Electronic Supplementary Information (ESI)

Preparation of Organic-Inorganic Hybrid Fe-MoO$_x$/Polyaniline Nanorods as Efficient Catalysts for Alkene Epoxidation

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Experimental section:

The precursor of $Mo_3O_{10}(C_6H_5NH_3)_2{\cdot}2H_2O$ nanowires was prepared through co-precipitation process. 2.48 g of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$) was dissolved in 40 ml of distilled water, and 3.34 g of aniline was added into the above solution. Afterwards, aqueous HCl (1 M) was dropwise added with magnetic stirring at room temperature until white precipitate appeared (pH 4~5). After a reaction with stirring at 50 °C in oil bath for 2 hours, the product was filtrated and washed with ethanol, and dried at 50 °C. Other precursors of $Mo_8O_{24}(C_6H_5NH_3)_4{\cdot}2H_2O$ bulks and $Mo_6O_{19}(C_6H_5NH_3)_2$ needles were obtained through the similar process except changing the pH level to 2 and 1, respectively.

The synthesis of Fe-MoO$_x$/PANI nanorods was conducted as follow: 0.672 g of $Mo_3O_{10}(C_6H_5NH_3)_2{\cdot}2H_2O$ nanowires were dispersed in 20 mL of H_2O, and then 10 mL aqueous solution containing 0.162 g of $FeCl_3$ was added, using 1M HCl to adjust the pH level to 1. After treating at 50 °C for 2 hours, the deep-green product was filtrated and washed with water for 3 times, and then dried at 50 °C overnight. The synthesis of Fe-MoO$_x$/PANI employing with other precursors of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, $Mo_8O_{24}(C_6H_5NH_3)_4{\cdot}2H_2O$ and $Mo_6O_{19}(C_6H_5NH_3)_2$ was carried out through the similar process.

MoO$_x$/PANI nanorods were synthesized as follow: 0.672 g of $Mo_3O_{10}(C_6H_5NH_3)_2{\cdot}2H_2O$ nanowires were dispersed in 40 mL of H_2O, and then 0.572 g $(NH_4)_2S_2O_8$ was added. Afterwards, 1 M HCl aqueous solution was added until pH =1. After 5 hours reaction at room temperature, the deep-green product was filtrated and washed with water, and then dried at 50 °C overnight.

MoO_3 nanowires were obtained through calcining $Mo_3O_{10}(C_6H_5NH_3)_2{\cdot}2H_2O$ nanowires under air flow at 400 °C for 5 hours.

Physical measurement: XRD measurements were performed on a D8 Diffractometer from Bruker instruments (Cu Kα radiation, $\lambda = 0.154$ nm) equipped with a scintillation counter. TEM images were taken using a Zeiss EM 912Ω operated at an acceleration voltage of 120 kV. The samples were dispersed in ethanol by sonication and then supported onto a holey carbon film on a copper grid. EDS measurement for element mapping was carried out on FETEM (JEM-2100F). SEM measurement was performed on a LEO 1550 Gemini instrument. The samples were loaded on carbon coated stubs and coated by sputtering an Au/Pd alloy prior to imaging. The IR spectra were collected with a BIORAD FTS 6000 FTIR spectrometer, equipped with an attenuated total reflection (ATR) setup. Nitrogen sorption experiments were done with a Quantachrome Autosorb-1 or Quadrasorb at liquid nitrogen temperature, and data analysis were performed by Quantachrome software. All the samples were degassed at 150 ºC for 20 h before measurements. CHN elemental analysis was done using a Vario EL Elementar.

The epoxidation of cis-cyclooctene was carried out using t-butyl hydroperoxide (TBHP, 80 wt% in water) as an oxidizing agent. The experimental procedure is as follows: cis-cyclooctene (1.0 ml) and Mo-based catalyst (0.04 g) were stirred at ca. 60 ˚C in $CHCl_3$ (4.0 ml) and TBHP (2.4 ml) for 4 h. The product was analyzed by GC-MS using an internal standard technique. For the recycle test of Mo-catalysts, the catalyst was centrifuged out and washed with EtOH for 3 times, and then dried at 50 ˚C. The recycled catalysts were used the same as the process described above.

