Supporting Information

Enhancement of metal ion-induced hole transfer on water oxidation performance of $BiVO_4$ photoanode

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1.***Materials***

Bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$, 99 %), ammonium metavanadate (NH_4VO_3, 99 %), potassium iodide (KI, 99 %), ethyl alcohol (C_2H_5OH, 99.5 %), p-benzoquinone ($C_6H_4O_2$, 99 %), vanadyl acetylacetonate ($C_{10}H_{14}O_5V$, 99 %), dimethyl sulfoxide (C_2H_6SO, 99.5 %) were purchased from Shanghai Maclin Biochemical Technology Co., LTD. Nitric acid (HNO_3, 68 %) is purchased from Nanjing Chemical Reagent LTD. All reagents were not further purified.

2 ***Synthesis of $BiVO_4$ photoanode***

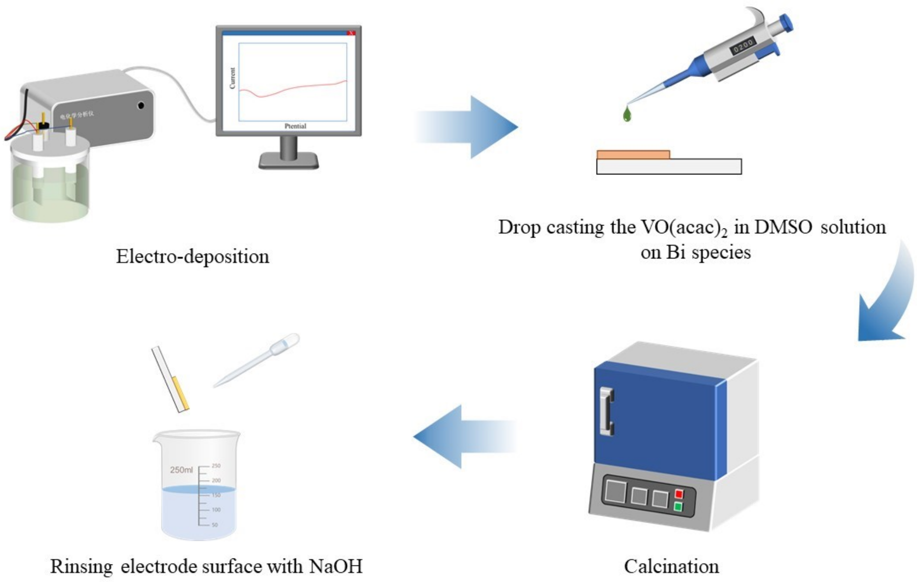
Firstly, 2 mmol $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in 50 mL KI solution (0.4 M) with continuously stirring. Then, HNO_3 solution was added dropwise to the mixture until the pH value to be 1.7, which was denoted as A solution. Meanwhile, 4.6 mmol p-benzoquinone was added to the 20 mL ethanol and the mixed solution was continuously stirred until obtaining the uniform brown-yellow solution, which was denoted as B solution. At last, A and B solution was mixed quickly with stirring until its color turned to be red. The homogeneous solution was then deposited on FTO with electrodeposition method, carried out for 180 s under a bias voltage of -0.1 V. The residual ions on electrode surface were washed by deionized water and dried in air. After that, 200 μL $VO(acac)_2$ DMSO solution (0.2 M) was slowly dropped onto the electrode, and subsequently heated at 450 °C for 2 hours. When cooled to room temperature, the electrode sheet was washed with 0.5 M NaOH solution to remove the V_2O_5 on the surface.

3 ***Electrochemical measurement***

The electrochemical test is carried out in Electrochemical Workstation (CHI 760e). The test system has three electrodes, among which, the $BiVO_4$ thin films electrode was used as the working electrode, the Ag/AgCl electrode was used as the reference electrode, and the platinum sheet electrode was used as the cathode. The electrolyte contains 1.25 mM $CoSO_4$ and 2.5 Mm $Fe_2(SO_4)_3$, respectively. A 300-W xenon lamp coupled with an AM 1.5G (light density 100 $mW \cdot cm^{-2}$) was used as a simulated-solar light source. In order to exclude Co^{2+}, Fe^{3+} which may interact with electrons at the cathode to have an effect on the experimental results, the tests were all carried out in an H-type electrolytic cell, with Nafion ion exchange membranes separating the two cells. Adjusting the pH of electrolyte to 2.4 in the two cells with H_2SO_4.

