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Electronic Supplementary Information

Self-assembly of urchin-like porphyrin/graphene microspheres for artificial photosynthetic production of formic acid from CO_2

Qi Li,[‡a] Qi Zeng,[‡ab] Lina Gao,[a] Zaka Ullah,[a] Hui Li,[c] Yufen Guo,[a] Weiwei Li,[a] Ying Shi,[c] Guanhong Tao,[*b] and Liwei Liu[*a]

[a] Key Laboratory of Nanodevices and Applications-CAS & Collaborative Innovation Center of Suzhou Nano Science and Technology, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou, Jiangsu, 215123, China.

[b] College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, Jiangsu, 215123, China.

[c] Institute of Atomic and Molecular Physics, Jilin University, Changchun, 130012, China.

* Correspondence should be addressed to Liwei Liu (lwliu2007@sinano.ac.cn) and Guanhong Tao (taogh@suda.edu.cn)

Experimental methods for the synthesis, optimization, and characterization of the photocatalyst materials

Photoelectrochemical measurements

A three-electrode system was used to measure the photoelectrochemical performance of the prepared samples using a CHI630D (CH Instruments, Inc., USA) electrochemical work station. The measurements were carried out in a 0.1 M NaCl solution containing 0.4 M Triethanolamine (TEOA) at room temperature. The same weight of TkisAPP, rGO, rGO microspheres, TkisAPP/G and TkisAPP/G microspheres was used as the working electrode, respectively. Platinum foil was utilized as the counter electrode and reversible AgCl/Ag was used as the reference electrode. Solar simulator (CHF-500W, TrusTech., China) was used as a light source. Light intensity was measured by VSLI standard incorporated Power & Energy Meter (PM100D, Thorlabs, USA).

Photochemical regeneration of NADH

The photochemical regeneration of NADH was performed within a quartz reactor under an inert atmosphere at room temperature, and a 500 W Xenon lamp was used (CHF-50 0W) as a light source. The reaction for photocatalytic regeneration of NADH was performed in a quartz reactor. The reaction was composed with β-NAD (1.24 μmol), rhodium complex (0.62 μmol), TEOA (1.24 mmol), and photocatalyst (0.5 mg) in 3.1 ml of sodium phosphate buffer (100 mM, pH 7.0). The regeneration of NADH was monitored through a spectrophotometer (PerkinElmer Lambda 750, USA).

Photosynthetic production of formic acid from CO_2

The photocatalyst (0.5 mg), β-NAD (1.25 μmol), rhodium complex (0.62 μmol), TEOA (1.25 mmol) and formate dehydrogenase (9 units) in 3.1 ml of sodium phosphate buffer (100 mM, pH 7.0), with TEOA (1.24 mmol) and continued bubbling into CO_2 (flow rate: 0.5 ml min^{-1}). After bubbling of CO_2 for 1 h in absence of light (light off), the reactor was exposed to visible light (light on) by light source Xenon lamp (CHF-XM-500W) with a 400-800 nm cutoff filter. After completion of the reaction and filtering the mixture by silica gel column, the formic acid was detected by high performance liquid chromatography.