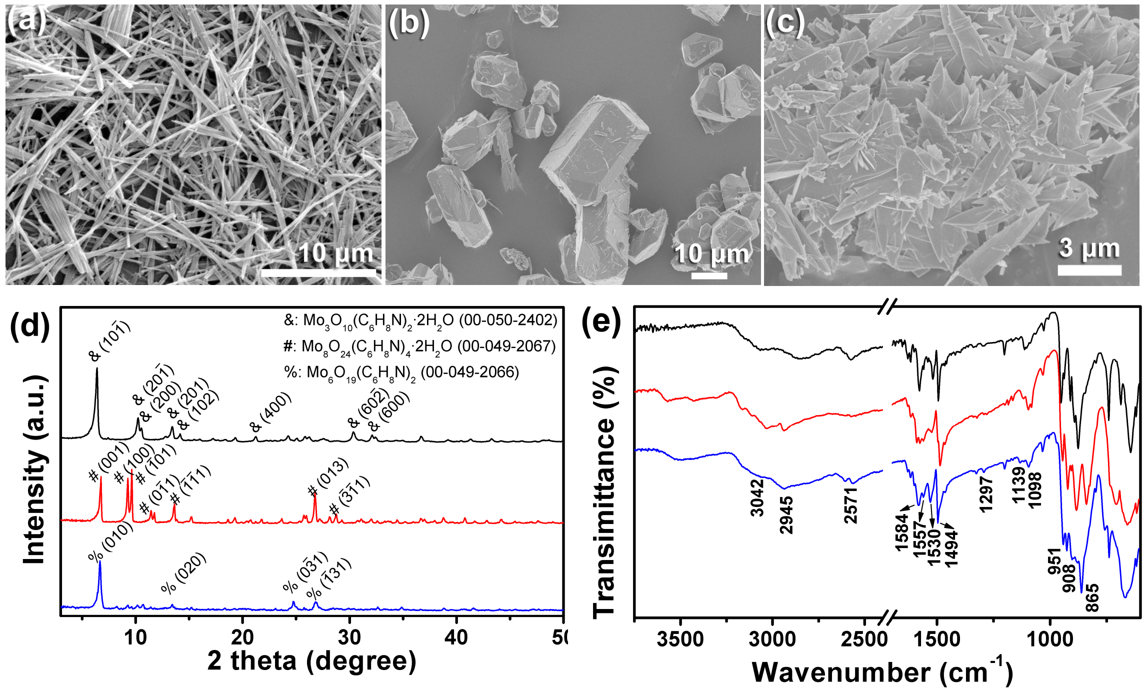

Fig. S1 SEM images of (a) $Mo_3O_{10}(C_6H_5NH_3)_2\cdot 2H_2O$ nanowires, (b) $Mo_8O_{24}(C_6H_5NH_3)_4\cdot 2H_2O$ bulks and (c) $Mo_6O_{19}(C_6H_5NH_3)_2$ needles precursors. (d) XRD patterns and (e) FT-IR spectra of (black) $Mo_3O_{10}(C_6H_5NH_3)_2\cdot 2H_2O$ nanowires, (red) $Mo_8O_{24}(C_6H_5NH_3)_4\cdot 2H_2O$ bulks and (blue) $Mo_6O_{19}(C_6H_5NH_3)_2$ needles. All the precursors present obvious aniline-molybdate hybrid components in their IR spectra. Taking $Mo_6O_{19}(C_6H_5NH_3)_2$ as example, the bands around 3042 and 2945 cm^{-1} are ascribed to the stretching vibration of C–H in benzene ring, and those at 1584, 1557, 1530 and 1494 cm^{-1} should be assigned to the characteristic vibration of benzene ring. The absorptions at 2571 and 1139 cm^{-1} are due to the stretching vibration of $–NH_3^+$ and C–N, respectively, while the peak of 1098 cm^{-1} is associated with the C–H bending vibration of benzenoid rings. Meanwhile, the stretching vibration of Mo=O and Mo–O bonds in molybdate are clearly detected at 951, 908 and 865 cm^{-1}.

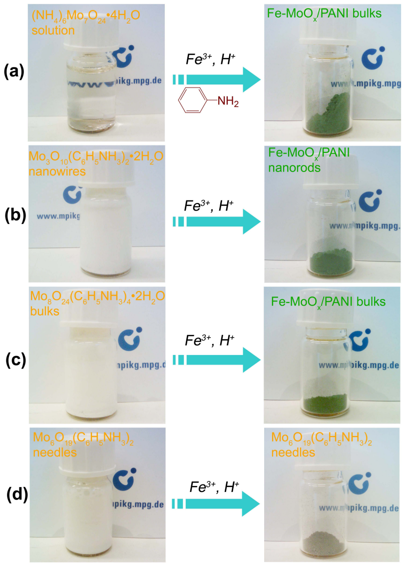

Fig. S2 Photographs for the synthetic process employing various precursors of (a) $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ solution, (b) $Mo_3O_{10}(C_6H_5NH_3)_2\cdot 2H_2O$ nanowires, (c) $Mo_8O_{24}(C_6H_5NH_3)_4\cdot 2H_2O$ bulks and (d) $Mo_6O_{19}(C_6H_5NH_3)_2$ needles.

