Supporting Information

Polyoxometalate-based crystalline tubular microreactor: redox-active inorganic-organic hybrid materials producing gold nanoparticles and catalytic properties

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S1 Materials and Measurements

All the chemicals were obtained from commercial sources, and were used without further purification. Deionized water was used for all experiments. Elemental analyses (C, H and N) were measured on a Perkin-Elmer 2400 CHN elemental analyzer; Mo, Zn, Mn, P and Au were determined with ICP-OES Spectrometer (USA). IR spectrum was performed in the range 4000–400 cm^{-1} using KBr pellets on an Alpha Centaurt FT/IR spectrophotometer. The X-ray powder diffraction (XRPD) data were recorded on a Bruker D8 Advance diffractometer. Thermogravimetric analysis (TGA) of the samples was performed using a Perkin-Elmer TG-7 analyzer heated from room temperature to 700 ºC under nitrogen at the heating rate of 5 $°C \cdot min^{-1}$. UV/Vis spectroscopy was performed with a Varian Cary 50 spectrophotometer in the range of 250–800 nm. XPS analysis was performed on a thermo ECSALAB 250 spectrometer with an Al $K\alpha$ (1486.6 eV) achromatic X-ray source running at 15 kV. The XPS binding energy (BE) was internally referenced to the aliphatic C(1s) peak (BE, 284.6 eV). Field-emission scanning electron microscopy (FE SEM) images were obtained with a XL30 ESEM FEG microscope.

S2 Single-crystal X-ray diffraction

Suitable single crystal of **IFMC-100** was selected and mounted onto the end of a thin glass fiber using Fomblin oil. Single crystal X-ray diffraction data for **IFMC-100** were recorded on a Bruker APEXII CCD diffractometer with graphite-monochromated Mo K_α radiation (λ = 0.71069 Å) at 293 K. Absorption corrections were applied using multi-scan technique. The structure was solved by Direct Method of SHELXS-97[1] and refined by full-matrix least-squares techniques using the SHELXL-97 program[2] within WINGX.[3] Those hydrogen atoms attached to lattice water molecules were not located. The P(4) position is disordered into two parts with a total occupancy of 1. Hydrogen atoms on im ligand were placed on calculated positions and included in the refinement riding on their respective parent atoms.

Anisotropic thermal parameters were used to refine all non-hydrogen atoms except for part of oxygen and carbon atoms.

S3 the redox titration experiments

Firstly, prepare $KMnO_4$ solution (its concentration is approximately 0.01 $mol \cdot L^{-1}$). Note: The solution should be boiled for 2 hour in order to deoxidize, filtrated and then stored in a brown bottle. Secondly, calibrate the concentration of $KMnO_4$ solution with $Na_2C_2O_4$. Note: (a) addition of 25 drops H_2SO_4 (18 $mol \cdot L^{-1}$) to each sample solution; (b) 70 °C water bath. Thirdly, determine of the oxidation state of Mo. The titration method is similar with the second step; the only difference is that the sample is the mixture of a certain amount of **IFMC-100** and $Na_2C_2O_4$ or **Au@IFMC-100** and $Na_2C_2O_4$.

Conclusion: The redox titration of **IFMC-100** and **Au@IFMC-100** were carried out in acidic solutions against standardized $KMnO_4$ solution. The results showed that the oxidation state of Mo is ca. 5.0 in **IFMC-100** and ca. 5.1 in **Au@IFMC-100**, respectively, suggesting that the Mo was partially oxidized to +6 in **Au@IFMC-100**.

S4 Catalytic reduction of $K_3Fe(CN)_6$

The reduction of $K_3Fe(CN)_6$ was carried out in a quartz cuvette and monitored using UV/Vis spectroscopy at room temperature. In a typical reaction, 7.5 mg of **Au@IFMC-100** samples was added into 500 μL of 8×10^{-3} $mol \cdot L^{-1}$ $K_3Fe(CN)_6$ aqueous solution, followed by the rapid addition of 1000 μL of 4×10^{-2} $mol \cdot L^{-1}$ freshly prepared ice-cold $NaBH_4$ solution. The solution was then quickly subjected to UV/Vis measurement. As the reaction proceeds, the color of the solution changed from yellow to colorless. To further investigate the reusability of the **Au@IFMC-100** as catalysts, the used **Au@IFMC-100** was separated from the solution with centrifugation after the whole reduction process was complete. Similar to the above reduction process, the obtained **Au@IFMC-100** were redispersed in 500 μL of 8×10^{-3} $mol \cdot L^{-1}$ $K_3Fe(CN)_6$ and 1000 μL of 4×10^{-2} $mol \cdot L^{-1}$ ice-cold fresh $NaBH_4$.

