

Supporting Information

Efficiency enhancement via tailoring energy level alignment induced by vanadium ion doping in organic/inorganic hybrid solar cells

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Note 1. CV characteristics

The CV characteristics of the bare TiO₂ and V-doped TiO₂ films are shown in Figure S1. One couple of peaks for oxidation and reduction potentials appear in the CV characteristics curves for the valence band (VB) edge and the conduction band (CB) edge, respectively. The CB and VB can be calculated using the formula: CB (or VB) (eV) = -4.8 - (E - E_{1/2}) (eV), where E is a peak point of the redox potential,¹ E_{1/2} is the formal potential of F₂/F_c⁺ system of 0.09 V (E_{1/2} = 0.09 V) against Ag/Ag⁺ system.² Both oxidation and reduction waves are well displayed in the CV curves, implying that these semiconductor crystals have the capability to transport both electrons and holes. The electrochemical parameters of the bare and V-doped TiO₂ nanocrystalline thin film electrodes are summarized in Table S1. The results show that the energy gap of acceptor is affected little by vanadium doping, whereas the position of the CB and VB of the acceptor have changed largely. After vanadium doping, a notable reduction of the energy offset between the CB of TiO₂ and the lowest unoccupied molecular orbit (LUMO) energy level of the donor P3HT, *i.e.*, the CB-LUMO

offset, is obtained. That is, the narrow-down from 1.33 to 1.02 eV.

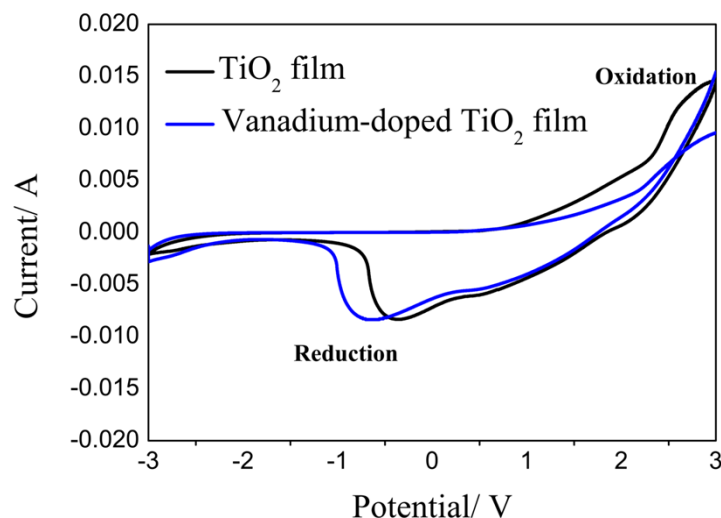


Figure S1. The CV behaviors of bare TiO₂ and V-doped TiO₂ electrodes in acetonitrile containing 0.1M TBAPF₆ at a sweep rate of 50 mV·s⁻¹.

Table S1. Electrochemical characteristics of the bare TiO₂ and V-doped TiO₂ at 5wt%

Electrodes	E _{peak} ^{red} (V)/CB(eV)	E _{peak} ^{ox} (V)/VB(eV)	E _g (eV)
TiO ₂	-0.38/-4.33	2.65/-7.36	3.03
V-doped TiO ₂	-0.69/-4.02	2.36/-7.07	3.05

Note 2 Mott-Schottky plots, UV-vis and Open circuit voltage

The origin of efficiency enhancement is closely related to the energy level alignment of TiO₂ induced by the incorporation of vanadium ions. In other words, the energy offset between conduction band (CB) of acceptor TiO₂ and lowest unoccupied molecular orbit (LUMO) of donor P3HT (i.e., CB-LUMO energy offset) is sensitive to the doping amount of vanadium species. The electrochemical characteristics for V-doped TiO₂ with different doping contents ranging from 0 wt%

to 7 wt% (relative to the amount of TiO₂) were carried out by Mott-Schottky plots and UV-vis and shown in Figure S2. Mott–Schottky plots (C^{-2} vs. V) are a standard means for the electrochemical characterization of semiconductor materials. For the n-type semiconductor, the relationship between the capacitance (C) and the applied potential (V) can be expressed by using Equation (S1):

$$C^{-2} = \frac{2}{A^2 \epsilon \epsilon_0 N_D} \left(V - V_{FB} - \frac{kT}{e} \right) \quad (S1)$$

in which N_D is the doping density, V_{FB} is the flat-band (FB) potential, k is the Boltzmann constant, T is the temperature, ϵ is the relative dielectric constant of the anodic film, ϵ_0 is the permittivity of free space, e is the charge of an electron, and A is the electrode area. The flat band potentials were determined by Mott-Schottky plots as obtained by a linear extrapolation to $C=0$, i.e., the intercept at the X axis,³⁻⁵ then the conduction band (CB) energy level was calculated with Ag/Ag⁺ as reference. The band gap was determined from the UV-vis absorption spectrum using the following relationship: $E_g=1240/\lambda$ eV. Finally, the valence band (VB) energy level was obtained and listed in Table S1. The CB, VB and band gap values of the acceptor are shown in Table S2. It can be observed that both the CB and VB values are elevated further with the increase of the initial vanadium content, which can give rise to enhanced charge transports at the interface of donor and acceptor and explain the almost linearly increase of PCE with the increase of vanadium species. However, when the initial loading of the vanadium species (i.e., sodium metavanadate) exceeds 5wt%, the conversion efficiency decreases at 7 wt% as demonstrated in Table 2. This decrease may be ascribed to the quenching of the luminescence that arises from the introducing of deleterious cross-relaxation by elevated doping levels.⁶ Therefore, when the initial loading of sodium metavanadate is 5wt% relative to the amount of TiO₂, the device exhibits the best performances.