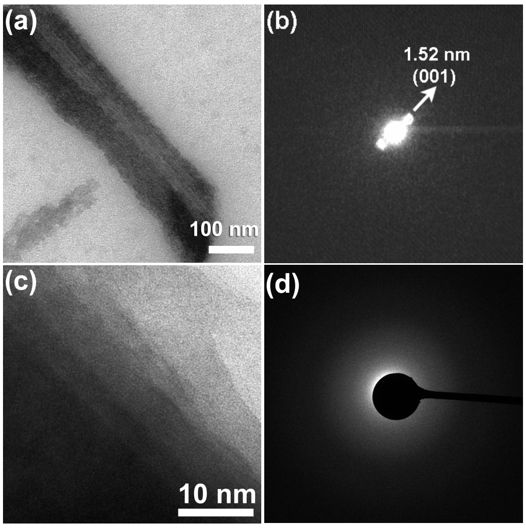

Fig. S3 (a) TEM image, (b) SAED pattern and (c) HR-TEM image of as-obtained Fe-MoO_x/PANI nanorods, and (d) SAED pattern obtained after HR-TEM. The SAED pattern (b) displays the diffraction of (001) in one dimension, which corresponds to the typical layered pattern in XRD investigation (Fig. 1d in manuscript). The HR-TEM image in c displays the ambiguous and destroyed lattice fringes, consistent with the diffused halo in its SAED pattern obtained after HR-TEM (d). It is indicated that the organic-inorganic hybrid crystal structure of Fe-MoO_x/PANI nanorods is not stable under electron-beam with high energy in HR-TEM.

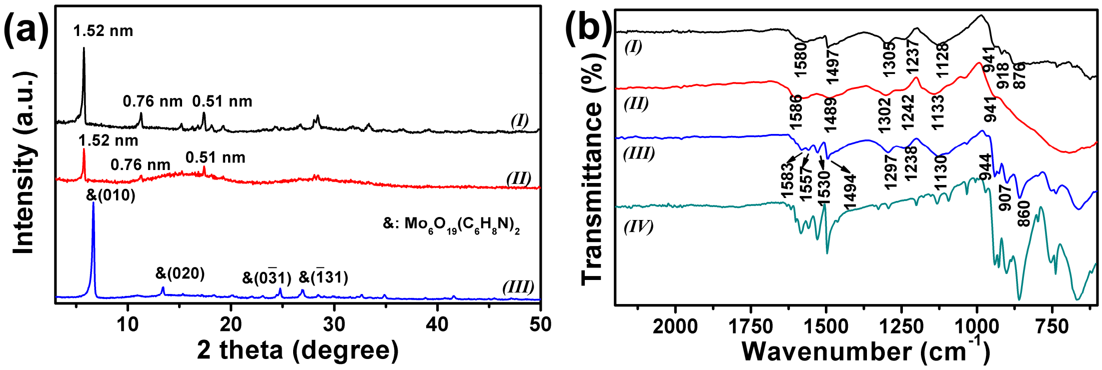

Fig. S4 (a) XRD patterns and (b) IR spectra of products fabricated using (I) $Mo_7O_{24}(NH_4)_6{\cdot}4H_2O$, (II) $Mo_8O_{26}(C_6H_5NH_3)_4{\cdot}2H_2O$ bulks and (III) $Mo_6O_{19}(C_6H_5NH_3)_2$ needles as precursors. The curve IV in b is the IR spectrum of $Mo_6O_{19}(C_6H_5NH_3)_2$ precursor.

