

Role of Cr(III) deposition during the photocatalytic transformation of hexavalent chromium and citric acid over P25 and UV100

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Cr(VI) and Cit adsorption on P25 and UV100

Adsorbed Cr(VI) and Cit concentrations in Fig. S1 were calculated by subtracting from $[\text{Cr(VI)}]_0$ and $[\text{Cit}]_0$ the concentration of each compound measured after stirring the TiO_2 suspension for 30 min in the dark. The difference between $[\text{Cr(VI)}]_0$ and $[\text{Cit}]_0$ and those measured after equilibration are ascribed to dark adsorption onto the TiO_2

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surface. In all cases the adsorption was never higher than 20% for Cr(VI) and Cit over both photocatalysts, with the only exception of $[\text{Cr(VI)}]_0 = 0.2 \text{ mM}$ with UV100, whose higher extent is due to the higher SSA and high $[\text{TiO}_2]/[\text{Cr(VI)}]_0$ and $[\text{TiO}_2]/[\text{Cit}]_0$ ratios.

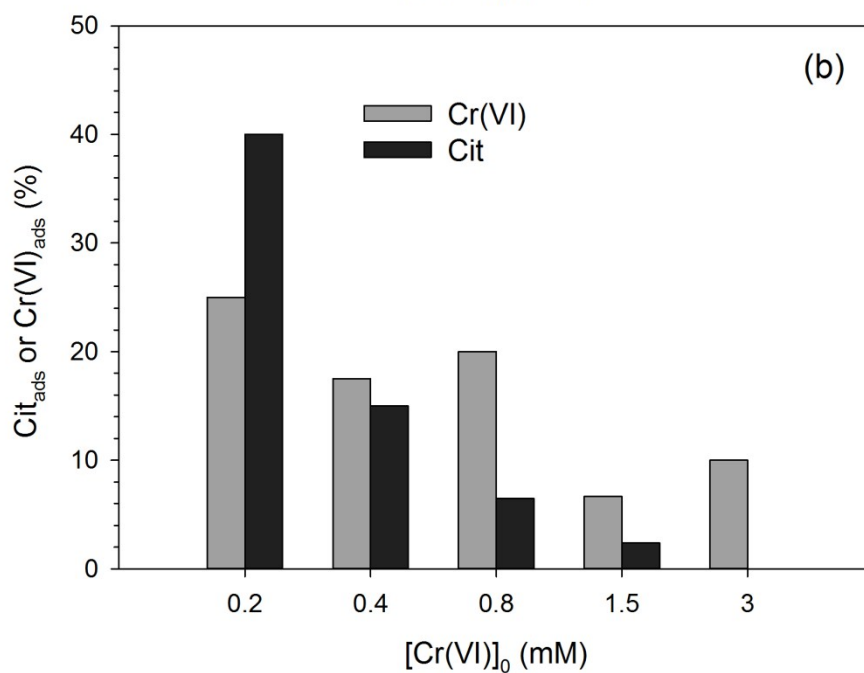
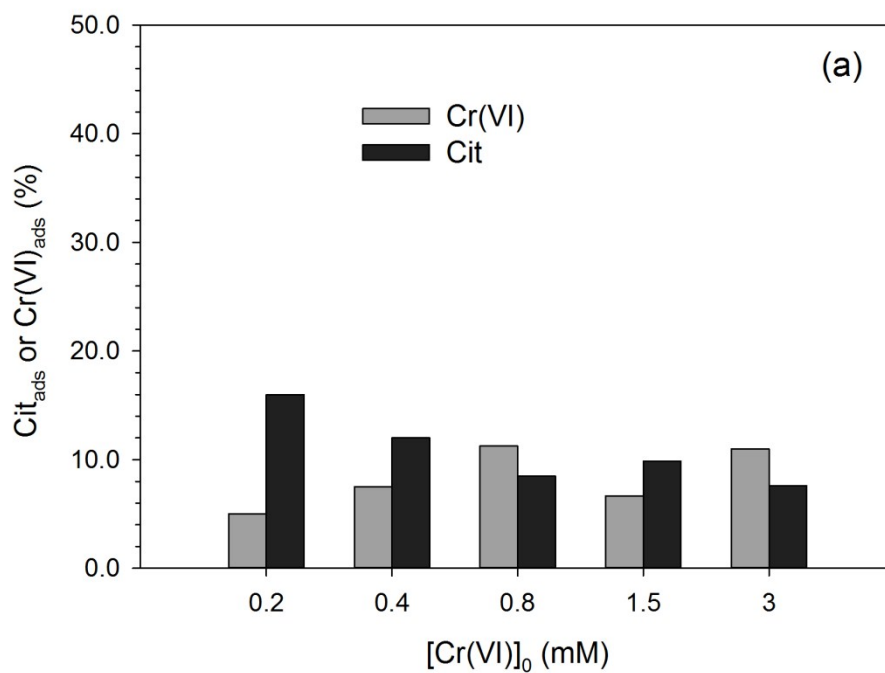