The solution was measured using UV/Vis spectroscopy quickly. The abovementioned procedures were repeated 6 times. As shown in Fig. 3, the catalytic activity almost remains in the six runs of reaction, revealing the good stability of the catalyst. The absorption spectra of the solution were measured in the range of 300-800 nm. The rate constants of the reduction process were determined through measuring the change in absorbance at 420 nm as a function of time.

S5 Catalytic reduction of 4-nitrophenol (4-NPh)

The reduction of 4-NPh by $NaBH_4$ was chosen as a model reaction to test the catalytic activity of **Au@IFMC-100**. In general, the reaction proceeded under ambient conditions. The 4-NPh solution exhibited a strong absorption peak at 317 nm in neutral or acidic conditions. Upon the addition of $NaBH_4$ solution, the absorption peak of 4-NPh changed from 317 to 400 nm immediately, corresponding to the color change of light yellow to yellow-green due to the formation of 4-nitrophenolate ion (Fig. S9).[4] To a mixture of 2.3 mg of $NaBH_4$ dispersed in 1 mL ice-sold distilled water, 1 mL of 0.12×10^{-3} $mol\cdot L^{-1}$ 4-NPh was added. To this solution, 30 mg of catalyst (**Au@IFMC-100**) was added. After **Au@IFMC-100** was added, the characteristic absorption peak of 4-nitrophenolate ion at 400 nm gradually decreased, while a new peak at ~300 nm, ascribed to 4-APh, appeared.[5] The peak of the 4-nitrophenolate ions diminished after 600 s. The absorption spectra of the solution were measured in the range of 250-550 nm. The rate constants of the reduction process were determined through monitoring the change in absorbance at 400 nm as a function of time.

The reaction of 4-NPh with $NaBH_4$ in the presence of **IFMC-100** has also been performed under similar condition. The result suggests that **IFMC-100** can hardly catalyze this reaction (Fig. S10).

S6 Figures in Supporting Information

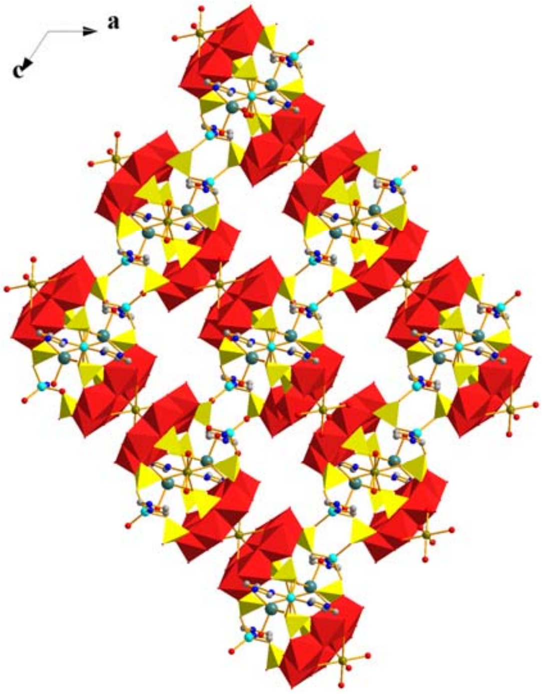


Fig. S1 The 1D channel observed running parallel to the *b* axis in **IFMC-100**.

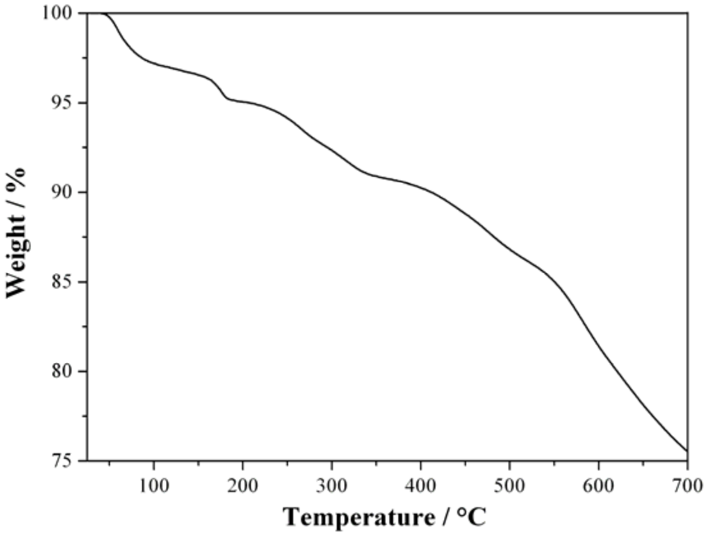


Fig. S2 The TGA curve of **IFMC-100** measured under N_2 atmosphere at the heating rate of 5 °C·min^{-1}.