4 ***Density functional theory (DFT) calculation***

The calculations were performed based on the Guassian 09D[1] by taking advantage of the pbe0/tzvp and pbe0/def2tzvp with GD3BJ and spin symmetry breaking, while the implicit solvation mode was applied to describe the solvent effect with the water. The molecular orbital of the HOMO and LUMO for the two compounds, calculated and displayed by the Multiwfn 3.8 with VMD 1.9.3.[2]



Schematic diagram of preparation of $BiVO_4$ electrode sheet

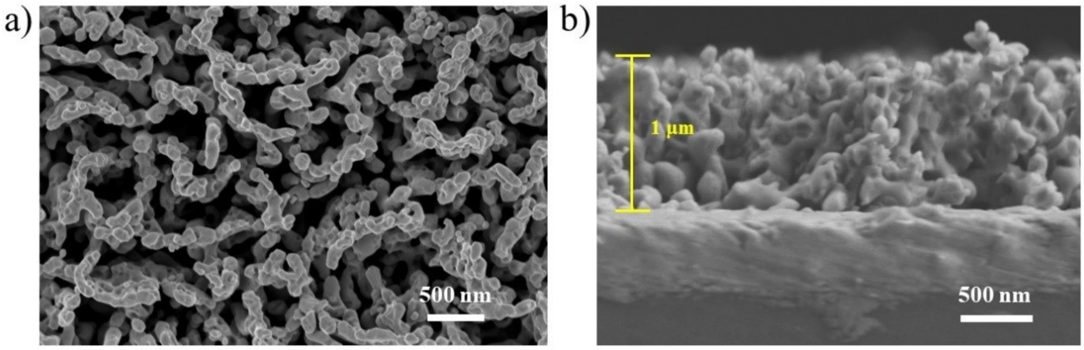


Fig. S1 a) Top surface SEM topography, b) cross-section SEM topography of $BiVO_4$ thin film

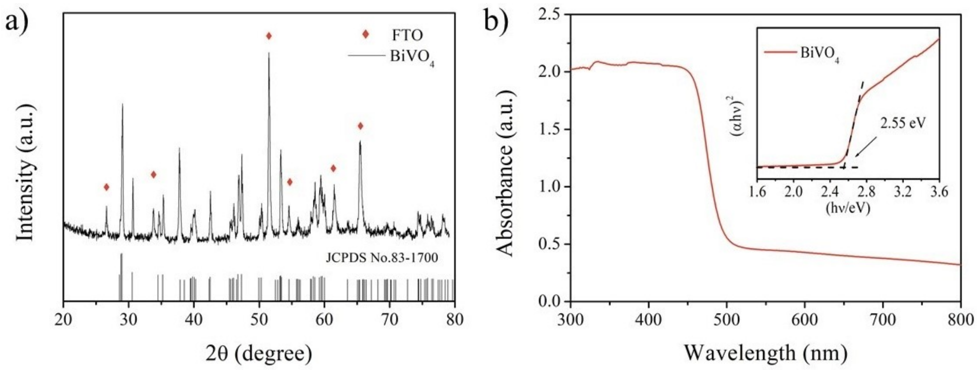


Fig. S2 a) XRD pattern (the characteristic peaks of FTO are marked in the red diamond), b) UV-vis absorption spectrum and Tauc plot of the $BiVO_4$ film

