Enhanced Photocatalytic Activity of Perovskite $NaNbO_3$ by Oxygen Vacancies Engineering

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Experimental section

Materials Characterization: Field-emission scanning electron microscope (FESEM, Hitachi SU8010) and high-resolution transmission electron microscopy (HRTEM, JEM-F200) are employed to analyze the morphology and microstructure. Phase structure was analyzed by using the X-ray diffraction measurement (XRD, SMARTLAB, Cu Kα). The powders were detected by X-ray photoelectron spectra (XPS ESCALab Xi+ photoelectron spectrometer). The electron paramagnetic resonance (EPR) spectra were characterized by a JES-FA200 spectrophotometer. UV-vis diffuse reflectance spectroscopy (DRS) were recorded using a UV-visible spectrophotometer with an integrating sphere attachment (PE Lambda950, PerkinElmer) and $BaSO_4$ as a reference. The photoluminescence (PL) spectra of the samples were measured on a fluorescence spectrometer (FLUOROLOY-3) under a laser excitation of 300 nm. The nitrogen (N_2) adsorption-desorption isotherms at 77 K were recorded by a Micromeritics Quadrasorb si-3 nitrogen adsorption apparatus (USA). The Electrochemical impedance spectrum (EIS) and Mott–Scotty plots were carried out by an electrochemical workstation (CHI660B, CH Instruments) with a typical three-electrode configuration, that Ag/AgCl (saturated KCl) was used as reference electrode and 0.5 mM $CuSO_4$ aqueous solution as electrolyte.

Photocatalytic activity measurements. Photo-degradation-rate were investigated by loading 50 mg of the photocatalysts into the breaker containing 50 ml of MB aqueous solution (10 ppm). The suspension was stirred in the dark for 60 min to attain the desorption–adsorption equilibrium and then exposure to the visible-light irradiation equipped from a 100 mW/cm^2 xenon lamp with a 400 nm cut-off filter. During the photodegragation process, about 1 ml suspension were taken with an equal interval of 30 min and analyzed by a UV-vis spectrophotometer after filtering photocatalysts completely. Moreover, the as-prepared annealed $NaNbO_3$ and reduced $NaNbO_3$ were measured at the same condition as the control group.

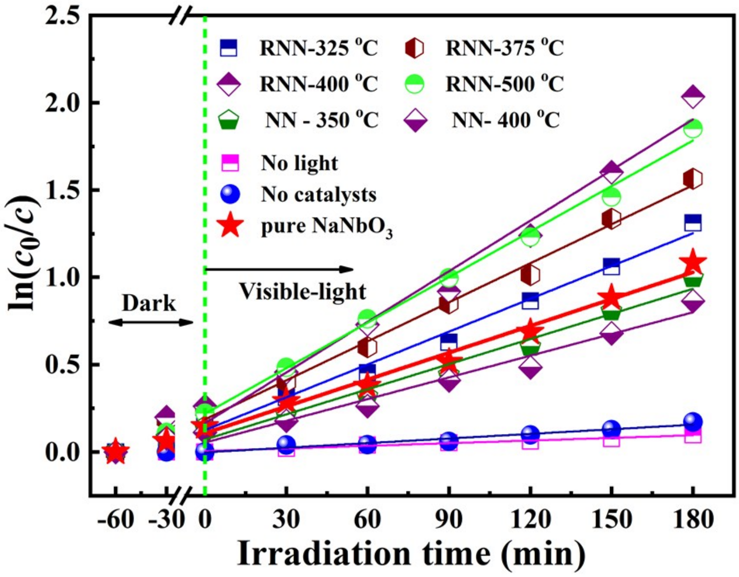


Fig. S1 The fitting plot of ln(c_0/c) plot versus time under visible-light for the MB photocatalytic degradation rection.