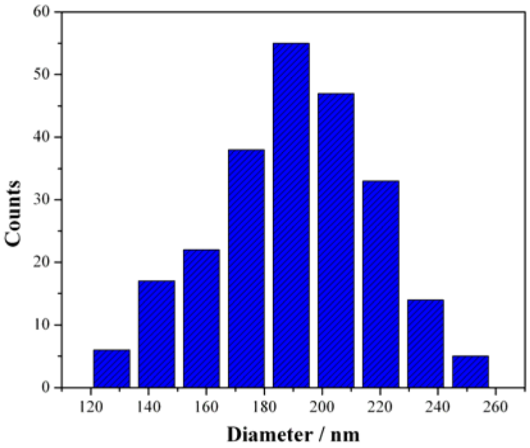


Fig. S3 The corresponding size distribution of Au nanoparticles.

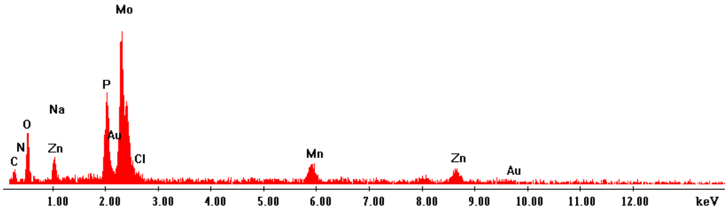
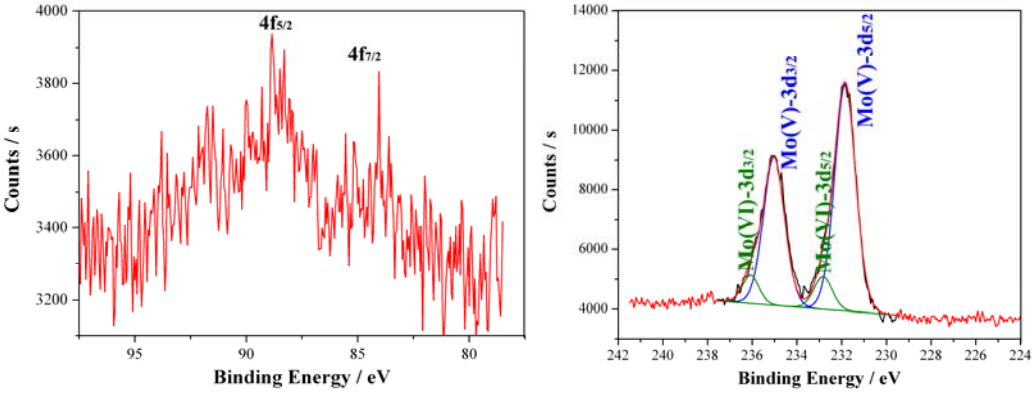


Fig. S4 EDS data for **Au@IFMC-100**.



(a)

(b)

Fig. S5 The XPS analysis of Au (a) and Mo (b) for **Au@ IFMC-100**.

Fig. S6 Color changes for $K_3[Fe(CN)_6]$ solutions before (left) and after (right) catalytic reaction. The red solid in quartz cuvette (right) are **Au@IFMC-100**.

