−} induced delay of Cu²⁺ reduction to Cu⁰ on P25 TiO₂ has been reported [21]. Interestingly, the mixed solution of 1 mM NO₃[−] and 3 mM Cu²⁺ is more efficient than 3 mM Cu²⁺ solution, because NO₃[−] hardly forms a complex with Cu⁺. Among several cupric salts, however, Cu(ClO₄)₂ is the most efficient, as observed for phenol oxidation on anatase (Fig. S5). This work shows that the formation of a copper complex with anions weakens the positive effect of copper ions on organic oxidation in TiO₂ photocatalysis. On the other hand, we must point out that inorganic ions are efficient and low-cost co-catalysts for organic oxidation in TiO₂ photocatalysis, but they cause an obviously secondary pollution for wastewater treatment.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s43630-021-00083-1>.

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Declarations

Conflict of interest There are no conflicts to declare.

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