Platinum Nanoparticles Loaded Bismuth Oxide: An Efficient Plasmonic Photocatalyst Active under Visible Light

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Electronic Supplementary Information (ESI):

Fig. S1a and Fig. S1b show field emission scanning electron microscopy (FE-SEM) images of Bi_2O_3 and Pt/Bi_2O_3, respectively, revealing the smooth surface of Bi_2O_3 was eroded after photodeposition of Pt. In order to identify where the Pt particles are, transmission electron microscopy (TEM) was employed. Fig. S1c shows a typical TEM image of the edge of Pt/Bi_2O_3. The corresponding EDS spectra indicate that Pt NPs are practically assembled from a number of NPs with diameters ranging from 5 to 10 nm, because in the real line circle (floc-like aggregates), the major element is determined to be Pt, whereas in the dashed circle (smooth surfaces) there is only Bi element without any Pt traces.

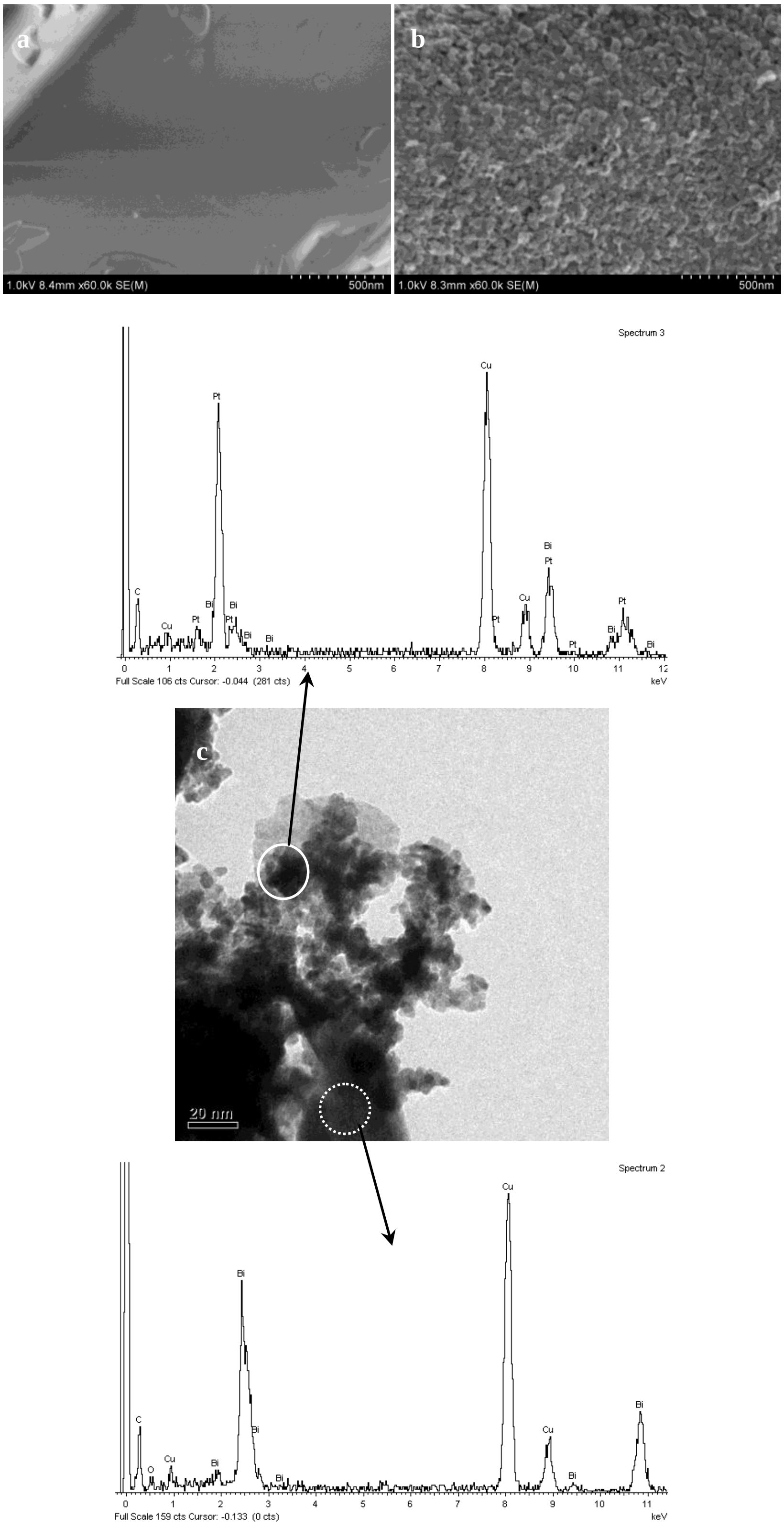

Fig. S1 FE-SEM images of bare Bi_2O_3 (a) and Pt/Bi_2O_3 (b); TEM image of Pt/Bi_2O_3 (c) with its corresponding EDS spectra.

