Supporting Information

Liquid Metal/Metal Oxide Frameworks with Incorporated Ga_2O_3 for Photocatalysis

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Experimental detail

Synthesis of Ga_2O_3 nanoparticles: Ga_2O_3 nanoparticles were prepared by a solvothermal method reported earlier[1] and this method was modified slightly for this work.[1] In a typical synthesis procedure, 0.5 g of $Ga(NO_3)_3 \cdot xH_2O$ was dissolved in 2 ml of concentrated hydrochloric acid. It was evaporated repeatedly by adding water. To this 4.5 ml of ethylene glycol was added and the pH of the solution was adjusted to 10. A jelly like liquid was obtained and was transferred into a 9 ml autoclave. The autoclave was filled up to 80% with water. The overall water to ethylene glycol ratio was 2:3. The autoclave was kept in an oven at 195 °C for 6 hours and then cooled to room temperature. A white precipitate was obtained and washed with water and ethanol respectively. The solid product was dried in an oven at 80 °C.

Synthesis of LM/MO frameworks suspensions and Ga_2O_3 nanoparticles suspensions: Galinstan (Geratherm Medical AG, Geschwenda, Germany) was chosen as the source of LM/MO frameworks suspensions. 20 µL of bulk galinstan (108.9 mg) was added into 3 ml of DI water, yielding a concentration of 36.3 mg/ml. They were kept in a sonication bath (UNISONICS AUSTRALIA, FXP10DH, 240V AC, 5V, 50 Hz) at 25 °C for 20 min. 10 mg of Ga_2O_3 nanoparticles was added into 3 mL of DI water, yielding a suspension with a concentration of 3.33 mg/ml.

Synthesis of photocatalytic samples: For the samples consist of LM/MO frameworks and Ga_2O_3 nanoparticles, the amount of LM/MO frameworks was fixed and the amount of Ga_2O_3 nanoparticles was varied. 3.3 µl, 16.3 µl and 32.6 µl of Ga_2O_3 nanoparticle suspensions were added into 150 µl (~5.45 mg) of LM/MO frameworks suspensions and they were co-sonicated for 5 min, yielding different weight percentages of 0.2%, 1% and 2% (wt%), respectively. 150 µl

of LM/MO frameworks suspensions and 1.64 ml (~5.45 mg) of Ga_2O_3 nanoparticle suspensions were chosen as comparisons. Each working electrode was made by drop-casting the sample solution onto a fluorine doped tin oxide (FTO) glass substrate (1cm × 2cm) and dehydrated at 70 °C for 20 min.

Ga_2O_3	5.45mg
LM/MO	5.45mg
0.2 wt% Ga_2O_3	5.45mg(LM/MO) + 11μg(Ga_2O_3)
1 wt% Ga_2O_3	5.45mg(LM/MO) + 54μg(Ga_2O_3)
2 wt% Ga_2O_3	5.45mg(LM/MO) + 109μg(Ga_2O_3)

Photocatalytic activity: The samples were placed in the congo red (CR) solution for obtaining the time-concentration charts in order to assess and compare the photocatalytic properties. All samples were put in a quartz vial containing 2 ml of 10 μM CR, which was placed 15 cm away from a simulated solar lamp (Abet Technologies LS-150). The duration of a whole photocatalytic procedure was 120 min. During the procedure, the absorbance of CR solution at 500 nm was measured every 30 min in order to determine the photodegradation rate. 500 nm was chosen as a reference. The repeated photocatalysis experiments were carried out with fresh dye (congo red) solution for every cycle. Each cycle lasted 120 min (only responses from 0 to 60 min were shown).

Mott–Schottky measurements: Based on a three–electrode configuration, Mott–Schottky experiments were performed using a CH Instruments (CHI 413A) electrochemical analyzer. 0.3 M sodium sulfate solution with a pH of 7.0 was chosen as the electrolyte. Substrates with deposited LMMO frameworks and Ga_2O_3 nanoparticles were used as working electrodes. The

reference electrode was Ag/AgCl (aqueous 3 M KCl) and a platinum electrode was used as the auxiliary electrode.

