

Supporting Information

Energy Efficient Photodegradation of Azo Dyes with TiO₂ Nanoparticles Based on Photoisomerization and Alternate UV-visible Light

Hao Zhang, Da Chen, Xiaojun Lv, Ying Wang, Haixin Chang and Jinghong Li*

Department of Chemistry, Key Laboratory of Bioorganic Phosphorus Chemistry &

Chemical Biology, Tsinghua University, Beijing 100084, China;

Email: jhli@mail.tsinghua.edu.cn

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* Corresponding Author. Email: jhli@mail.tsinghua.edu.cn; Tel & Fax: +86-10-62795290.

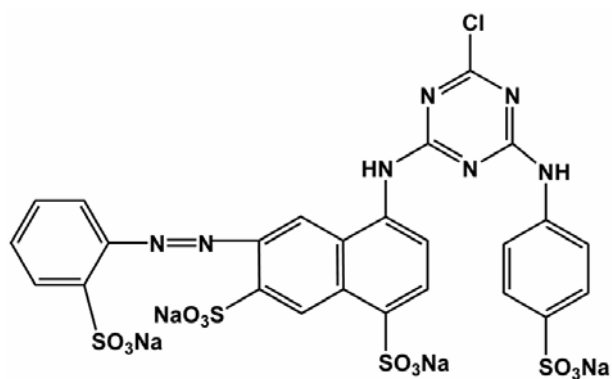


Figure S1 Molecular structure of Brilliant Reactive Red K-2G.

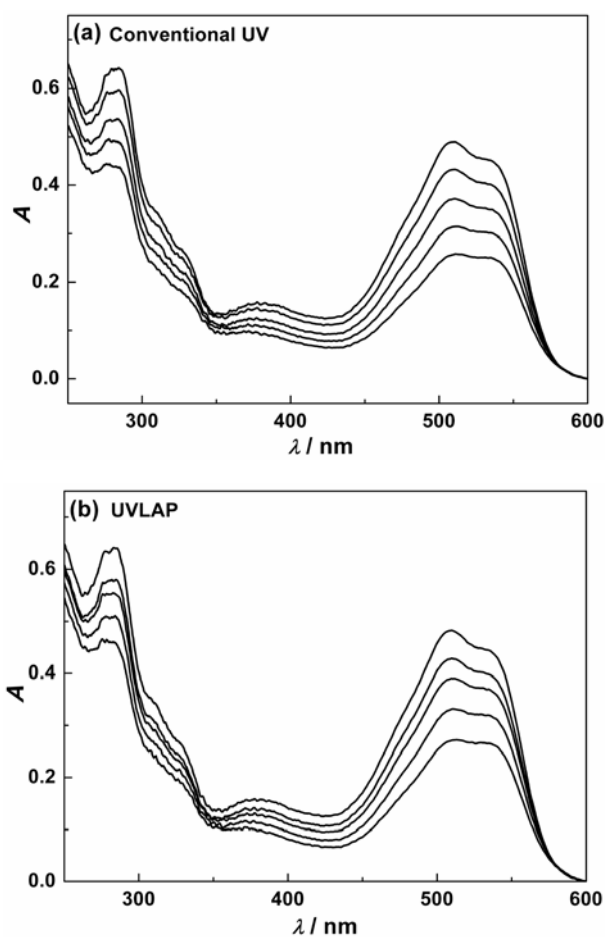


Figure S2 UV-visible absorption spectra changes of K-2G under (a) UV conventional and (b) UVLAP photocatalysis. In both modes, the changes were recorded at given time interval (1 h). Both in (a) and (b), the absorbance decreased with the extension of the time of photocatalysis.

Discussion about the role of visible light irradiation and the natural of UVLAP

It is noteworthy that the UVLAP process cannot be considered as a simple combination of the conventional UV photocatalysis based on the direct TiO₂ band-gap photoexcitation during the UV irradiation period and the dye-sensitized photocatalysis, triggered by electron transfer from the visible-light-excited dye molecules to the TiO₂ conduction band during the visible light irradiation period. Otherwise, the photodegradation rate constant k_{UVLAP} should be equal or approximate to the value of $(2/3 k_{\text{conventional}} + 1/3 k_{\text{visible light}})$, *i.e.*, 11.9% h⁻¹, where $k_{\text{visible light}}$ was the rate constant of photocatalysis with indoor natural light as the only light source, since the photodegradation reactions followed the first order kinetics and the time for UV irradiation was twice of that for visible light irradiation during the UVLAP. Actually, the k_{UVLAP} was significantly larger, and thereby the role of visible light irradiation in the UVLAP process was much more than a simple light source for dye-sensitized photocatalysis and the improvement in the energy efficiency should be attributed to other factors. In addition, the results of the control experiments of UV-Dark Alternate Photocatalysis (UDAP) and UV-and-visible Light Photocatalysis (UVLP) also verified the suggestion. (See Figure S3 and Table S1)

