Electronic Supplementary Information

Aquatic plant inspired hierarchical artificial leaves for highly efficient photocatalysis

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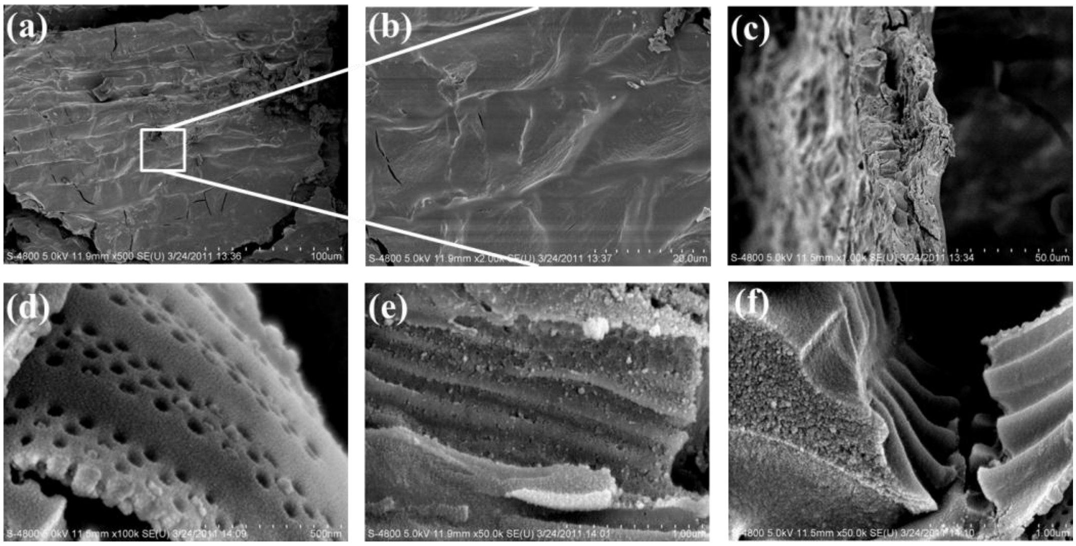

Fig. S1. SEM images of TiO_2 replicas (Ti-r*V*), showing the hierarchical structures can be perfectly inherited from the delicate structure of leaves.

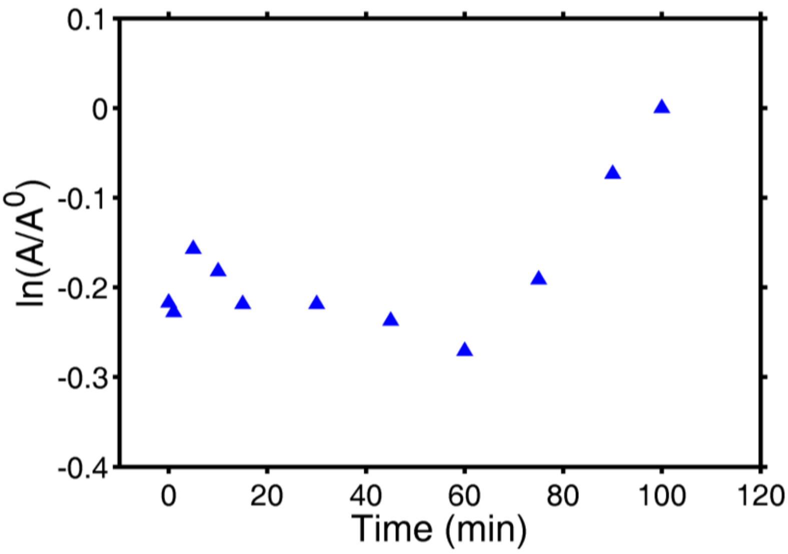

Fig. S2. Reaction kinetics of Methylene blue (MB) photodegraded by Ti-rV under irradiation of solar simulator equipped with 420 nm cut off filters.