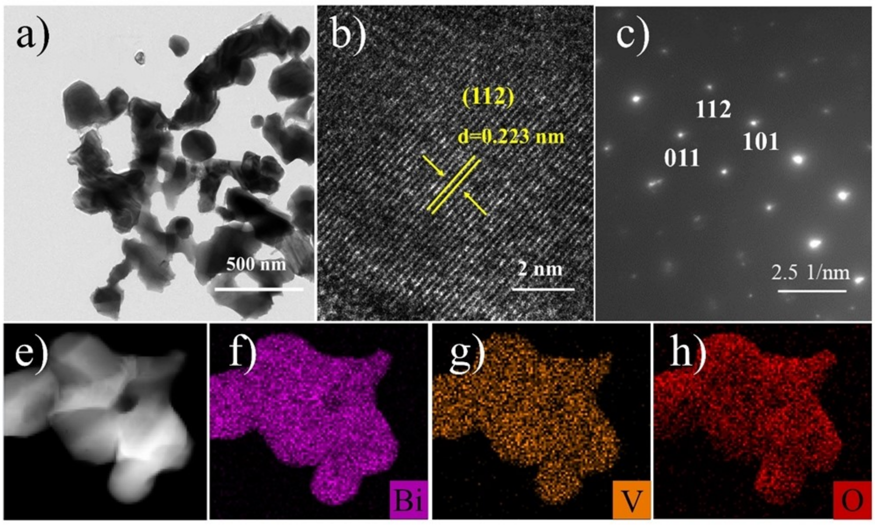


Fig. S3 a) TEM, b) HRTEM image, c) SAED, e-h) EDS elemental mappings (Bi, V and O) of the selected particle in e)

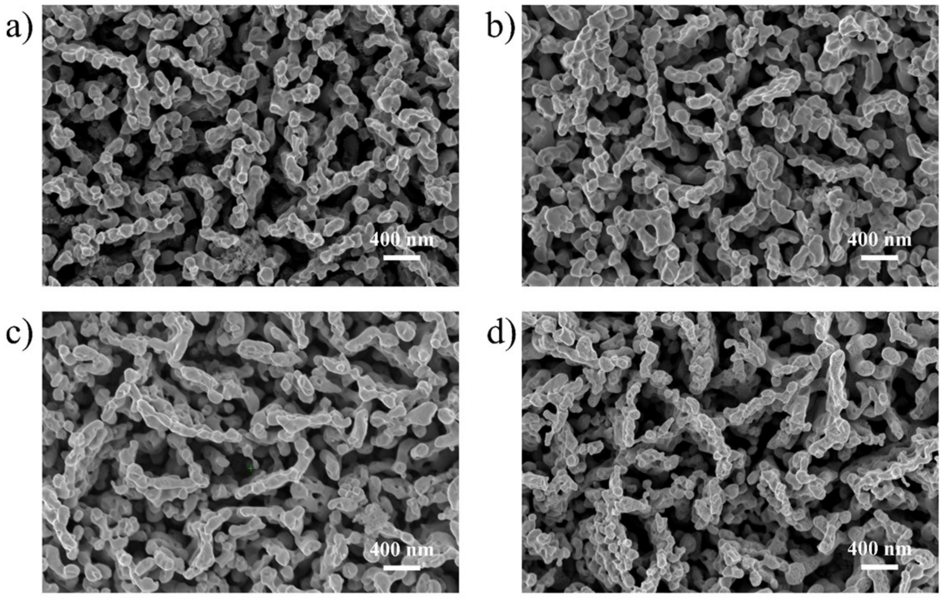


Fig. S4 SEM of $BiVO_4$ after testing in a) Na_2SO_4, b) Na_2SO_4+$CoSO_4$, c) Na_2SO_4+$Fe_2(SO_4)_3$, d) Na_2SO_4+$Fe_2(SO_4)_3$+$NiSO_4$ electrolytes