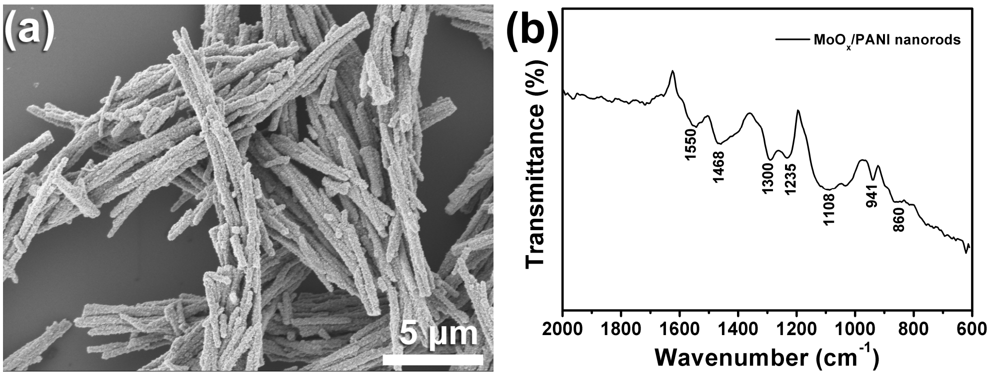

Fig. S5 (a) SEM image and (b) FT-IR spectrum of MoO_x/PANI nanorods synthesized from $Mo_3O_{10}(C_6H_5NH_3)_2{\cdot}2H_2O$ nanowires using $(NH_4)_2S_2O_8$ as initiator. In IR spectrum, the absorptions at 1550 and 1468 cm^{-1} are associated with the stretching vibration of quinonoid and benzenoid rings, respectively. The peaks at 1300 and 1235 cm^{-1} are assigned to C-N stretching vibration in quinonoid–benzenoid–quinonoid and benzenoid units, and the peak at 1108 cm^{-1} is attributed to bending vibrations of C-H in quinonoid and benzenoid rings. On the other hand, the bands at 941 and 860 cm^{-1} are associated with the stretching vibration of Mo=O and Mo-O-Mo in molybdate.

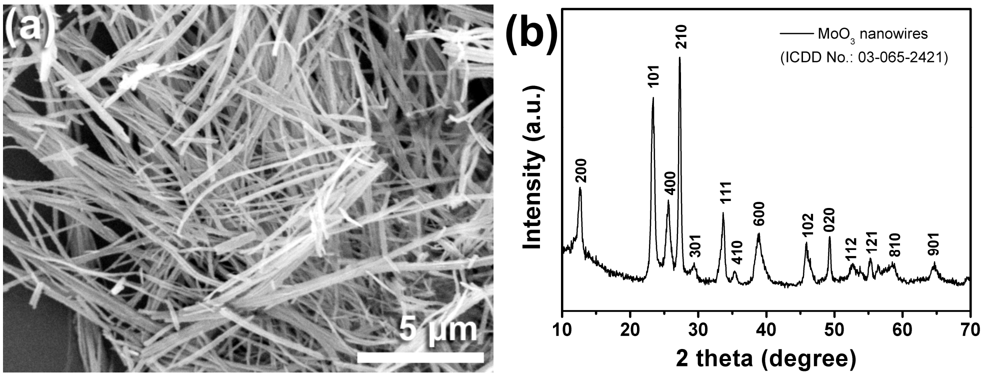

Fig. S6 (a) SEM image and (b) XRD pattern of MoO_3 nanowires obtained through calcining $Mo_3O_{10}(C_6H_5NH_3)_2 \cdot 2H_2O$ nanowires under air flow at 400°C for 5 hours.

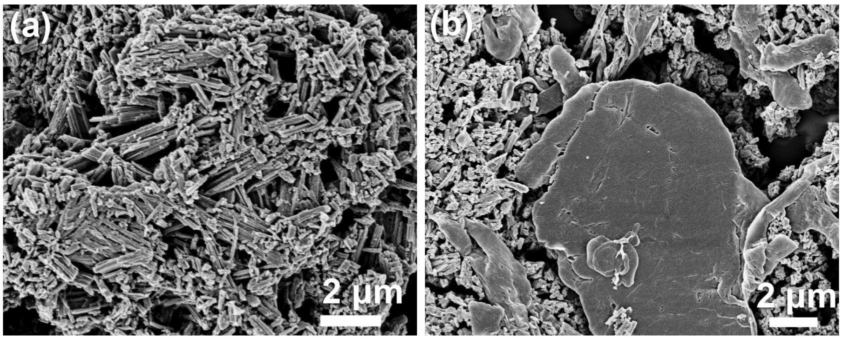

Fig. S7 SEM images of (a) Fe-MoO_x/PANI and (b) MoO_x/PANI nanorods after 3rd cycle for cyclooctene epoxidation.