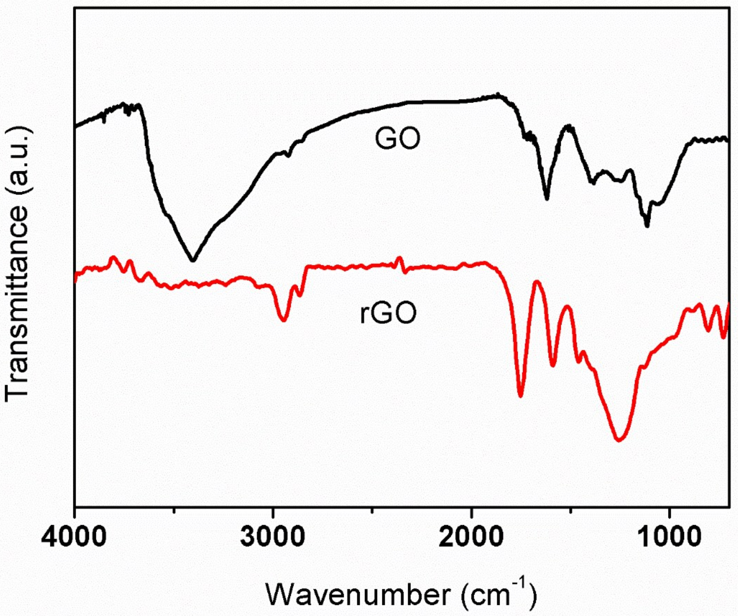

Fig. S1 The FTIR spectra of pure GO, and rGO. After the reduction of GO with citric acid at microwave oven, there was a dramatic decrease in the intensities of the peaks corresponding to the oxygen functionalities, such as the –C-O-C stretching vibration peak at 1100 cm^{-1} and the -OH deformation vibration peaks at 3408 cm^{-1}and 1394 cm^{-1}. The intensity of the C-O peak at 1249 cm^{-1} was also decreased slightly in the rGO. However, the C=O stretching peak at 1740 cm^{-1} was remained unchanged significantly in the rGO. This is attributed to the partial reduction of GO to graphene.

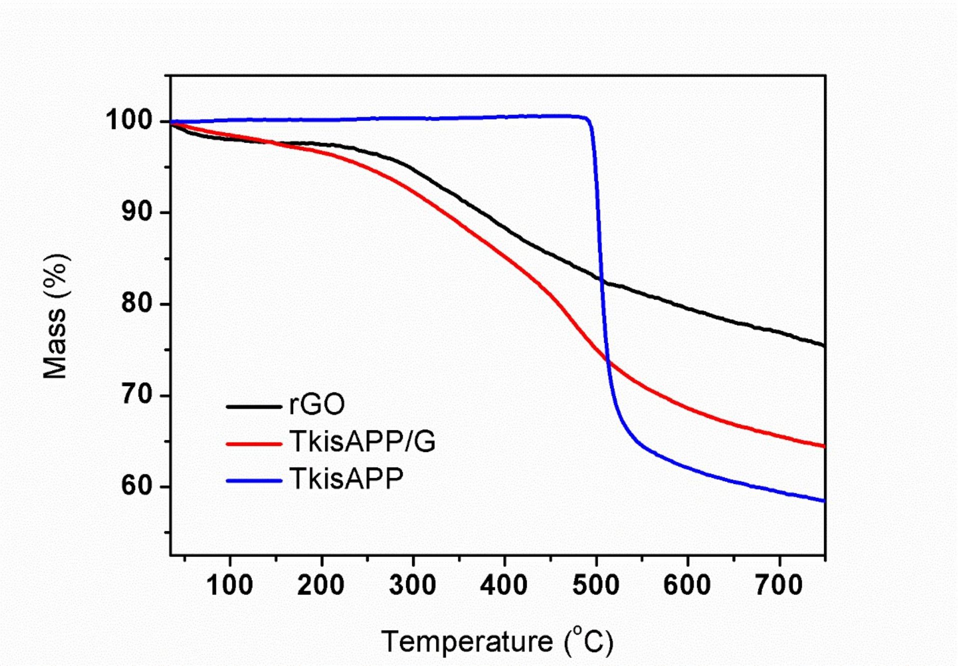

Fig. S2 Thermogravimetric analysis (TGA) was used to investigate the thermal properties of TkisAPP/G, as shown above. The curves for TkisAPP were quite stable in temperature range 25-500 °C. Contrary to this, a slight weight loss of rGO and TkisAPP/G occurred at 100 °C. This was due to the loss of residual water between the adjacent hydrophilic graphene sheets. The mass loss above 200 °C was attributed to the decomposition of oxygen functional groups –COOH, and carbon networks, as evidenced by the FTIR spectra and XPS analysis (Fig. 2). According to the TGA data, the TkisAPP/G showed thermal stabilities similar with rGO. These features of TkisAPP/G account for 26.1 % of the initial weight loss.