Characterization: We utilized a FEI Nova NanoSEM and a HRTEM (JEOL 2100F) for SEM and TEM spectroscopy, respectively. A Bruker D8 DISCOVER micro-diffractometer was used for X-ray diffraction. For XPS measurements, a VG-310F instrument using Al non-monochromated X-rays (20 kV, 15 mA) with a hemispherical energy analyser was set at a pass energy of 100 eV for the survey spectrum and 20 eV for the peak scans. A VARIAN 50 Bio UV-Visible spectrophotometer was used for UV-Vis spectroscopy.

Table S1. Raw data of repeatability of photocatalysis

Time (min)	C/C_o (Cycle 1)	C/C_o (Cycle 2)	C/C_o (Cycle 3)	C/C_o (Cycle 4)
0	**1**	**1**	**1**	**1**
30	**0.2727**	**0.2705**	**0.2692**	**0.2683**
60	**0.0287**	**0.0289**	**0.0288**	**0.0282**
90	**0**	**0**	**0**	**0**
120	**0**	**0**	**0**	**0**

S1. Cross section of LM/MO framework film

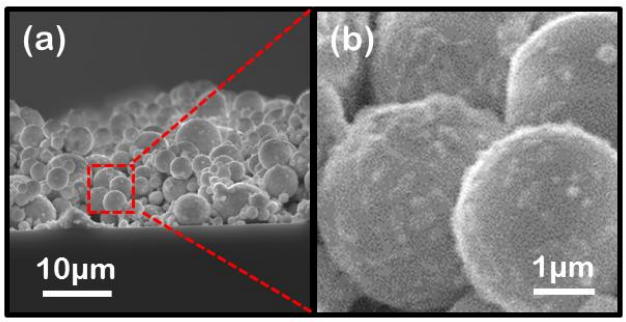

Figure S1. (a) SEM image of cross section of drop-casted LM/MO framework film. (b) The magnified picture.

S2. XRD of Ga_2O_3 nanoparticles

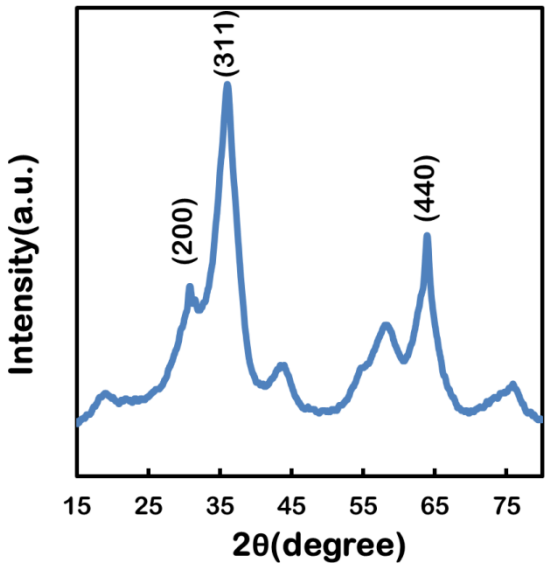

Figure S2. XRD spectrum of solvothermally synthesized Ga_2O_3 nanoparticles.

Figure S2 shows the X-ray diffraction (XRD) spectrum of solvothermally synthesized Ga_2O_3 nanoparticles. The pattern is consistent to that of γ-Ga_2O_3 which has been previously reported.[2]

S3. Low magnification images of LM/MO frameworks with different loadings of Ga_2O_3 nanoparticles