Fig. S2 shows X-ray diffraction patterns of 2.0 wt % Pt/Bi_2O_3 and that of the reference Bi_2O_3. The diffraction peaks of Bi_2O_3 were shifted to a lower-angle side with Pt loading. The successive shift of the XRD pattern was partly ascribed to the occupation of interstitial sites in Bi_2O_3 by Pt NPs. Pt traces around 46 ° and 55 ° can also be recognized in the XRD patterns, as indicated by the black arrows. All diffraction peaks of bare Bi_2O_3 are assigned to bismite crystallized in monoclinic form corresponding to JCPDS files (No. 41-1449.), namely, α-Bi_2O_3.

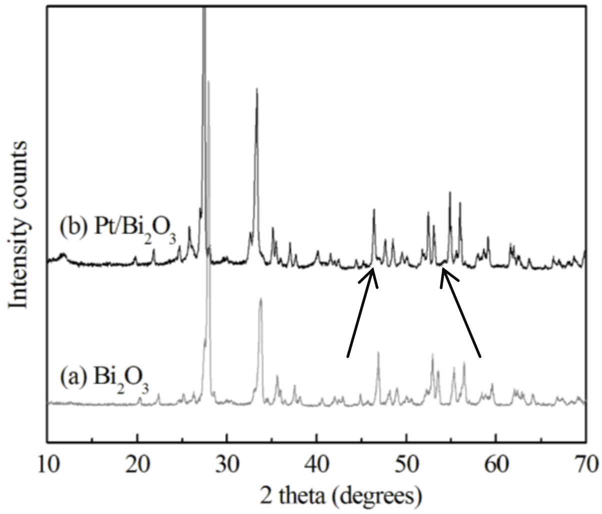

Fig. S2 X-ray diffraction patterns of (a) Bi_2O_3 and (b) Pt/Bi_2O_3.

In order to analyze the chemical composition of the catalysts and to determine the chemical state of Pt, XPS survey was conducted. The XPS spectrum and the high-resolution XPS spectra are compared in Fig. S3. The binding energies of the Pt 4f band were 71.0 and 74.2 eV (Fig. S3b), respectively, suggesting that Pt NPs are comprised of metallic Pt (71.2 eV) on the catalyst surface.[1] For bare Bi_2O_3, the peaks centered at 163.9 eV and 158.6 eV are assigned to Bi 4f 5/2 and Bi 4f 7/2 region (Fig. S3c).[2] For Pt/Bi_2O_3, the peaks assigned to Bi 4f 5/2 and Bi 4f 7/2 region shift to 164.228 eV and 159.028 eV (Fig. S3d).

