Electronic Supplementary Material (ESI) for RSC Advances

Supplementary Information

Plasmon-enhanced hydrogen evolution on Au-$InVO_4$ hybrid microspheres

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Experimental details

Synthesis of $InVO_4$ hollow microshpheres: In a typical procedure, while stirring, 0.5 mmol of $InCl_3$ was initially dissolved in 50 mL ultrapure water, followed by the addition of 0.5 mmol of NH_4VO_3. Then 0.3 mL of 1 M aqueous ethanolamine solution was added into the mixture. The resultant suspension was sealed in a 100 mL teflon-lined stainless-steel autoclave. The autoclave was heated to and maintained at 160 ºC for 12 hours, and allowed to cool to room temperature. The product was collected after centrifugation, washed with water repeatedly, and then dried in a vacuum oven.

Synthesis of Au-$InVO_4$ hybrid microshpheres: 60 mg of the as-prepared $InVO_4$ powder was suspended in 20 mL ultrapure water followed by the addition of 5 mL aqueous solution of 0.01 M L-cysteine. The mixture was subjected to sonication for 30 minutes followed by the addition of different amount of 3 mM $HAuCl_4$ aqueous solution (2.5, 5, 10 mL for 2, 4, 7.5 wt% Au-$InVO_4$, respectively). After vigorous

stirring for another 30 minutes, different amount of 0.05 M L-ascorbic acid aqueous solution (5, 10, 20 mL for 2, 4, 7.5 wt% Au-$InVO_4$, respectively) was quickly added into the solution. The reaction was allowed for rapid stirring for 3 hours. The products were separated via centrifugation, washed with water repeatedly, and dried in a vacuum oven.

Synthesis of Pt-$InVO_4$ hybrid microshpheres: Platinum nanoparticles are grown on the $InVO_4$ hollow microspheress follows: 60 mg of the as-obtained $InVO_4$ powder was suspended in 20 mL ultrapure water followed by the addition of 5 mL aqueous solution of 0.01 M L-cysteine. The mixture was allowed for sonication for 30 minutes followed by introducing 5 mL aqueous solution of 3 mM H_2PtCl_6. After vigorous stirring for another 30 minutes, 10 mL aqueous solution of 0.05 M L-ascorbic acid was quickly added into the solution. The reaction was allowed for rapid stirring for 3 hours. The products were separated via centrifugation, washed with water repeatedly, and dried in a vacuum oven.

Characterization: X-ray powder diffraction (XRD) patterns were recorded on a Shimadzu XRD-6000 X-ray diffractometer (Cu Kα source) at a scan rate of 1 °/min with the 2θ range from 10 to 70°. The field emission scanning electron microscopy (FESEM) images and energy dispersive X-ray spectra (EDX) were taken with a JEOL JSM-7600F scanning electron microscope equipped with energy dispersive X-ray analysis system. Transmission electron microscopy (TEM) images were recorded on a JEOL JEM-2100F transmission electron microscope at an accelerating voltage of 200 kV. UV–vis diffuse reflectance spectra (DRS) were recorded on a Lambda 750

UV/Vis/NIR spectrophotometer (Perkin Elmer, USA). X-ray Photoelectron spectroscopy (XPS) measurement was performed on a Thermo Scientific Theta Probe XPS with monochromatized Al Kα (*hv*=1486.6 eV) source.

Photocatalytic hydrogen evolution from water splitting: Typically, 10 mg of the prepared Au-$InVO_4$ hybrid microshperes were suspended in 10 mL aqueous solution of 0.1 M L-ascorbic acid. The pH value was adjusted to 4.0 by using 1 M NaOH aqueous solution. The suspension was purged with nitrogen for 3 hours to drive away the residual air before sealed in a quartz flask. The photocatalytic hydrogen evolution was carried out by irradiating the suspension with a 300-W xenon lamp (MAX-302, Asahi Spectra, USA) coupled with a UV cut-off filter (λ > 420 nm). The gas product composition was analyzed every 30 min by an Agilent 7890A gas chromatograph (GC) with TCD detector.