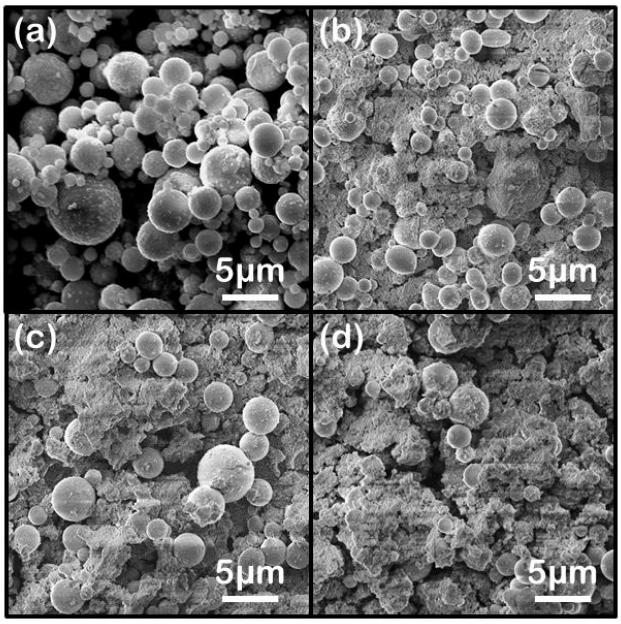

Figure S3. SEM images of LM/MO frameworks with different loadings of Ga_2O_3 nanoparticles: (a) 0 wt%, (b) 0.2 wt%, (c) 1 wt%, and (d) 2 wt%.

S4. UV-vis reflectance and transmission spectra of LM/MO with incorporated Ga_2O_3 nanoparticles

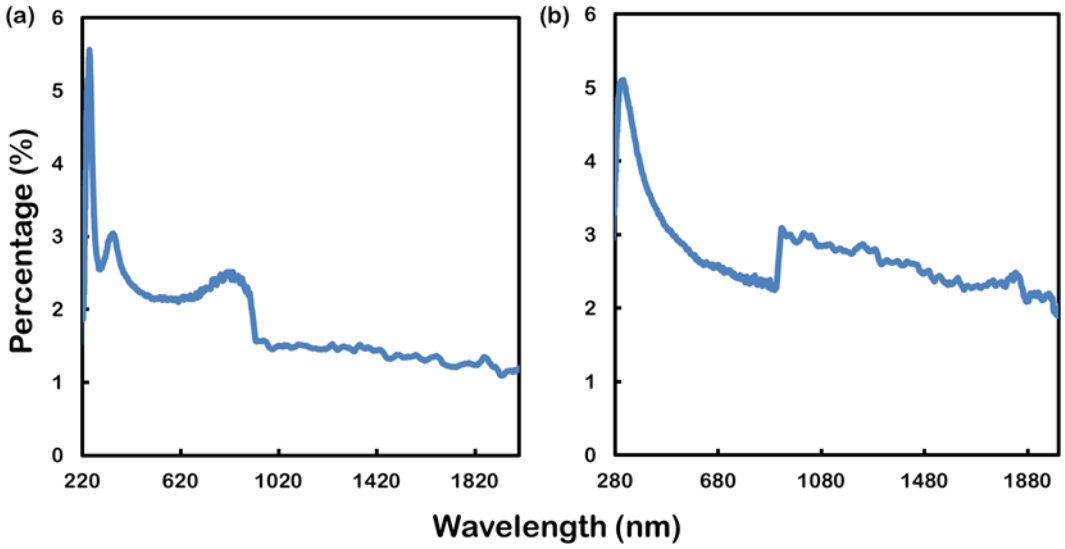

Figure S4. UV–vis (a) reflectance and (b) transmission spectra of LM/MO framework with 1 wt% Ga_2O_3 nanoparticles.

The references used for reflectance and transmission measurements are aluminum standard (>99.5% reflectance) and glass (~100% transmission) substrates, respectively. It is shown that around 2% of incoming light is reflected and about 2.5% of the light transmitted through the sample in the visible light range, which means nearly 95 % of light is absorbed.

S5. Photocatalytic activities of LM/MO frameworks with different loadings of Ga_2O_3 nanoparticles

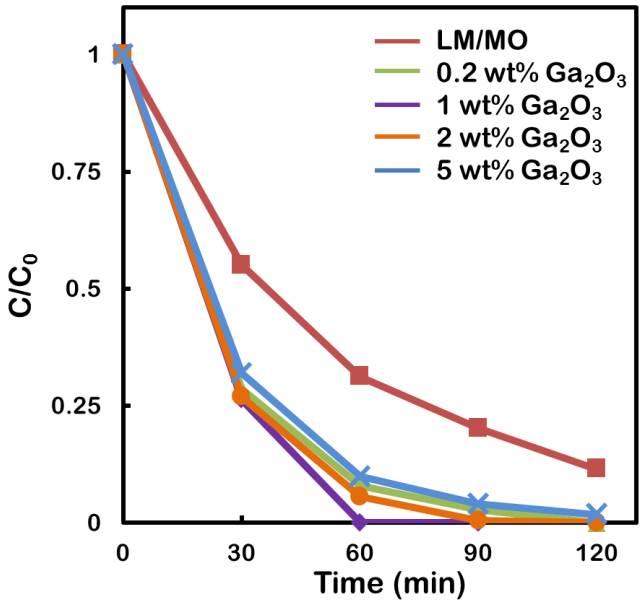

Figure S5. Degradation of 10 µM CR in the presence of LM/MO frameworks and LM/MO frameworks with incorporated different loadings of Ga_2O_3 nanoparticles.