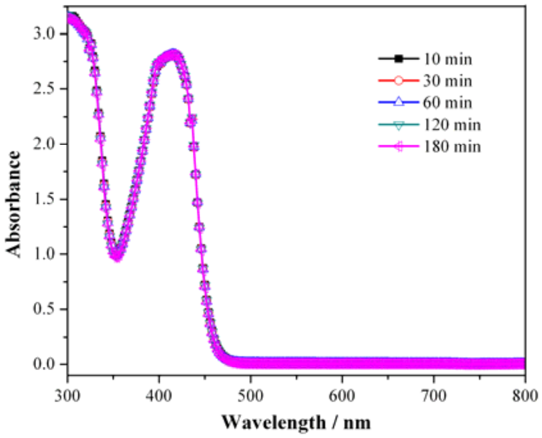
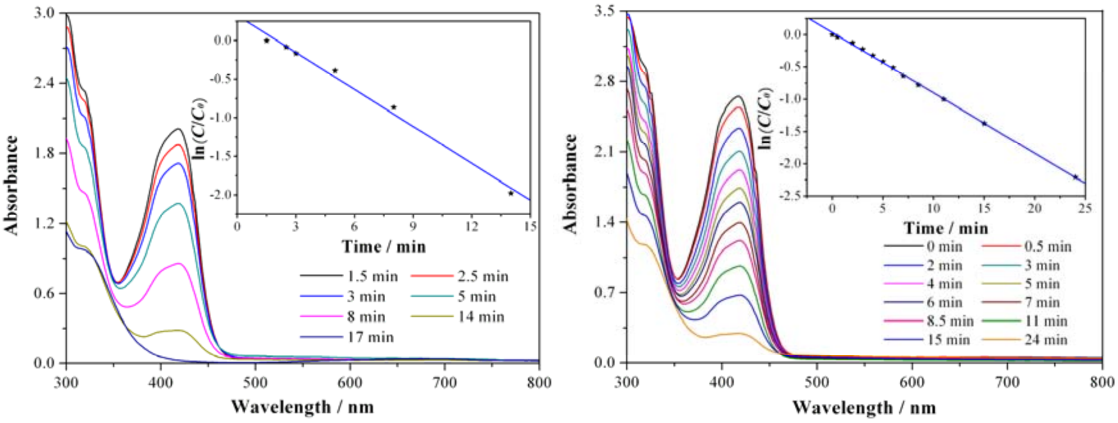
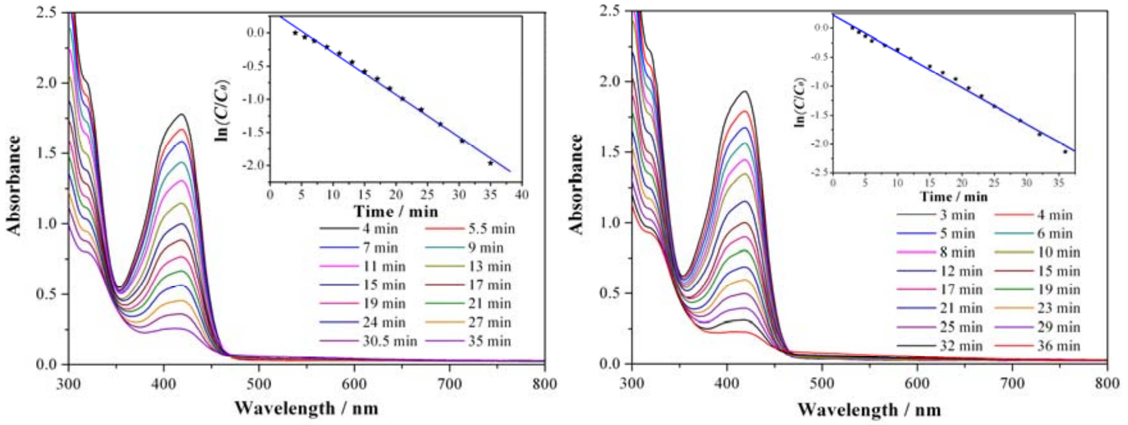


Fig. S7 UV/Vis spectra of only $K_3[Fe(CN)_6]$ and **Au@IFMC-100** in aqueous solution measured at different time.



(a) (b)



(c)

(d)

Fig. S8 UV/Vis spectra of the reduction of $K_3[Fe(CN)_6]$ by $NaBH_4$ in the presence of **IFMC-100** determined at different time, (a) for the 1st run, the rate constant k is 15.95×10^{-2} min^{-1}; (b) for the 2nd run, the rate constant k is 9.35×10^{-2} min^{-1}; (c) for the 3rd run, the rate constant k is 6.38×10^{-2} min^{-1}; (d) for the 4th run, the rate constant k is 6.26×10^{-2} min^{-1}.