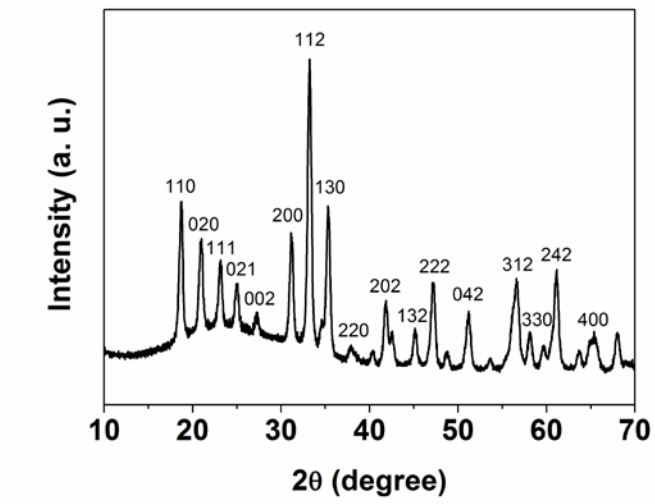

Fig. S1 XRD pattern of $InVO_4$ microspheres (JCPDS No. 48-0898).

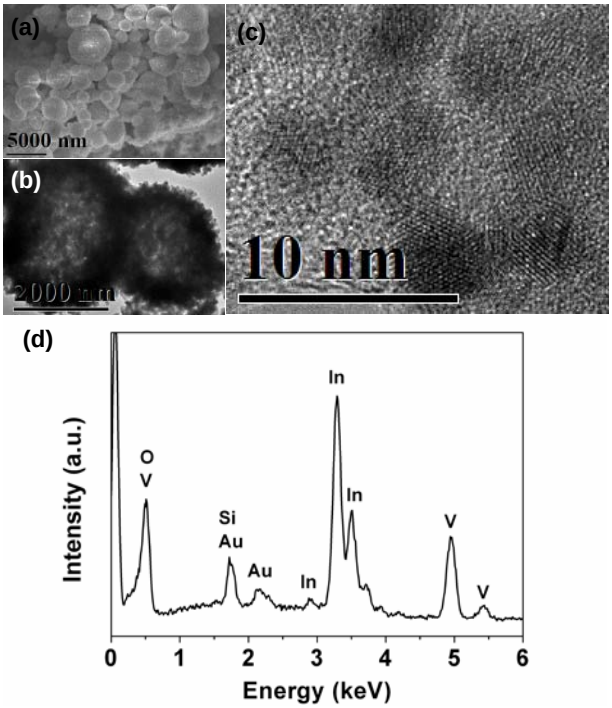

Fig. S2 characterization of 2 wt% Au-$InVO_4$ microspheres: (a) SEM image; (b) TEM image; (c) TEM image from the edge of a single Au-$InVO_4$ microsphere; (d) EDX spectrum.

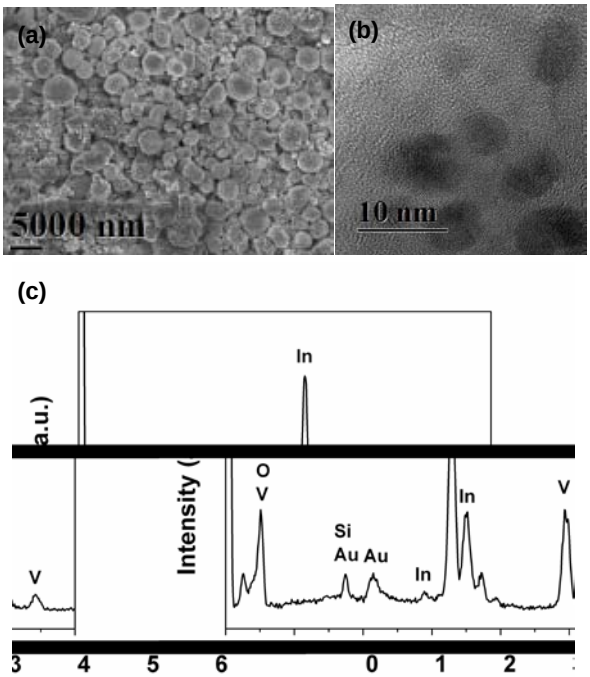

Fig. S3 characterization of 4 wt% Au-$InVO_4$ microspheres: (a) SEM image; (b) TEM image from the edge of a single Au-$InVO_4$ microsphere; (c) EDX spectrum.