S6. Photocatalytic activities of aluminium particles with incorporated 1 wt% Ga_2O_3 nanoparticles

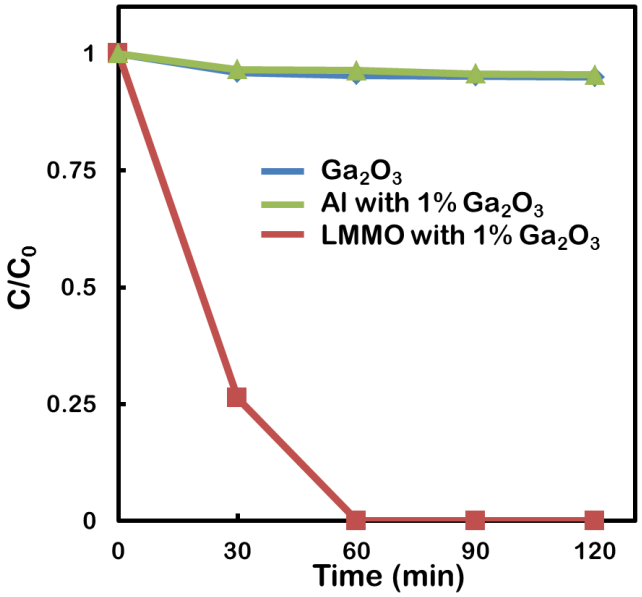

Figure S6. Degradation of 10 µM CR in the presence of Ga_2O_3 nanoparticles, LM/MO frameworks with incorporated 1 wt% Ga_2O_3 and aluminium particles with incorporated 1 wt% Ga_2O_3 nanoparticles.

The weight of aluminium particles is kept the same as LM/MO frameworks. It is observed that the photocatalytic efficiency of aluminum particles with 1 wt% Ga_2O_3 is very low, and is almost the same as the sample made of pure Ga_2O_3 nanoparticles.

S7. Linear sweep voltammogram of LM/MO framework with incorporated 1 wt% Ga_2O_3 nanoparticles

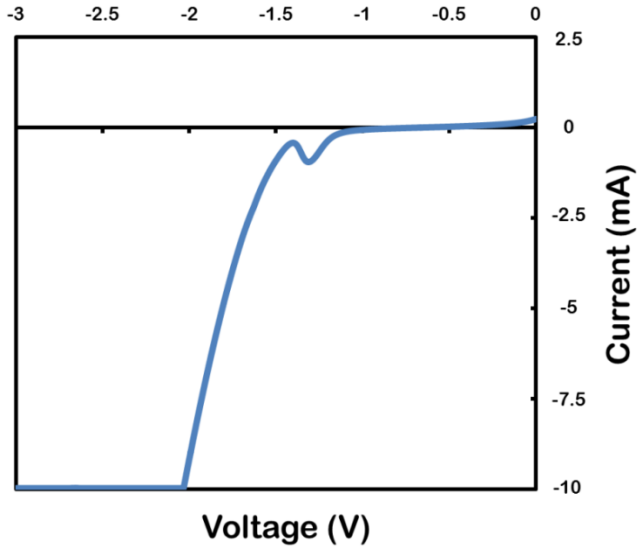

Figure S7. Linear sweep voltammogram of LM/MO framework with incorporated 1 wt% Ga_2O_3 nanoparticles.

As can be seen in Figure S7, during the sweep, the response is capacitive from 0 to −1.2 V range. For voltages lower than −1.2 V, a peak can be observed, which can be ascribed to the reduction of sub-stoichiometric gallium oxide. When the applied voltage is below −1.4 V, the current increases dramatically and hydrogen evolution is observed. For voltages more negative than −2 V, the current is beyond the maximum measurement value, so the plot shows an overflow.