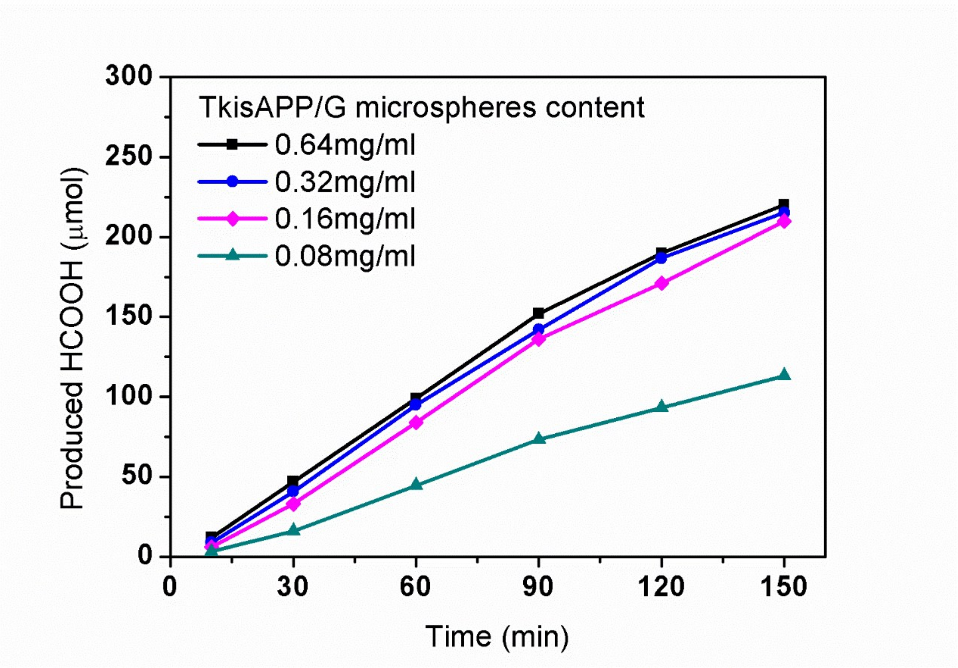

Fig. S3 The influence of TkisAPP/G microspheres concentration on production of formic acid from CO_2.

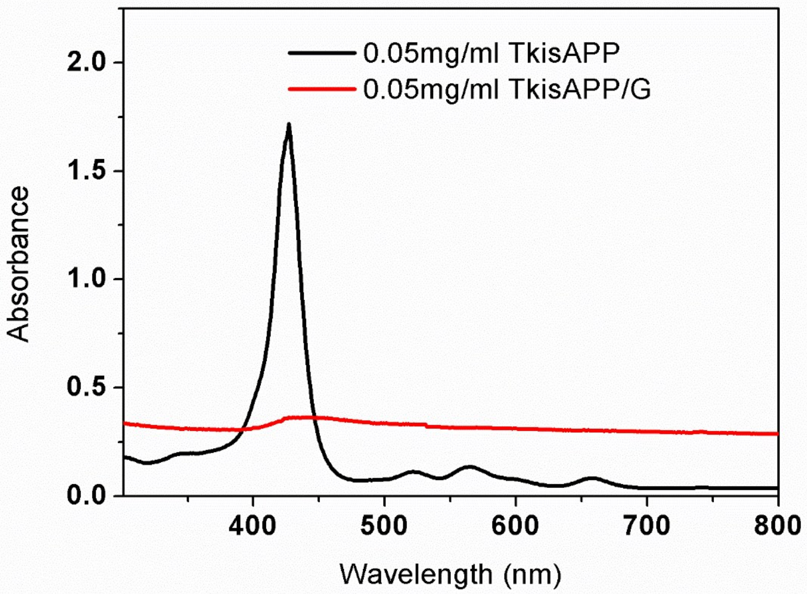

Fig. S4 Absorption of the TkisAPP/G and TkisAPP.