Fig. S1. Cr(VI) and Cit removed (MR = 2.5) after 30 min of stabilization in the dark in a TiO₂ suspension (1 g L⁻¹) at pH 2 and under air bubbling. (a) P25; (b) UV100.

Impact of the homogeneous photochemical removal of Cr(VI) in the presence of Cit

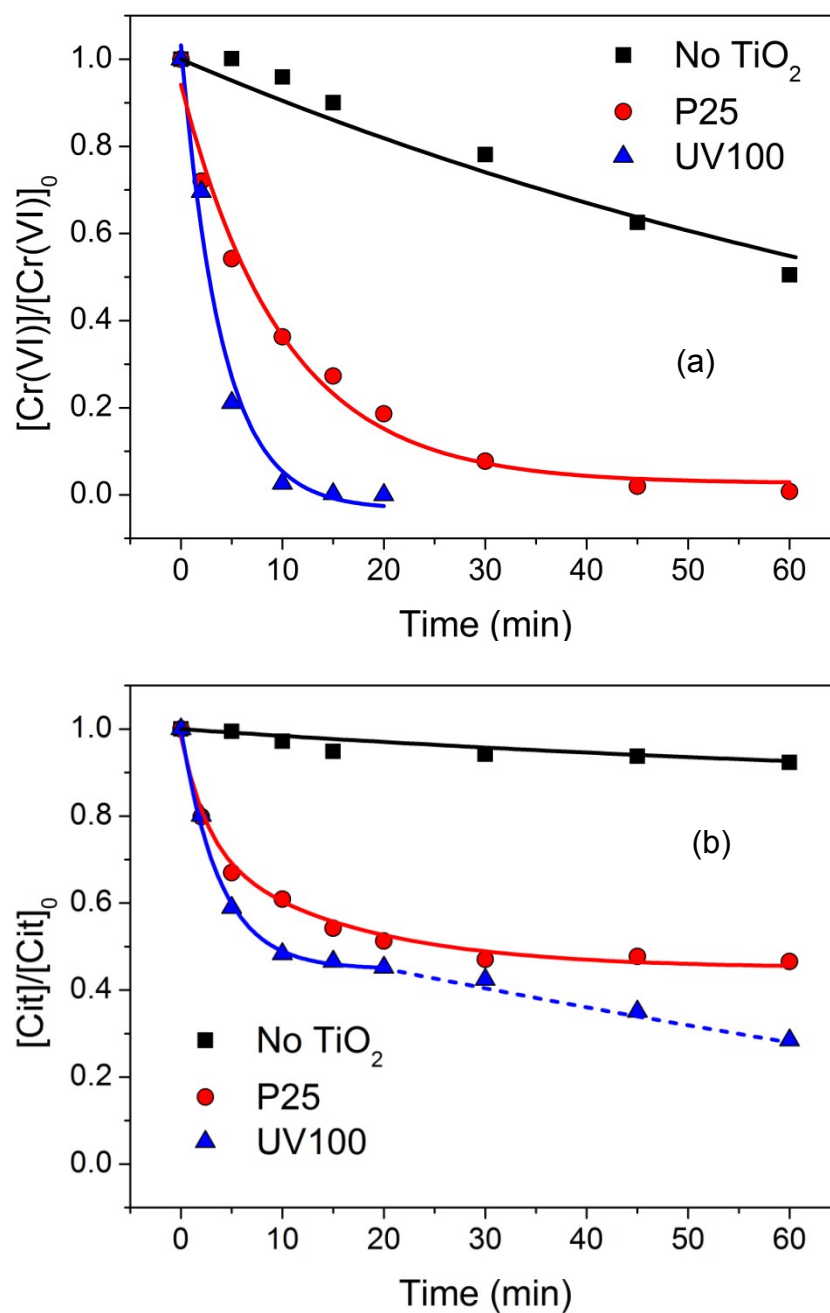


Fig. S2. Temporal profiles of (a) $[\text{Cr(VI)}]/[\text{Cr(VI)}]_0$ and (b) $[\text{Cit}]/[\text{Cit}]_0$ under UV irradiation in the absence and in the presence of P25 and UV100. Conditions: $[\text{Cr(VI)}]_0 = 0.8 \text{ mM}$, $[\text{Cit}]_0 = 2.5 \text{ mM}$, $[\text{TiO}_2] = 0 \text{ or } 1 \text{ g L}^{-1}$, UV irradiation ($310 < \lambda/\text{nm} < 410$, $\lambda_{\text{max}} = 351 \text{ nm}$; $q_{n,p}^0/V = 15.2 \text{ } \mu\text{einstein s}^{-1} \text{ L}^{-1}$). The solid lines are the fitting of the experimental points to a pseudo-first order rate law. The dashed lines represent Cit degradation after Cr(VI) total removal fitted to a LH rate law.

Photocatalytic reactions over P25 and UV100

The experimental points of $[\text{Cr(VI)}]$ and $[\text{Cit}]$ evolution up to total removal of Cr(VI) by HP over P25 and UV 100 (solid lines in Fig. 1) were fitted using a pseudo-first order rate. The values of the kinetic parameters can be seen in Tables S1 and S2 ($R^2 \geq 0.94$).

Table S1. Kinetic parameters extracted from the HP experiments with P25 up to complete Cr(VI) removal using a pseudo-first order rate. Conditions of Fig. 1(a).

$[\text{Cr(VI)}]_0$ (mM)	k_1 (min^{-1})	R^2	
		Cr(VI)	Cit