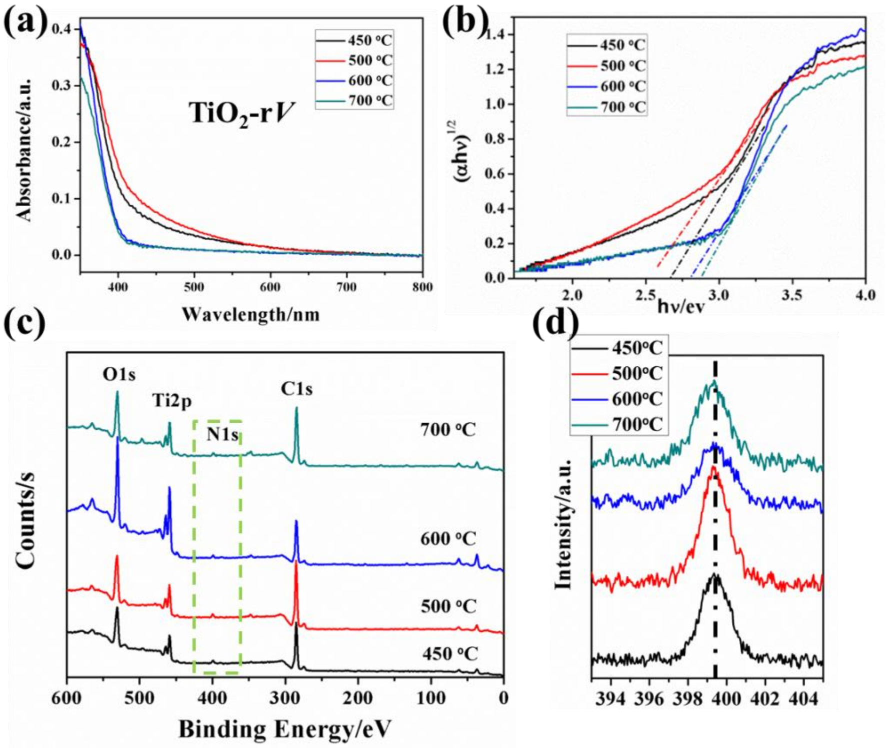

Fig. S3. (a) The diffuse reflectance spectroscopy of Ti-rV under different calcination conditions. (b) The corresponding Tauc-plot derived from the DRS data, indicating the estimated bandgap of the obtained TiO_2. (c) XPS spectrum of Ti-rV under different calcination conditions and (d) the corresponding N1s binding energy spectrum.

We expect the elements (N, C and S) in the leaves can be effectively incorporated into TiO_2 and alter the absorbance onset of pristine TiO_2 into visible light region. The diffuse reflectance absorbance spectra of the Ti-r*V* replicas under four different calcination conditions were measured to verify the above speculation, as illustrated in Fig. S3. Interestingly, the absorbance onsets of the replica under calcination temperature of 450 °C and 500 °C were even red-shifted to 650 nm. However, the replica under calcination temperature of 600 and 700 °C were only red-shifted to 435 nm. We further calculate the corresponding bandgap from the Tauc plot using the data derived from the diffuse reflectance absorbance spectra according to the equation below:

$$(\alpha h\nu)^n \propto h\nu - E_g \tag{1}$$

However, the visible light absorbance doesn’t necessarily contribute to the visible-light photocatalytic activity. As previously analyzed by Asahi, the effective substitutional doping form for the incorporated Nitrogen element is a prerequisite for realizing the visible light photocatalysis. In order to analyze the component in the TiO_2 replica, XPS (Fig. S3 c and d) was employed to characterize the samples under four above mentioned calcination conditions. From Figure S3c, it can be concluded that the biogenic self-doping has indeed incorporated N elements into the TiO_2 replica. But, combining with the N1s binding energy spectrum (as illustrated in Fig. S3d), we can know that the N element in the TiO_2 takes the interstitial doping form with the binding energy of 399.4 eV, which cannot contribute to visible light activity.[1] Some previous researches referred that the biogenic template can lead to the concurrent effective doping for visible light photocatalysis. But our results don't support this conclusion. We think that the different aquatic plant kinds and even treatment procedures and calcination conditions lead to the difference in visible light photocatalytic activity for Ti-Si and TiO_2.

Table S1. Parameters derived from N_2 adsorption-desorption isotherm and its photocatalytic performance

Sample	**$S_{BET}{}^{a}$/ (m^2/g)**	**V^{b}/ (cm^3/g)**	**$D_{BJH}{}^{c}$/ (nm)**	**Crystal size/ (nm)**	**Rate constants/ (min^{-1})**
Ti-Si-r*V*-650	167.1	0.227	4.9	9.1	0.2622
Ti-r*V*-600	59.7	0.084	5.8	9.9	0.0745
nc-TiO2	58.5	0.132	6.4	15.1	0.0133

[a] BET surface area calculated from the linear part of the BET plot (P/P0=0.1-0.2). [b] Total pore volume, taken from the volume of N_2 adsorbed at (P/P0=0.977). [c] Average pore diameter, estimated using the adsorption branch of the isotherm and the Barrett-Joyner-Halenda (BJH) formula.

Reference

1. J. B. Varley, A. Janotti and C. G. Van de Walle, *Adv.Mater.*, 2011, **23**, 2343-2347.