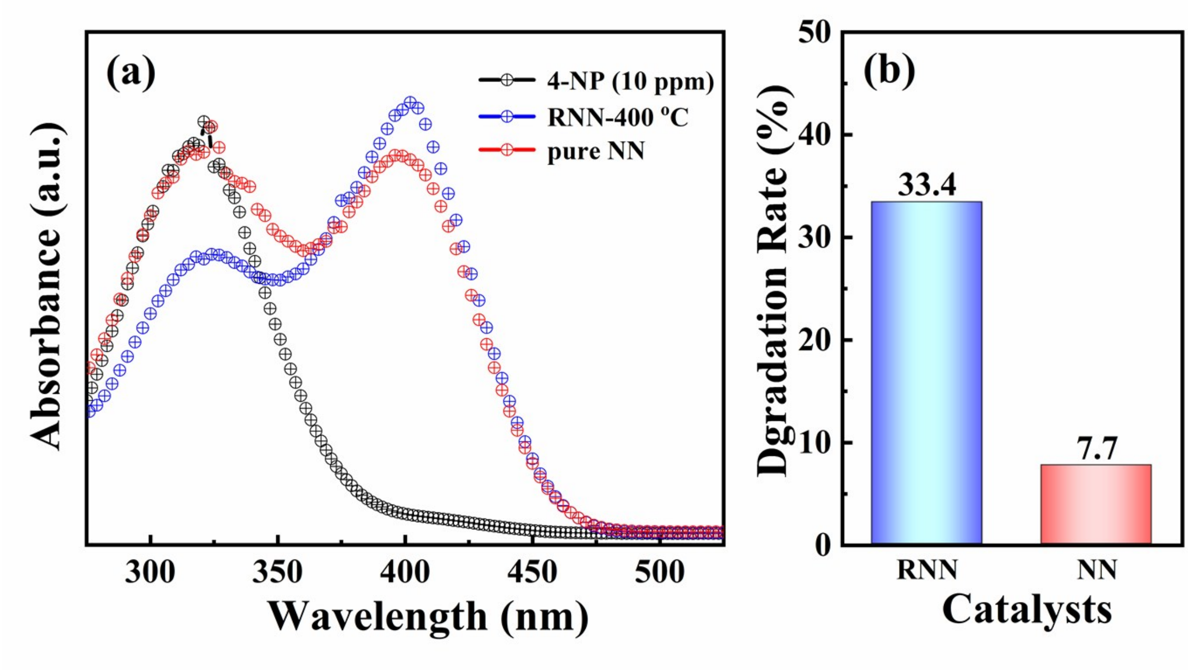


Fig. S2 The photo-degradation activity of RNN-400 °C and NN as catalysts for 4-NP (10 ppm) after simulated sun-light irradiation of 2.5 h.