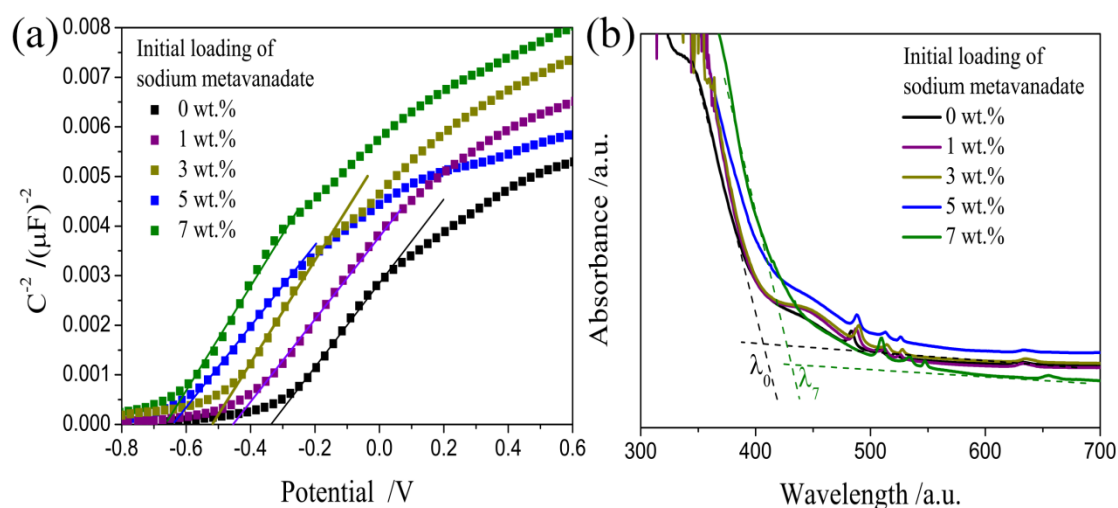


Figure S2. (a) Mott-Schottky plots of the different films. Mott-Schottky measurements were done at the frequency of 1 kHz in the aqueous solution of 0.05 M Na₂SO₄. (b) The UV-vis diffuse reflectance spectra of the films with different doping concentration.

Table S2 Electrochemical parameters for the different initial loading amounts of sodium metavanadate

V-TiO ₂ (wt. %)	0 wt%	1 wt%	3 wt%	5 wt%	7 wt%
V _{FB} (V vs Ag/Ag ⁺)	-0.33	-0.45	-0.52	-0.63	-0.66
CB (V vs vacuum level)	-4.38	-4.26	-4.19	-4.08	-4.05
E _g (eV)	3.04	3.02	3.02	2.95	2.87
VB (V vs vacuum level)	-7.42	-7.28	-7.21	-7.03	-6.92

The CB values were determined by Mott-Schottky plots and the band gap was estimated from the UV-vis diffuse reflectance spectrum using $1240/\lambda$ (eV), then the VB values were derived from CB and band gap values.

According to the following relationship,⁷

$$V_{oc} = |HOMO_D| - |LUMO_A| - \frac{kT}{q} \ln \left(\frac{N_{eff}^2}{np} \right) \quad (S2)$$

where $HOMO_D$ is the highest occupied molecular orbital (HOMO) of the donor, $LUMO_A$ is the LUMO of the acceptor, k is the Boltzmann constant, q is the elementary charge, T is temperature, N_{eff} is the effective density of state, and n and p are the concentrations of electrons and holes, respectively. If the third term is neglected, V_{oc} is determined by the energy-level difference between the $|HOMO_D|$ and $|LUMO_A|$. One route to improve V_{oc} is to raise the CB energy level of the acceptor (*i.e.*, to decrease $|LUMO_A|$), which will simultaneously reduce the energy offset between the CB energy level of acceptor and LUMO energy level of donor. On the other hand, the enhanced J_{sc} from 6.97 to 7.80 mA cm⁻² after doping can be ascribed to the reduction of the ‘excess’ CB-LUMO energy offset and hence the faster electron transport at the interface. For given 5wt% doping of vanadium species, as observed from Table S1 and S2, the CB, VB and band gap E_g obtained from the CV characteristics are in reasonable agreement with those determined from the UV-vis and Mott-Schottky method, indicating that the results obtained in this work are reliable.

SUPPLEMENTARY REFERENCE

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