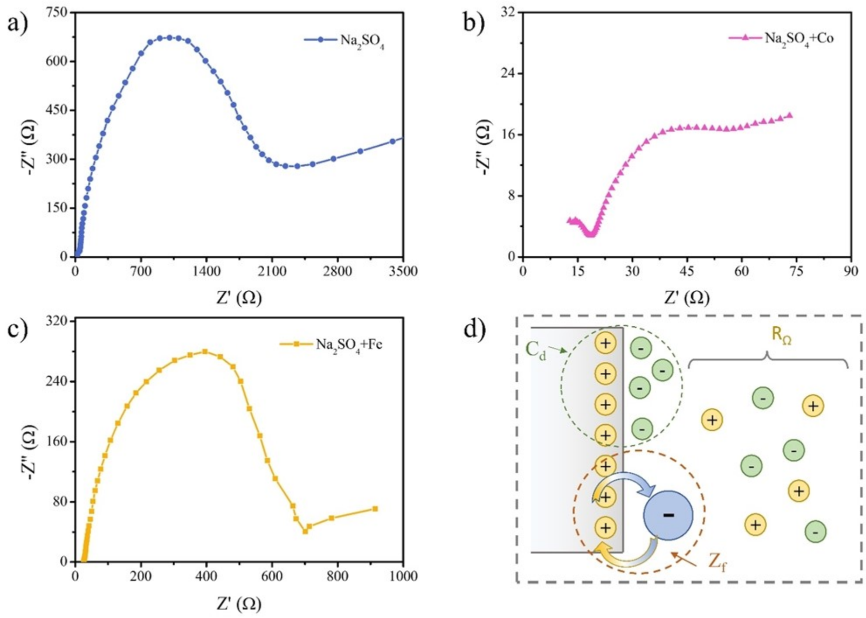


Fig. S5 EIS curve of $BiVO_4$ in a) Na_2SO_4 electrolyte, b) Na_2SO_4+$CoSO_4$ electrolyte, c) Na_2SO_4+$Fe_2(SO_4)_3$ electrolyte under light, d) schematic diagram of electrochemical process

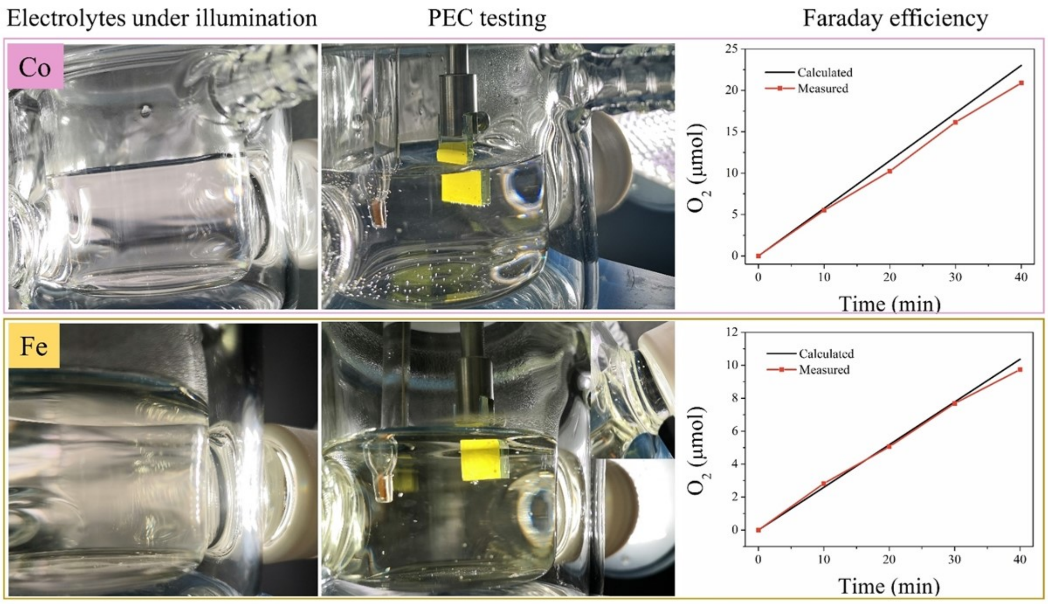


Fig. S6 Optical photos of different electrolytes under illumination, optical photos of $BiVO_4$ photoanode tested in different electrolytes, and Faraday efficiency