0.2	0.61	1.00	0.99
0.4	0.35	0.99	0.99
0.8	0.10	0.99	0.94

1.5	0.05	0.99	0.99
3	0.03	0.99	0.99
0.8, no TiO ₂	0.01	0.98	0.93

Table S2. Kinetic parameters extracted from the experiments with UV100 up to complete Cr(VI) removal using a pseudo-first order rate. Conditions of Fig. 1(b).

[Cr(VI)] ₀ (mM)	k ₁ (min ⁻¹)	R ²	
		Cr(VI)	Cit
0.2	1.39	1	0.999
0.4	0.63	0.999	0.981
0.8	0.26	0.979	0.995
1.5	0.11	0.981	0.992
3	0.04	0.990	0.973
0.8, no TiO ₂	0.01	0.977	0.934

The experimental points of Cit consumption after total removal of Cr(VI) (dashed lines in Fig. 1) were fitted with eq. (S1)). The values of the kinetic parameters can be seen in Tables S3 and S4 ($R^2 \geq 0.98$).

$$t = \frac{([Cit]_0' - [Cit])}{k_{phot}^{Cit}} + \frac{\ln([Cit]_0'/[Cit])}{k_{phot}^{Cit} K^{Cit}} \quad (S1)$$

where $k_{\text{phot}}^{\text{Cit}}$ is the photocatalytic rate constant for Cit degradation, K^{Cit} is the “Langmuir” constant and $[\text{Cit}]_0'$ is the Cit concentration after complete Cr(VI) removal.

Table S3. Kinetic parameters extracted from the experiments with P25 after complete Cr(VI) removal using eq. (S1)). Conditions of Fig. 1(a).

[Cr(VI)] ₀ (mM)	Cit			<i>R</i> ²
	[Cit] ₀ ' (mM)	$k_{\text{phot}}^{\text{Cit}}$ (mM min ⁻¹)	K^{Cit} (mM ⁻¹)	
0	2.00	0.033	11	0.991
0.2	0.19	0.005	>100	0.998
0.4	0.43	0.002	>100	0.989

$k_{\text{phot}}^{\text{Cit}}$ was not calculated for $[\text{Cr(VI)}]_0 \geq 0.8$ mM because there was still a measurable amount of Cr(VI) remaining after 90 min of irradiation.