In Figure 5(a), the Mott–Schottky plot is linear from 0 to −1.2 V. Once the applied voltage reaches below −1.2 V, the Mott–Schottky plot loses its linear relationship, which can be ascribed to the same electrochemical reactions seen during the I-V measurements.

S8. Cyclic voltammogram of LM/MO framework with incorporated 1 wt% Ga_2O_3 nanoparticles

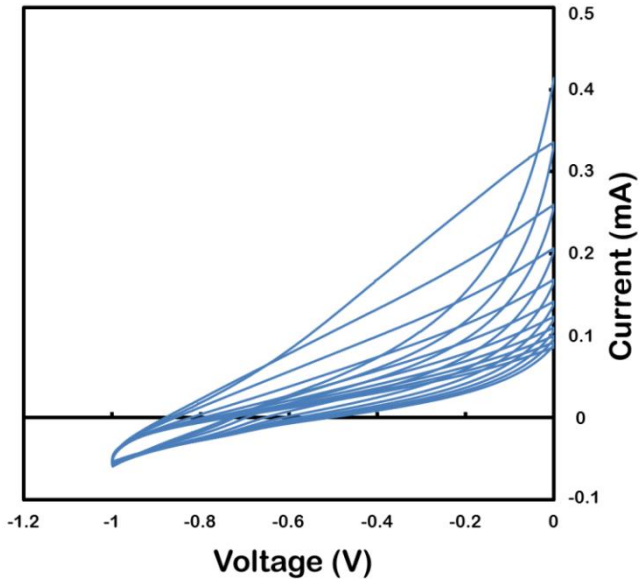

Figure S8. Cyclic voltammogram of LM/MO framework with incorporated 1 wt% Ga_2O_3 nanoparticles.

The first 10 cycles of cyclic voltammograms of LM/MO frameworks with incorporated 1 wt% Ga_2O_3 nanoparticles are shown in Figure S8. After about 8 cycles, the sample was relatively stabilized. The voltage range is from 0 to −1 V. In this range, no metallic stripping peaks are observed and the response appears to be capacitive in nature.

S9. XPS valence band spectra of Ga_2O_3 nanoparticles, LM/MO frameworks and LM/MO frameworks with different loadings of Ga_2O_3 nanoparticles.

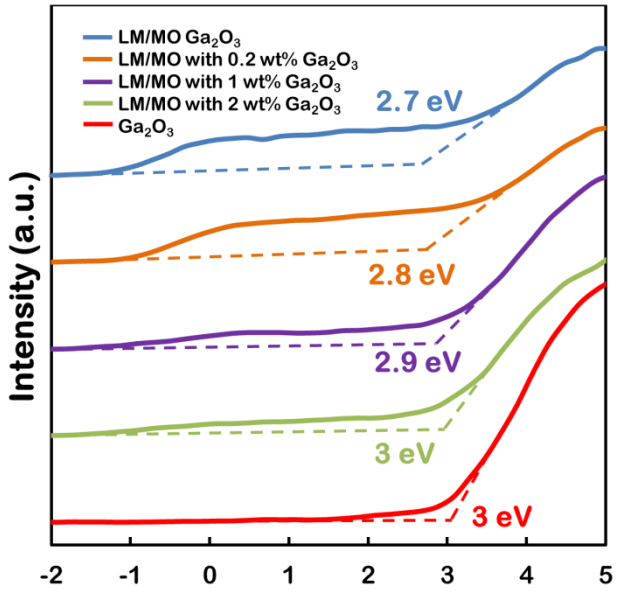

Figure S9. XPS valence band spectra of Ga_2O_3 nanoparticles, LM/MO frameworks and LM/MO frameworks with different loading of Ga_2O_3 nanoparticles.

REFERENCES

(1) Sinha, G.; Patra, A., Generation of Green, Red and White Light From Rare-Earth Doped Ga_2O_3 Nanoparticles. *Chem. Phys. Lett.* **2009**, *473*, 151-154.

(2) Huang, C.-C.; Yeh, C.-S., GaOOH, and β- and γ-Ga_2O_3 Nanowires: Preparation and Photoluminescence. *New J. Chem.* **2010**, *34*, 103-107.