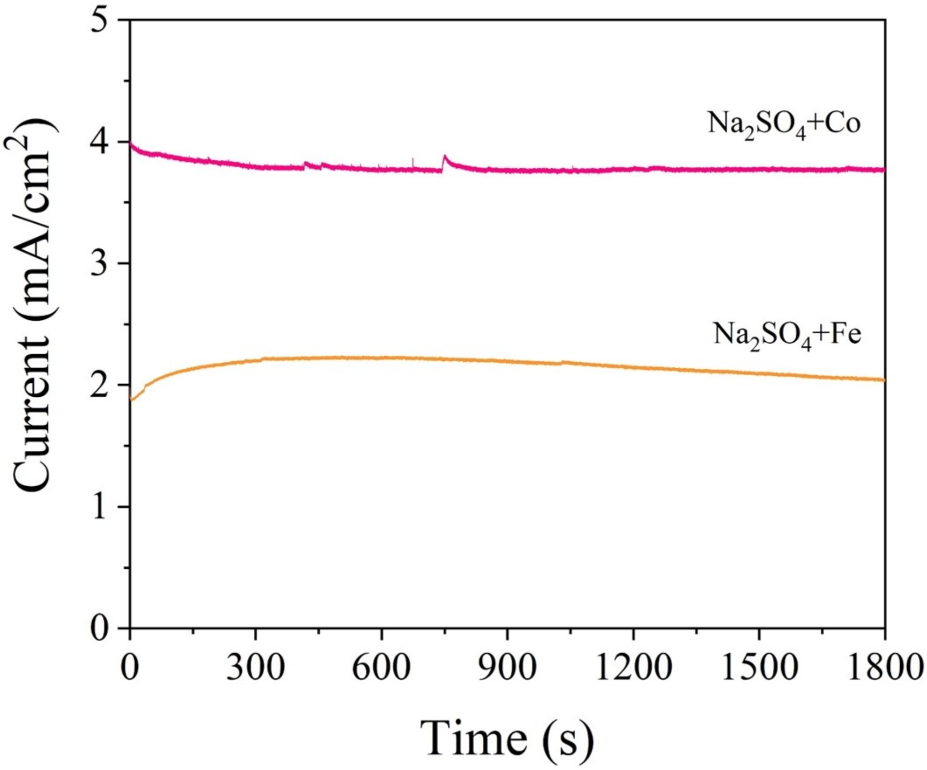


Fig. S7 I-t performance of $BiVO_4$ photoanode in electrolytes containing Co^{2+} or Fe^{3+}

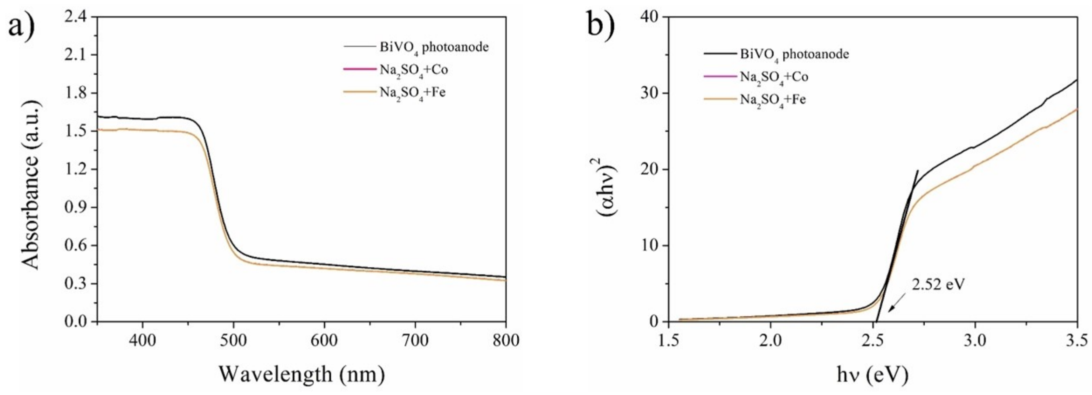


Fig. S8 UV-vis absorption spectrum and Tauc plot of the $BiVO_4$ film before and after testing in different electrolytes