Table S4. Kinetic parameters extracted from the experiments with UV100 after complete Cr(VI) removal using eq. (S1)). Conditions of Fig. 1(b).

[Cr(VI)] ₀	Cit
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(mM)	[Cit] ₀ ' (mM)	k _{phot} ^{Cit} (mM min ⁻¹)	K ^{Cit} (mM ⁻¹)	R ²
0	1.98	0.069	2.5	0.992
0.2	0.16	0.051	2.5	0.999
0.4	0.37	0.011	10.0	0.976
0.8	0.84	0.009	10.0	0.991
1.5	1.60	0.006	10.0	0.828

k_{phot}^{Cit} was not calculated for [Cr(VI)]₀ = 3 mM because there was still a measurable amount of Cr(VI) remaining after 90 min of irradiation.

OGA selectivity

OGA selectivity was calculated as follows:

$$\frac{([Cit]_0 - [Cit]_f - [OGA]_f) * 100}{[Cit]_0 - [Cit]_f} \quad (1)$$

where [Cit]₀ is the concentration of Cit at time "0", [Cit]_f is the concentration of Cit at the end of the experiment and [OGA]_f is the concentration of OGA at the end of the experiment.

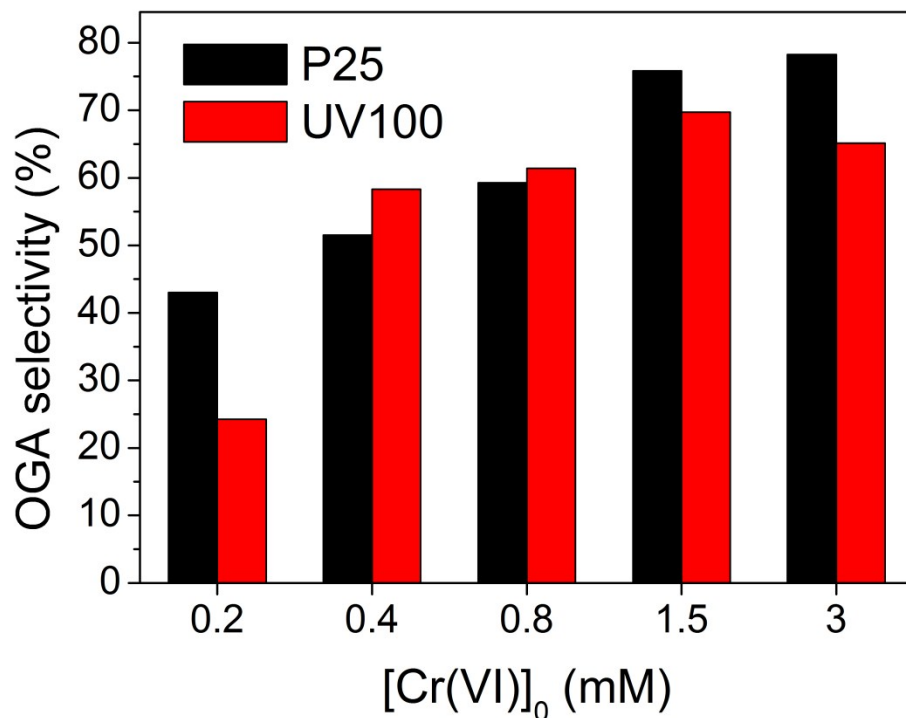


Fig. S3. Selectivity towards OGA formation by Cit degradation during the photocatalytic removal of Cr(VI) in the presence of Cit with P25 and UV100. Conditions of Fig. 1.