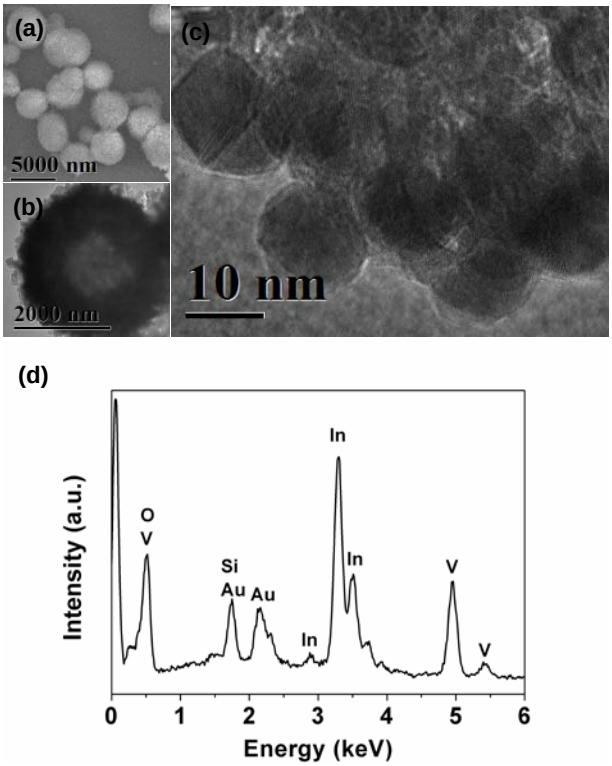

Fig. S4 characterization of 7.5 wt% Au-$InVO_4$ microspheres: (a) SEM image; (b) TEM image; (c) TEM image from the edge of a single Au-$InVO_4$ microsphere; (d) EDX spectrum.

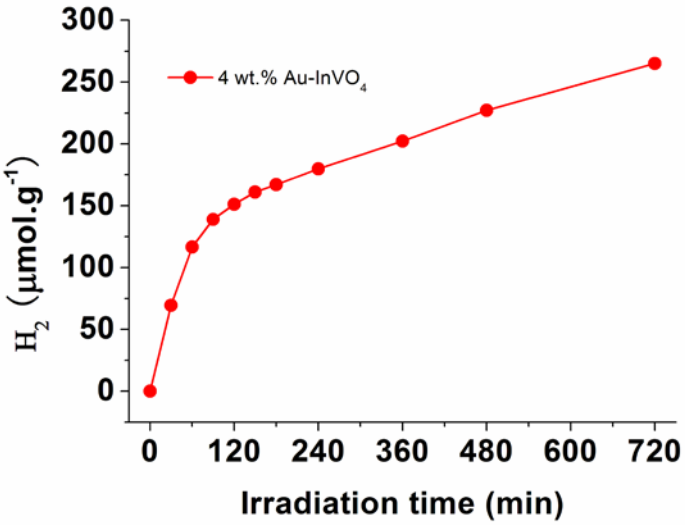

Fig. S5 Photocatalytic H_2 evolution versus visible-light ($\lambda > 420$ nm) irradiation time for 4 wt% Au-$InVO_4$ microspheres at pH 4.0.

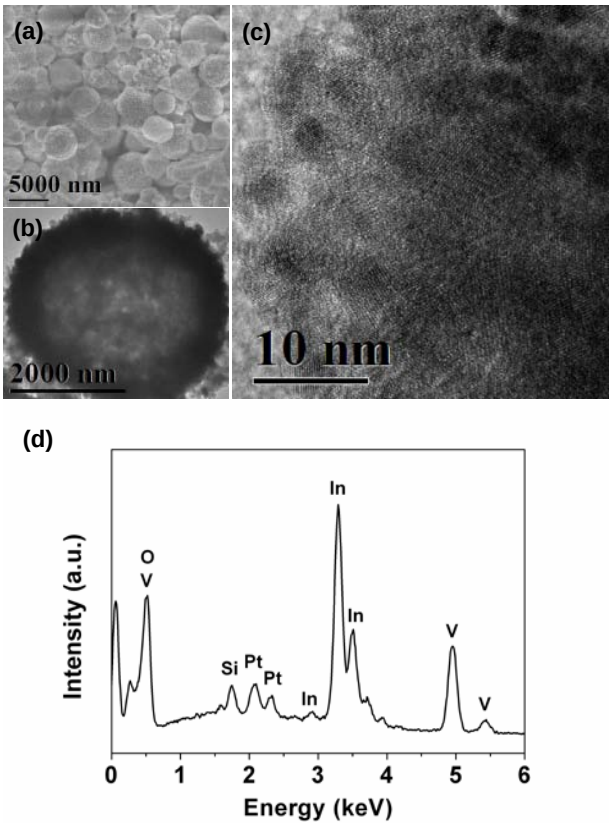

Fig. S6 characterization of 4 wt% Pt-$InVO_4$ microspheres: (a) SEM image; (b) TEM image; (c) TEM image from the edge of a single Pt-$InVO_4$ hollow microsphere; (d) EDX spectrum, the estimated Pt content is around 4 wt %.