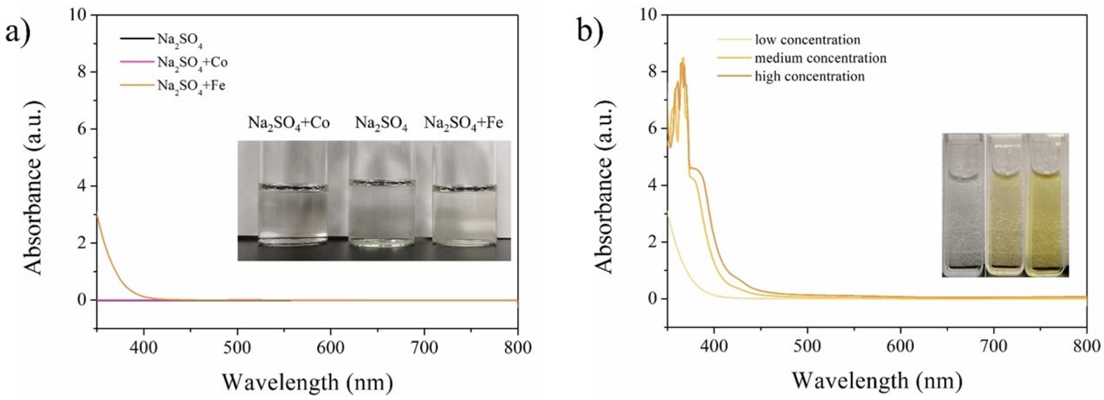


Fig. S9 a) UV-vis absorption spectrum and optical photos of different electrolytes, b) UV-vis absorption spectrum and optical photos of electrolytes with different Fe^{3+} concentrations

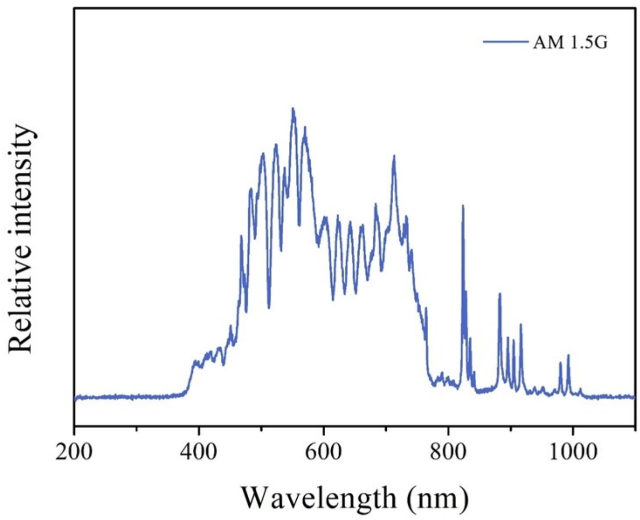


Fig. S10 Spectrum of a xenon lamp with an AM 1.5 filter

Table S1 The content of V element in solution after $BiVO_4$ photoelectrode was tested in different electrolytes

Filtrate	Concentration
Na_2SO_4	0.0103 mg/L
Na_2SO_4+$CoSO_4$	0.0095 mg/L
Na_2SO_4+$Fe_2(SO_4)_3$	0.0079 mg/L
Na_2SO_4+$Fe_2(SO_4)_3$+$NiSO_4$	0.0059 mg/L

Table S2 The content of metal ions in the electrolyte before and after the reaction

Sample number	Element	Concentration (mg/L)
1	Co	75.32
2	Co	78.23
3	Fe	176.60
4	Fe	177.70

*Samples 1 and 2 are Co^{2+}-containing electrolytes before and after the reaction, respectively; Samples 3 and 4 are Fe^{3+}-containing electrolytes before and after the reaction, respectively.

Table S3 The content of elements of sample

Sample number	Bi (mg/kg)	V (mg/kg)	Co (mg/kg)	Fe (mg/kg)
1	91.8	20.9	0	-
2	111.5	25.9	-	0

*Sample 1 and 2 are the $BiVO_4$ photoanode after testing in solutions containing Co^{2+} or Fe^{3+}, respectively.

References

1 R. A., M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria,M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian,J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. , K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian 09, Gaussian, Inc., Wallingford CT, 2016.

2 (a) T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580-592; (b) W. Humphrey, A. Dalke and K. Schulten, *J. Mol. Graphics*, 1996, **14**, 33-38.