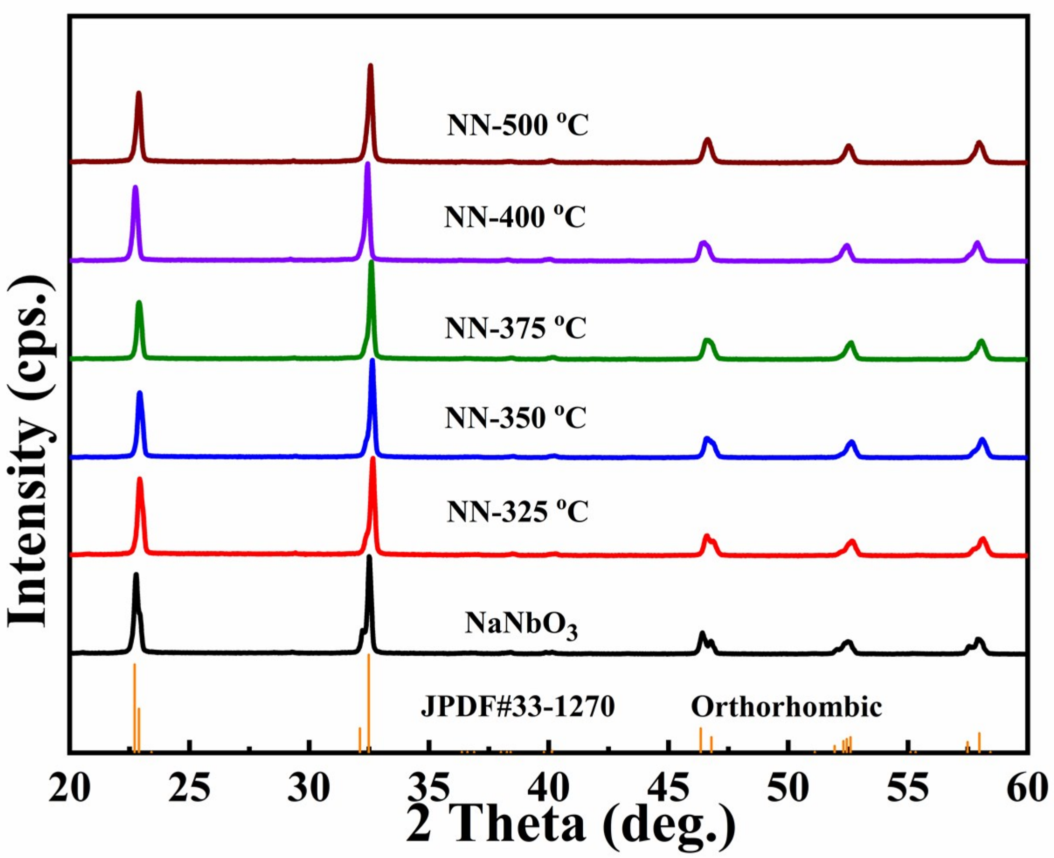


Fig. S3 XRD patterns of annealing $NaNbO_3$ at various temperatures