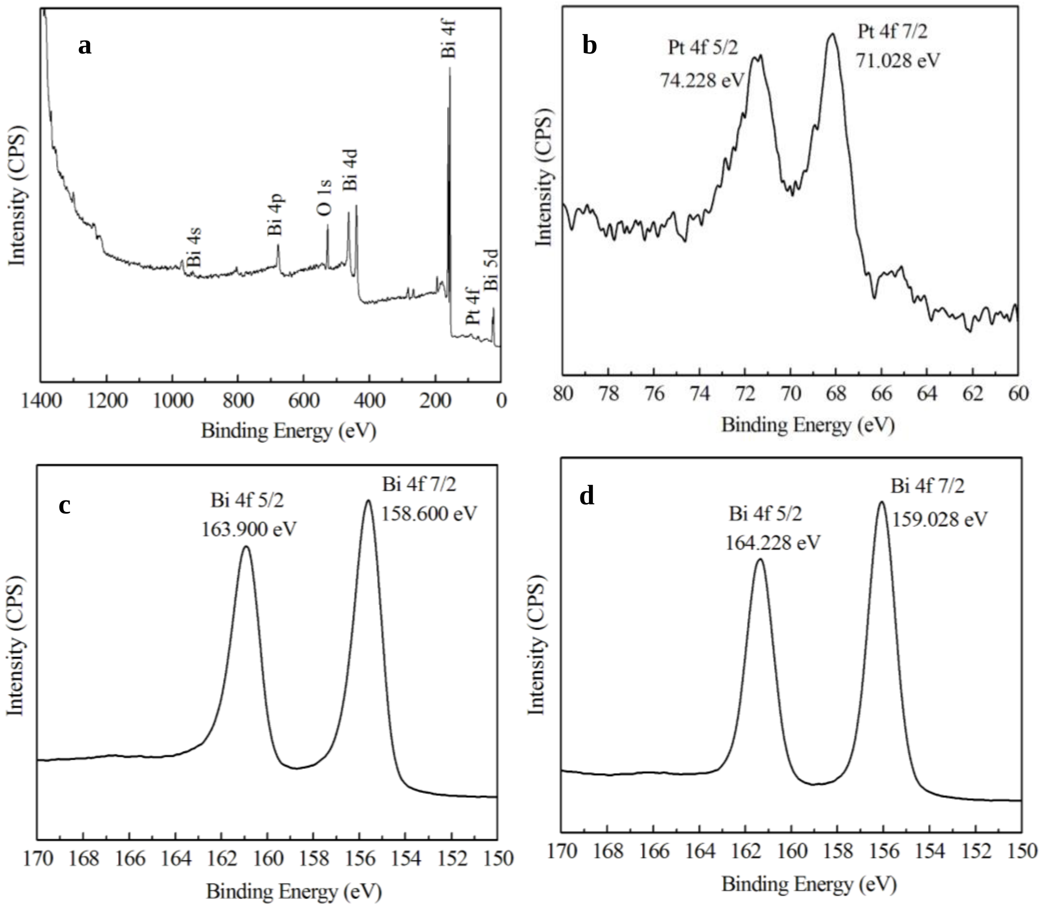

Fig. S3 XPS survey spectrum of (a) Pt/Bi_2O_3 and the high-resolution XPS spectra of (b) Pt 4f region, (c) Bi 4f region of bare Bi_2O_3 and (d) Bi 4f region of Pt/Bi_2O_3.

The reuse and stability of catalyst are two major concerns for a catalyst to be useful in practical applications. Thus life cycle tests need to be carried out to assess the stability and durability of Pt/Bi_2O_3. The detailed experimental procedure was as follows: after each 60 min reaction with methanol solution under visible light irradiation, the reacted solution was centrifuged, the upper liquid was removed and the residual Pt/Bi_2O_3 was dried at 80 ℃ for 5 h. The results are shown in the following Fig. S4. We can see that the CO_2 evolution rate over Pt/Bi_2O_3 slightly decreased after every cycle, which might due to the coagulation of the photocatalysts. This is the reason that we are now trying to prepare nanosized Bi_2O_3 for Pt deposition, which is supposed to enhance the stability of Pt/Bi_2O_3. However, in the present study, Pt/Bi_2O_3 can still be considered as a promising catalyst since it is a visible light driven photocatalyst with good photoactivity.

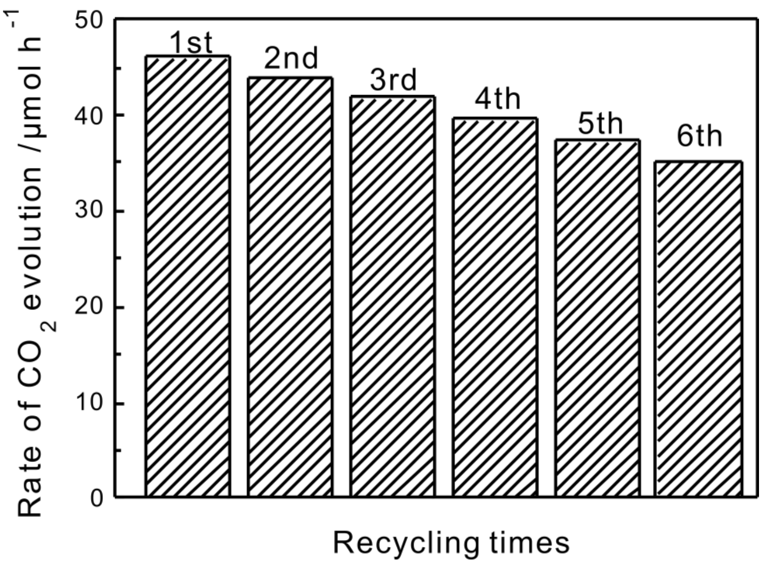

Fig. S4 Life cycle of Pt/Bi_2O_3 for the decomposition of methanol under visible light irradiation (λ > 400 nm) with ambient air.