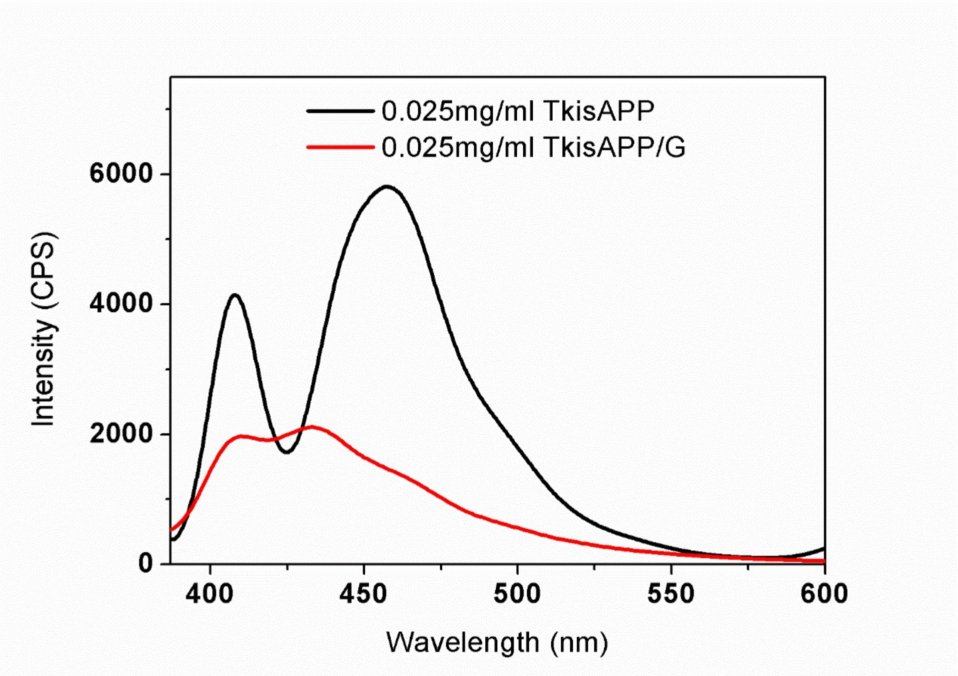

Fig. S5 The fluorescence (λ_{ex}=457nm) measurements of TkisAPP and TkisAPP/G.

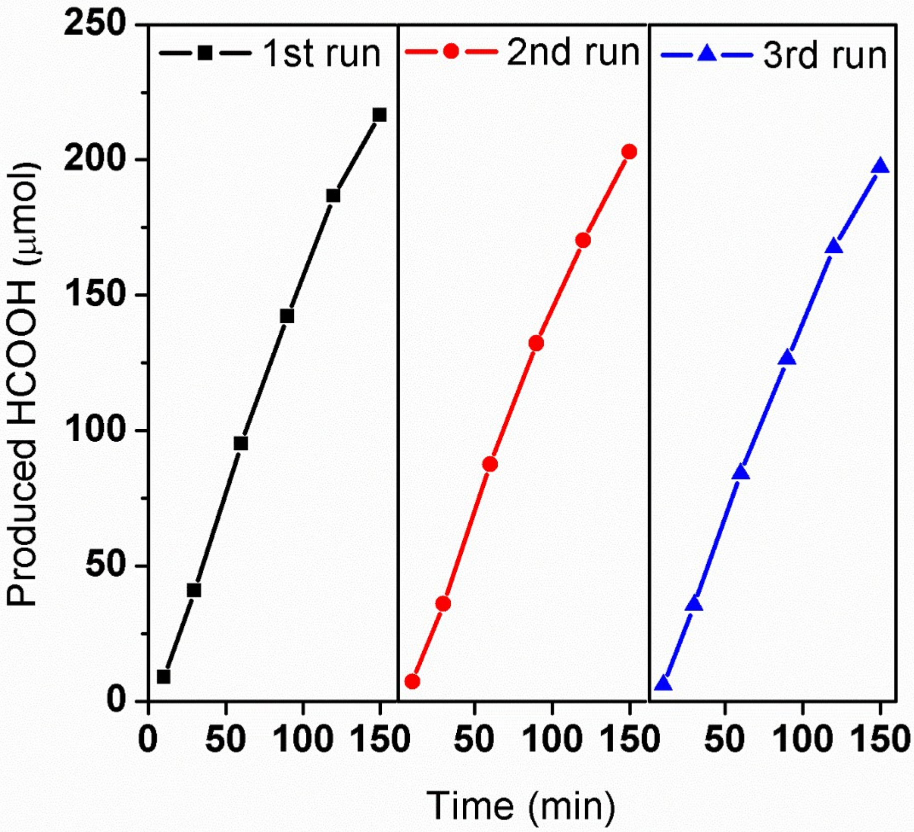

Fig. S6 Cycling measurements of visible-light driven artificial photosynthesis for production of formic acid from CO_2 by TkisAPP/G microspheres. The photocatalyst shows good photo-stability under visible light irradiation.

Table S1 Transient absorption kinetics lifetimes of TkisAPP and TkisAPP/G by global analysis. The meaning of proportion is the deviation percentage.

System	τ_1 (ps)	τ_2 (ps)
TkisAPP	22.03±7.74 (35.13%)	675.40±186.00 (27.5%)
TkisAPP/G	0.15±0.05 (35.3%)	33.78±7.94 (23.5%)

Table S2 Important reports on photocatalytic reduction of CO_2 to solar fuels/formic acid.

Light source	**Catalyst**	**Products**	**Efficiency (%)**	**Year**
Sunlight	Porphyrin/graphene microspheres	Formic acid	η: 0.5	2016 [Current Work]
Sunlight	r-STO/InP/[RuCP] system	Formic acid	η: 0.08	2013 [1]
Xe arc lamp	GaN	Formic acid	FE: 3	2011 [2]
Sunlight	[Ru-dcbpy]/NTa_2O_5	Formic acid	QE: 1.9	2010 [3]

η: Conversion Efficiency, QE: Quantum Efficiency, FE: Faradaic Efficiency

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