without any reducing agents.

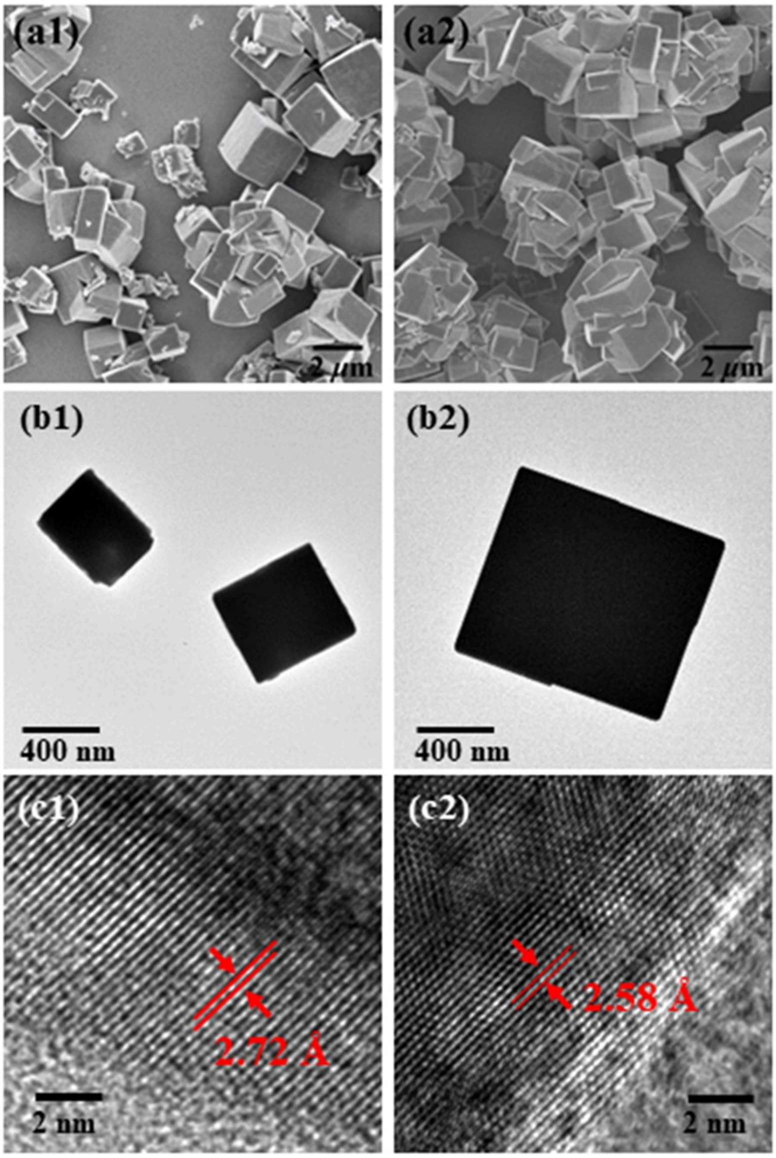
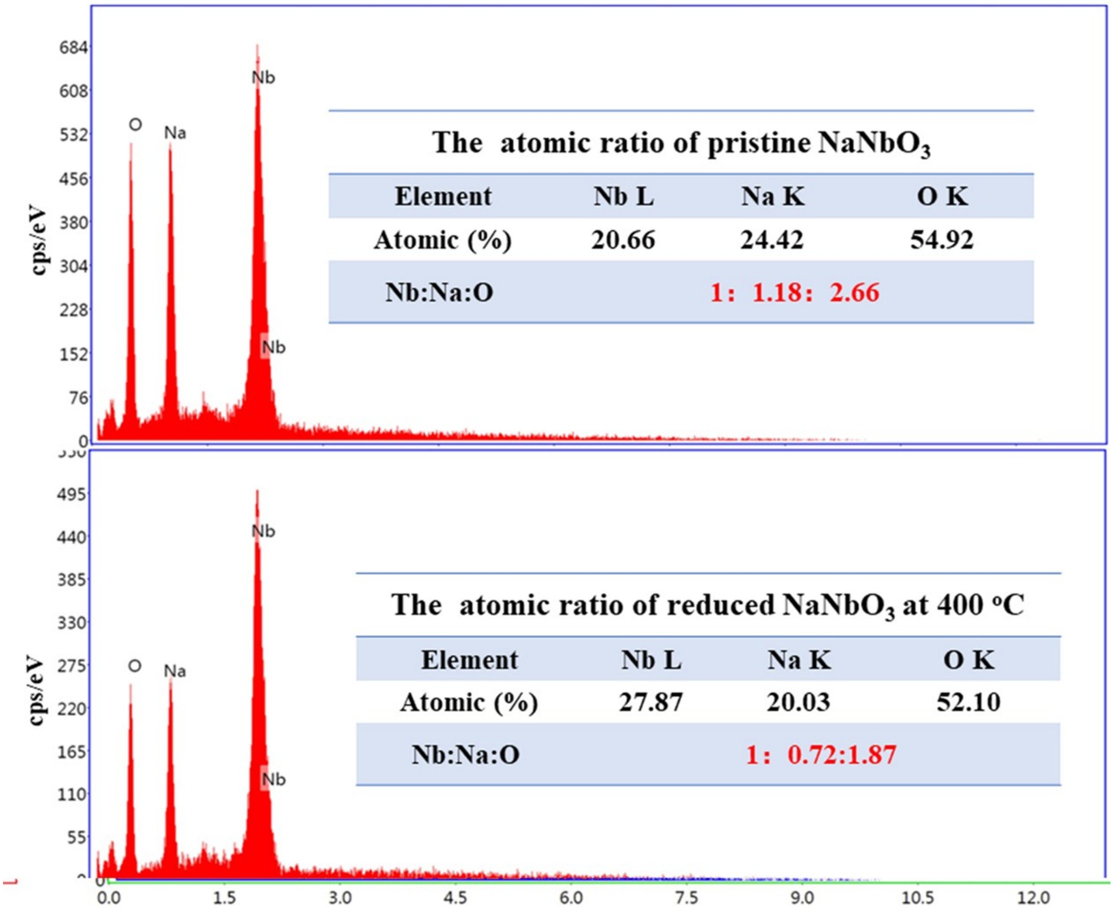