Fig. S5 shows the electron density on both Bi and O atoms. However, with smaller value of contour, the contribution from Bi atoms increases.

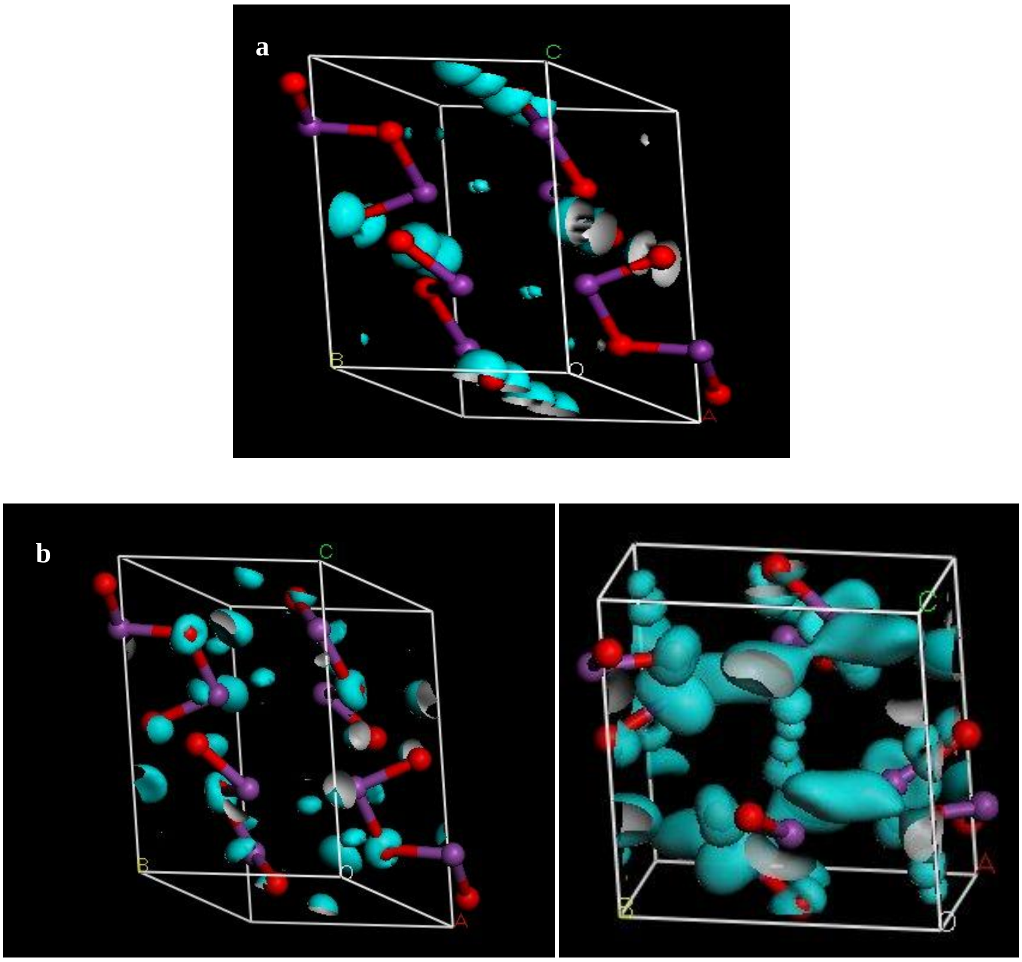

Fig. S5 (a) Electron density contour map for the valence band maximum (HOMO) of Bi_2O_3 and (b) electron density contour map for the conduction band minimum (LUMO) of Bi_2O_3.

References

1. T. Morikawa, T. Ohwaki, K. I. Suzuki, S. Moribe and S. Tero-Kubota, *Appl. Catal., B*, 2008, **83**, 56-62.
2. C. H. Wang, C. L. Shao, Y. C. Liu and L. Zhang, *Scripta Mater.*, 2008, **59**, 332-335.