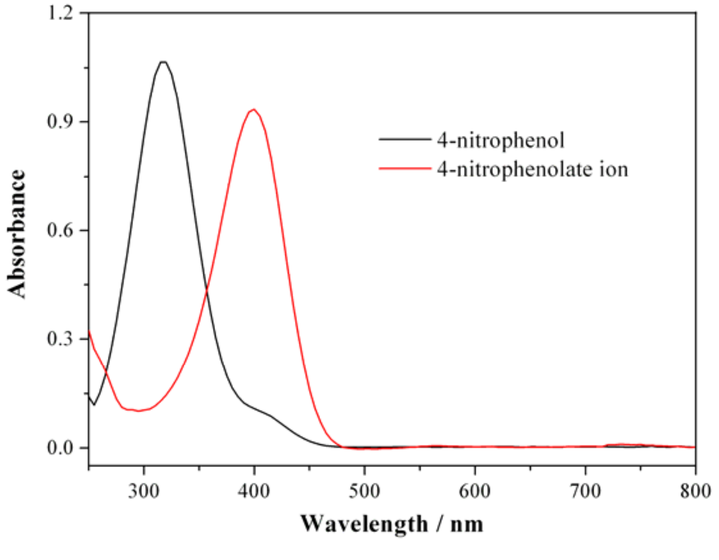


Fig. S9 The UV/Vis characteristic peaks of freshly prepared 4-nitrophenol and 4-nitrophenolate ion aqueous solution at 317 and 400 nm, respectively.

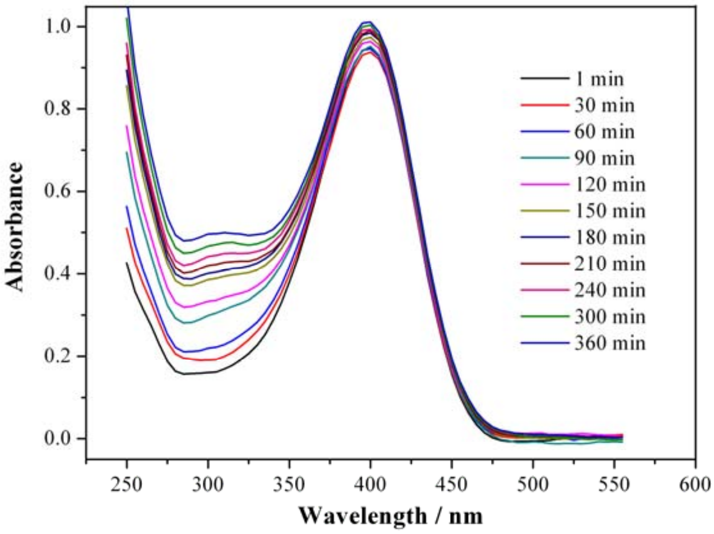


Fig. S10 UV/Vis spectra of 4-NPh and $NaBH_4$ in the presence of **IFMC-100** recorded at different time.

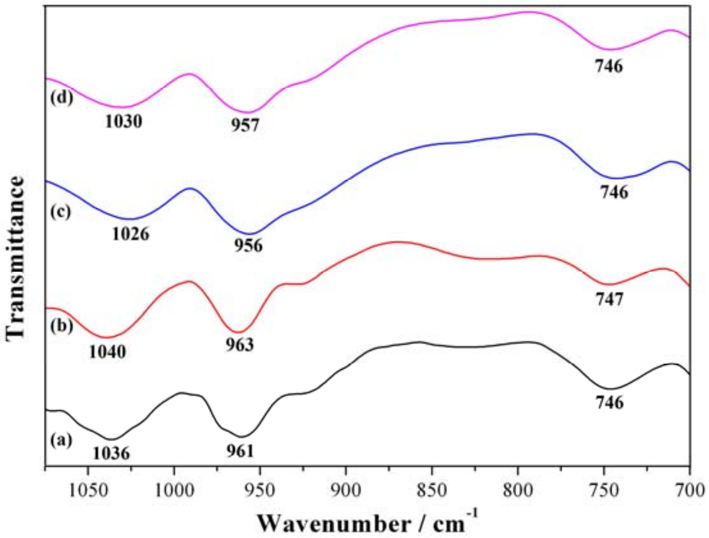


Fig. S11 The IR characteristic vibration peaks of (a) solid **IFMC-100**, (b) **Au@IFMC-100**, (c) and (d) **Au@IFMC-100** after catalyzed reduction of $K_3Fe(CN)_6$ and 4-NPh, respectively.

References

1 G. M. Sheldrick, SHELXS-97, *Programs for X-ray Crystal Structure Solution*, University of Göttingen: Göttingen, Germany, 1997.

2 G. M. Sheldrick, SHELXL-97, *Programs for X-ray Crystal Structure Refinement*, University of Göttingen: Göttingen, Germany, 1997.

3 L. J. Farrugia, WINGX, *A Windows Program for Crystal Structure Analysis*; University of Glasgow; Glasgow, UK, 1988.

4 S. Praharaj, S. Nath, S. K. Ghosh, S. Kundu and T. Pal, *Langmuir*, 2004, **20**, 9889–9892.

5 S. Tang, S. Vongehr and X. Meng, *J. Phys. Chem. C*, 2010, **114**, 977–982.