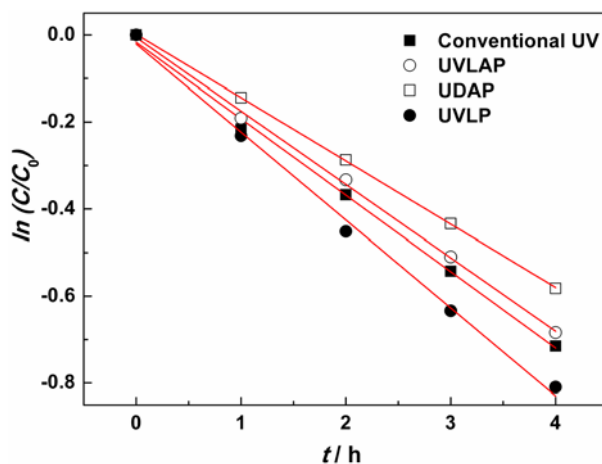


Figure S3 Absorption changes ($\lambda = 510$ nm) plots for the photocatalytic degradation of K-2G over TiO_2 films *via* different photocatalytic modes: conventional (■), UVLAP (○), UV-Dark Alternate Photocatalysis (UDAP) (□) and UV-and-visible Light Photocatalysis (UVLP) (●).

Table S1 Photodegradation rate constants k in the photodegradation of K-2G *via* different photocatalytical modes.

Photoreaction rate Constants k	vs. Time (% h^{-1})	$k/k_{\text{conventional}}$
$k_{\text{conventional}}$	17.6	100%
k_{UVLAP}	16.9	96.0%
k_{UDAP}	14.5	82.3%
k_{UVLP}	20.2	114.7%

To investigate the role of visible light irradiation in UVLAP and prove that azo dyes in the *trans* state was easier to be photodecomposed than the *cis* state, another

two kinds of photocatalytic modes were adopted and their photocatalytic rate constants were shown in **Figure S3** and **Table S1**. The first one was UV-Dark Alternate Photocatalysis (UDAP). In this strategy, the quartz vessel with K-2G dyes solution and TiO₂ film photocatalyst was placed in dark after the UV irradiation period. In detail, in each hour of photocatalysis, the alternation between UV light and dark condition followed the process (15 min UV - 10 min dark - 15 min UV - 10 min dark - 10 min UV). Similar to the UVLAP mode, in the UDAP strategy, K-2G dyes were photodegraded during UV light irradiation period with simultaneous transition from *trans* to *cis* state, and the backward reverse occurred under dark condition, since the *trans* state was more thermodynamically stable. As listed in Table S1, the photoreaction rate constant ($k_{UDAP}=14.5\% \text{ h}^{-1}$) was obviously higher than the 2/3 of the rate in conventional UV photocatalysis ($2/3 k_{conventional}=11.7\% \text{ h}^{-1}$). This enhancement should be ascribed to the higher degradation rate of dyes in *trans* state than in the *cis* one. In addition, UDAP showed lower rate than UVLAP, which may be due to the incomplete transition from *cis* to *trans* state under dark condition.

In another strategy (UVLP), both UV-and-visible Light were simultaneously used to conduct the photodegradation of K-2G over TiO₂, in other words, the quartz vessel containing K-2G solution and TiO₂ film was exposed to ambient indoor natural light during the UV light irradiation. Significant enhancement in the rate was observed in the UVLP compared to UV conventional photocatalysis with the same irradiation time. This improvement could not be simply attributed to the dye-sensitized photocatalysis under visible light, whose rate was almost negligible, as listed in Table 1. Moreover,

since the *trans* state was more thermodynamically stable than *cis* state, in the UVLP mode, a large amount of the dyes stayed in the *trans* state as a result of visible light irradiation and thereby a faster degradation was achieved in UVLP compared with conventional UV photocatalysis.

Overall, the results of the two strategies mentioned above supported the suggestion that the photocatalytic process of UVLAP should not be considered as simple combination of conventional UV photocatalysis and the dye-sensitized photocatalysis under visible light. Furthermore, the results also verified the crucial role of visible light irradiation and the isomerization of K-2G in its photodegradation.