Fig. S4 Morphology and lattice images of RNN-400 °C (a1-c1) and pristine NN (a2-c2) *via* FE-SEM (a1, a2), TEM (b1, b2) and HR-TEM (c1, c2) observation, respectively.



The atomic ratio of pristine $NaNbO_3$

Element	Nb L	Na K	O K
Atomic (%)	20.66	24.42	54.92
Nb:Na:O	1：1.18：2.66		

The atomic ratio of reduced $NaNbO_3$ at 400 °C

Element	Nb L	Na K	O K
Atomic (%)	27.87	20.03	52.10
Nb:Na:O	1：0.72:1.87		

Fig. S5 EDS spectra of pristine NN (top) and RNN-400 °C (bottom).

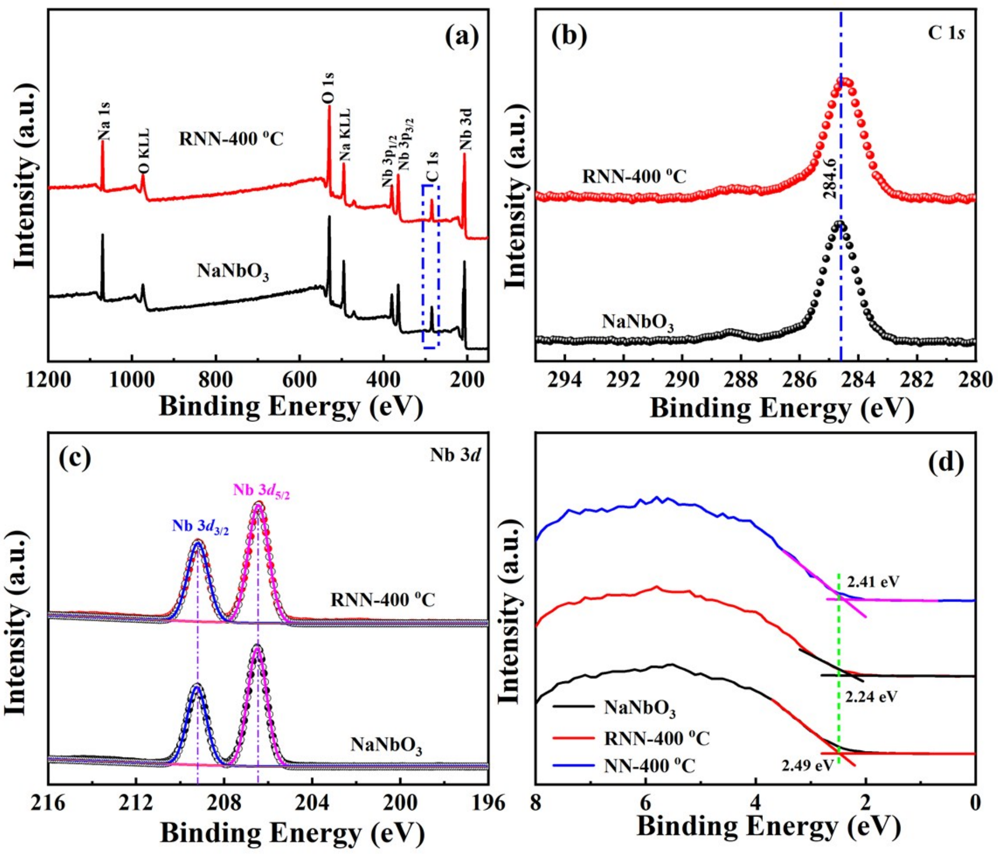


Fig. S6 (a) XPS survey scans of pristine NN and RNN-400 °C; (b) XPS core level spectra of C 1s and (c) XPS core level spectra of Nb 3d; (d) valance band XPS spectra of pristine NN, NN-400 °C and RNN-400 °C.

Notes: Full XPS spectra of the samples are shown in Fig. S6. Clear spectra indicate that the byproducts from $NaBH_4$ can be easily removed by washing with water and ethanol. For the high-resolution XPS spectra of Nb 3d of pristine NN and RNN-400 °C samples, as presented in Fig. S6 (c), the spectra were corrected relative to the standard carbon species (graphite) located at the binding energy of 284.6 eV. In addition, the Nb $3d_{3/2}$ and Nb $3d_{5/2}$ peaks centered at the binding energies of 209.25 and 206.50 eV, which is consistent with the reported Nb^{5+} in the $NaNbO_3$[1]. The electronic structure of as-prepared catalysts was explored using the valence band (VB) XPS. As unclosed in Fig. S6(d), the E_{VB} of the pristine $NaNbO_3$, RNN-400 °C and NN-400 °C samples were 2.49, 2.24 and 2.41 eV relative to the surface Fermi level, respectively.

