Supporting Information

Citrates/F- assisted phase control synthesis of TiO2 nanostructures and their photocatalytic properties

Zhiqiang Guo, Chao Li, Shuanglong Lu, Yue Pan*, Hongwei Gu*

5 Experimental Section

TEM of TiO\textsubscript{2} at different temperature

Figure S1A, S1B and S1C are corresponding to the temperature is 160 °C, 180 °C and 200 °C respectively. When the temperature is relatively low, crystalinity is not very good and it took more time to make the reaction proceed completely. When the temperature is high, the as-synthesized materials tend to aggregate together as shown in Figure S1C. So we choose 180 °C as the best temperature. As for the reaction time, if we quitted the reaction at an earlier stage, the precursor was not consumed thoroughly and if we quitted later, the material we obtained did not have notable changes. Therefore, we choose 18 h as the best reaction time.

20 UV-vis diffuse reflectance spectra of the as-synthesized TiO\textsubscript{2}

Figure S2. UV-vis diffuse reflectance spectra of the TiO\textsubscript{2} we synthesized. Reaction condition: \( r_c = 1:0.0125 \), 180 °C for 18 h.
The influence of pH value on the reaction process

We added possible species of titanium citrate anions and their transformations in the Ti citrate system under the influence of pH according to published papers.

\[
\begin{align*}
[Ti(H_2cit)_3]^{5-} + H^+ & \rightarrow [Ti(H_2cit)Hcit]^{4-} \\
[Ti(H_2cit)Hcit]^{4-} + H^+ & \rightarrow [Ti(H_2cit)Hcit]^{3-} \\
[Ti(H_2cit)Hcit]^{3-} + H^+ & \rightarrow [Ti(H_2cit)Hcit]^{2-} \\
[Ti(H_2cit)Hcit]^{2-} + H^+ & \rightarrow [Ti(H_2cit)Hcit]^{1-} \\
[Ti(H_2cit)Hcit]^{1-} + H^+ & \rightarrow [Ti(H_2cit)Hcit]^{0} \\
[Ti(H_2cit)Hcit]^{0} + H^+ & \rightarrow [Ti(H_2cit)Hcit]^2
\end{align*}
\]

Scheme S1. Possible Species of Titanium Citrate Anions ([Ti(cit)_3]^{5-}) and Their Transformations in the Ti Citrate System.

10 TEM of TiO₂ when more SC was added

If more SC was added into the solution, the fresh SC reacted with precipitates again and constructed a more stable sol.

15 Figure S2 TEM image of the TiO₂: the left one r_c=100:0, the right one r_c=100:15 (the reaction time and condition were 180°C and 18h).

The TEM image of TiO₂ (4 mmol NaCl was added)

20 We added the situation where 4 mmol NaCl worked as the regulating reagent. The TEM image is shown in Figure S3 and we can find the particle size and shape did not changed.
Figure S3. TEM image of the TiO$_2$ when 4 mmol of NaCl was added ($r_c=1:0.025$) and the reaction time and condition were 180 °C and 18h.