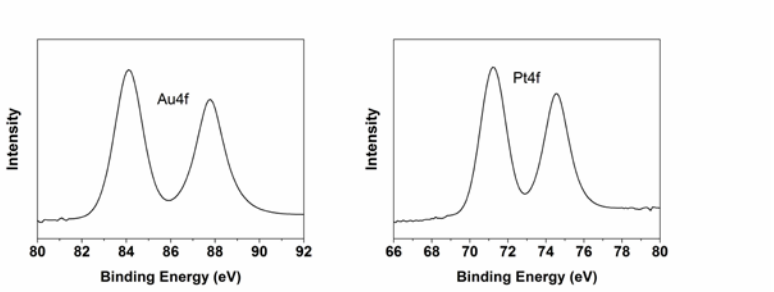

Fig. S7. The XPS spectra of the Au-InVO4 and Pt-InVO4 sample, showing the binding energy of Au 4f (84.1 and 87.8 eV) and Pt 4f (71.2 and 74.6 eV).

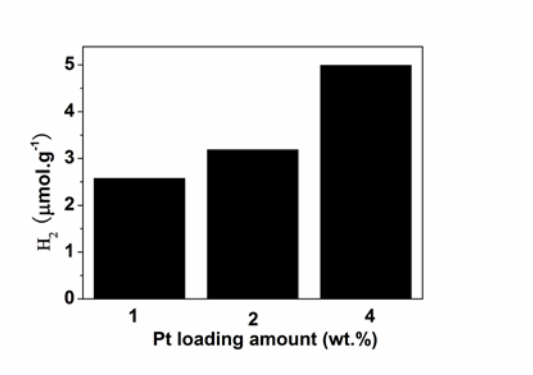

Fig. S8 Photocatalytic H_2 evolution amount at pH 4.0 after 3h visible-light ($\lambda > 420$ nm) irradiation for Pt-$InVO_4$ samples.

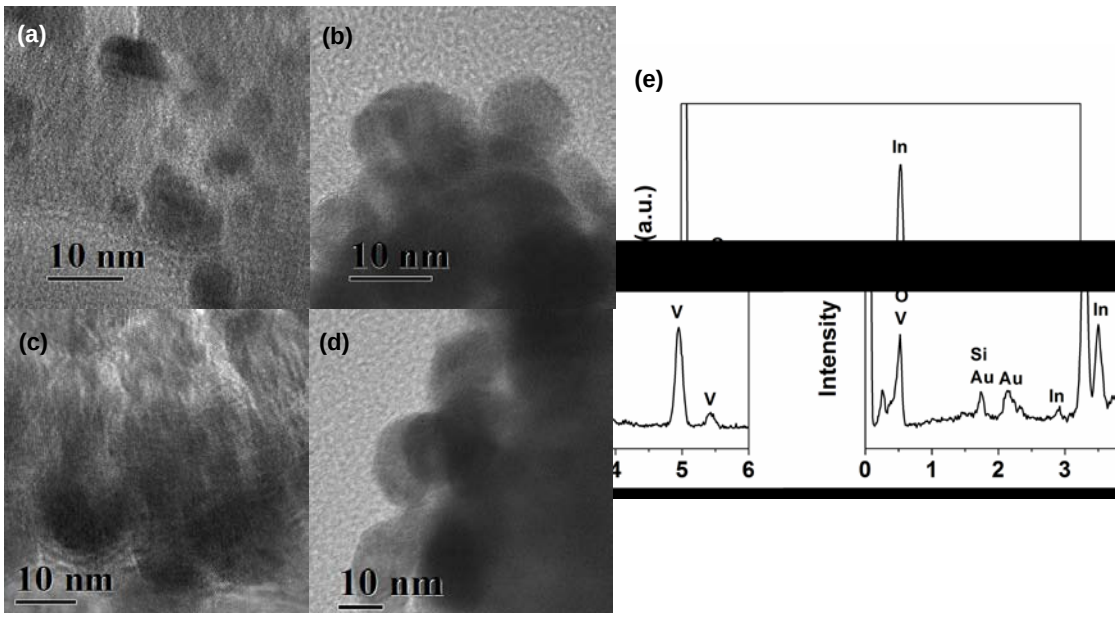

Fig. S9 TEM images for samples used in photocatalytic reaction after visible-light irradiation: (a) 2 wt% Au-$InVO_4$ at 3h; (b) 4 wt% Au-$InVO_4$ at 3h; (c) 7.5 wt% Au-$InVO_4$ at 3h; (d) 4 wt% Au-$InVO_4$ at 18h. (e) EDX spectrum for 4 wt% Au-$InVO_4$ after 18h visible-light irradiation.