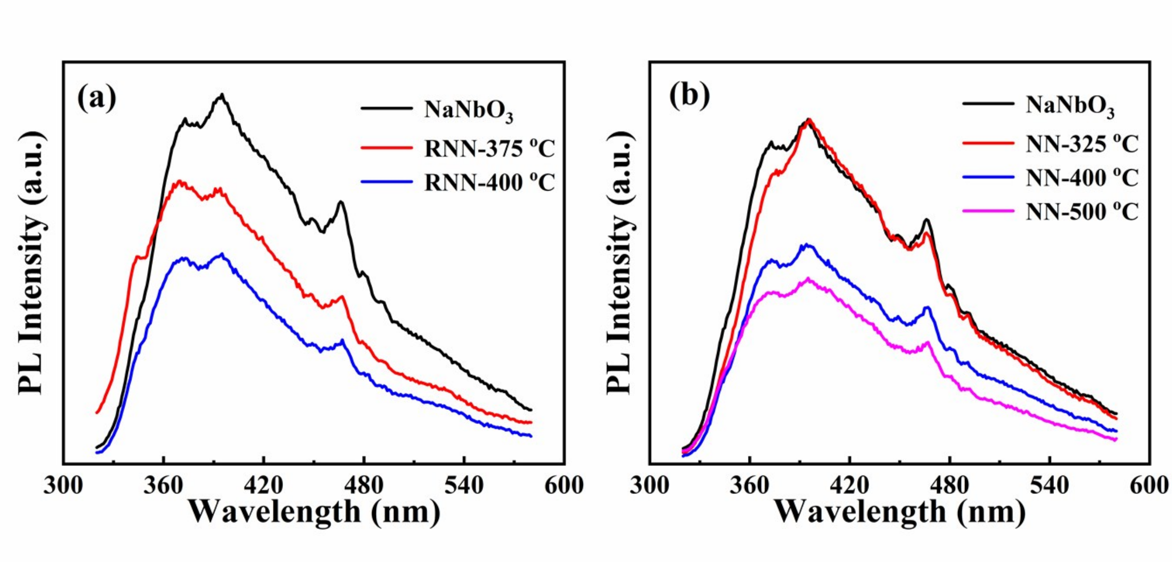


Fig. S7 PL emission spectrum of reduced $NaNbO_3$ and annealed $NaNbO_3$ as function of various temperatures.

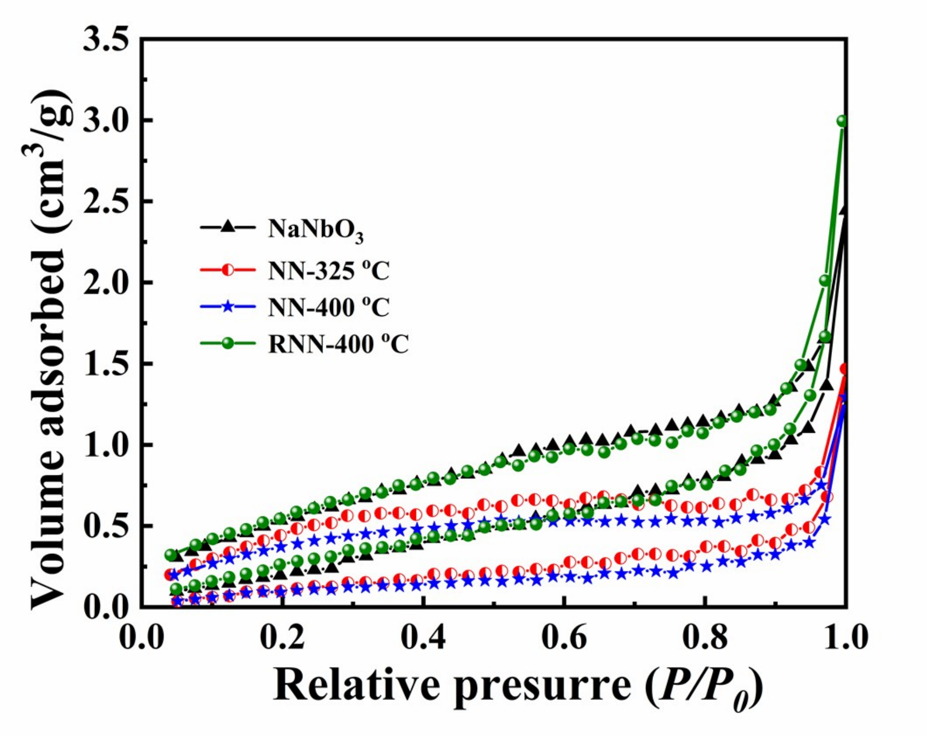


Fig. S8 N_2 adsorption-desorption isotherms curves of pristine $NaNbO_3$, NN-325 °C, NN-400 °C and RNN-400 °C.

Notes and references

1. H. You, X. Ma, Z. Wu, L. Fei, X. Chen, J. Yang, Y. Liu, Y. Jia, H. Li, F. Wang and H. Huang, *Nano Energy*, 2018, **52**, 351-359.