Time Resolved Microwave Conductivity

Time Resolved Microwave Conductivity (TRMC) is based on the measurement of the change of the microwave power reflected by a solid sample, $\Delta P(t)$, induced by its laser-pulsed illumination. The relative difference $\Delta P(t)/P$ can be correlated to the difference of conductivity $\Delta\sigma(t)$, according to:¹

$$\frac{\Delta P(t)}{P} = A\Delta\sigma(t) = Ae \sum_i \Delta n_i(t) \mu_i \quad (2)$$

where A is a sensitivity factor, e is the electron charge, $\Delta n_i(t)$ is the number of excess charge carriers i at time t , and μ_i is their mobility. In the specific case of TiO_2 , Δn_i is reduced to electrons in the conduction band because their mobility is much larger than that of holes.¹

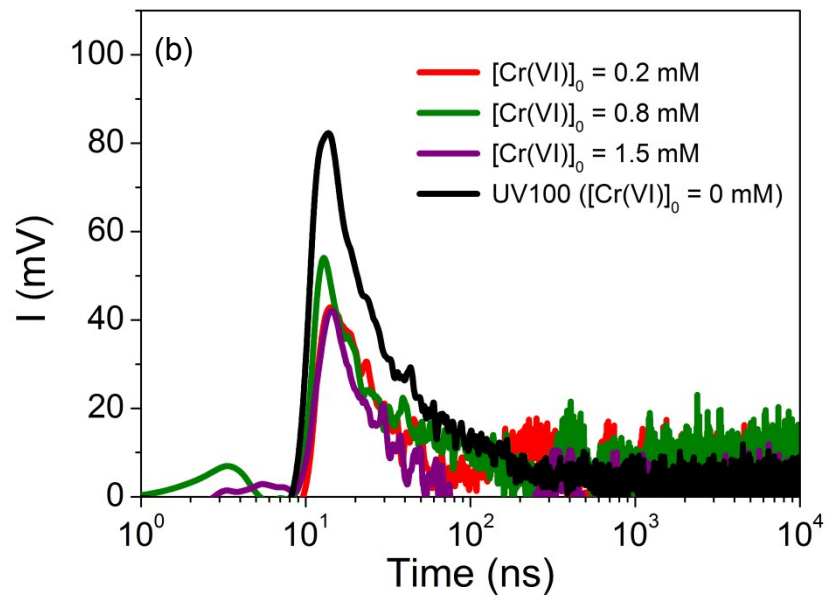
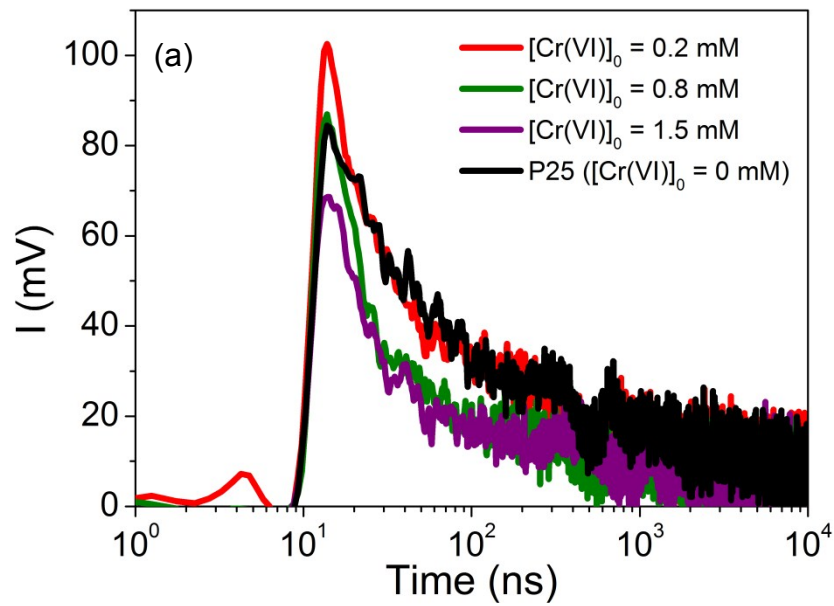


Fig. S4. TRMC temporal profiles for the solids obtained after Cr(VI) complete removal in HP runs with $[\text{Cr(VI)}]_0 = 0.2, 0.8$ and 1.5 mM and Cit (MR = 2.5) at pH 2 over (a) P25 and (b) UV100.

References

1 M. Kunst, F. Goubard, C. Colbeau-Justin, F. Wünsch, *Mater. Sci. Eng. C*, 2007, **27**, 19.