Electronic Supplementary Information (ESI) for:

Hydrogenative cyclization of levulinic acid into γ-valerolactone by photocatalytic intermolecular hydrogen transfer

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Assignment of isopropyl levulinate (IL) Based on the analysis with Gas Chromatograph-Mass Spectrometer (GC-MS), the mass spectrum of the appointed peak (RT=7.33 min) in Gas Chromatograph (GC) spectrum (Fig. S1) is consistent with IL standard MS spectrum collected in data base of GC-MS. The similarity reaches to 98%, shown in Fig. S2. We also prepared IL by acid catalytic route using mixture of LA/ isopropanol and analyzed it with GC and GC-MS. Its retention time (7.33 min) in GC is the same as the appointed peak and its mass spectrum is consistent with spectrum in Fig. S2a.

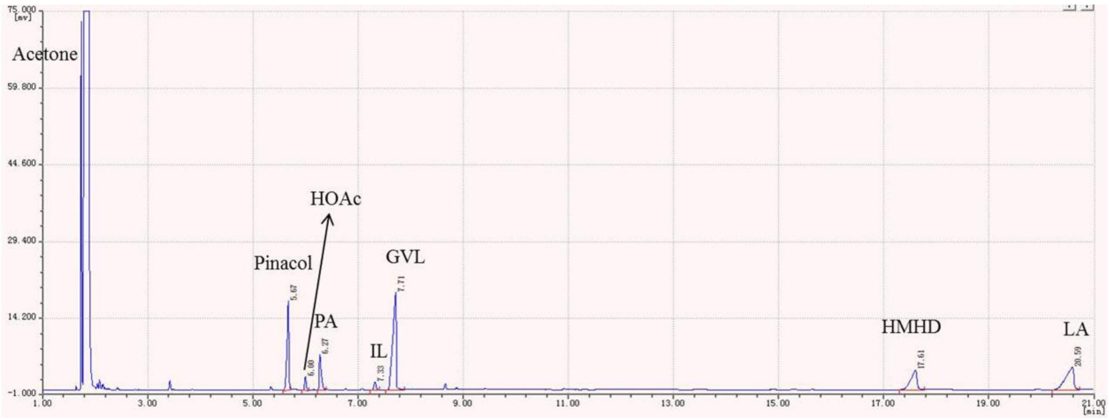


Figure S1. GC spectrum of liquid products.

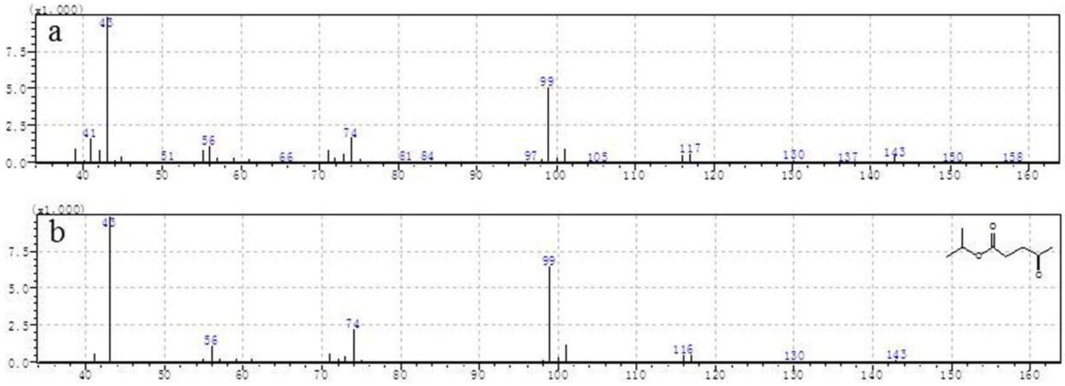


Figure S2. a) Measured mass spectrum; b) Standard mass spectrum collected in data base of GC-MS for isopropyl levulinate (IL).

Assignment of 6-hydroxy-6-methylheptane-2,5-dione (HMHD): GC spectrum (Fig. S1) displays that retention time of IL is 7.33 min, while another peak is located at retention time 17.61 min. Clearly, they are two different products. The mass spectrum (RT=17.61 min) shows in Fig.S3. By analysis of related ion fragments, it is well assign to 6-hydroxy-6-methylheptane-2,5-dione (HMHD).

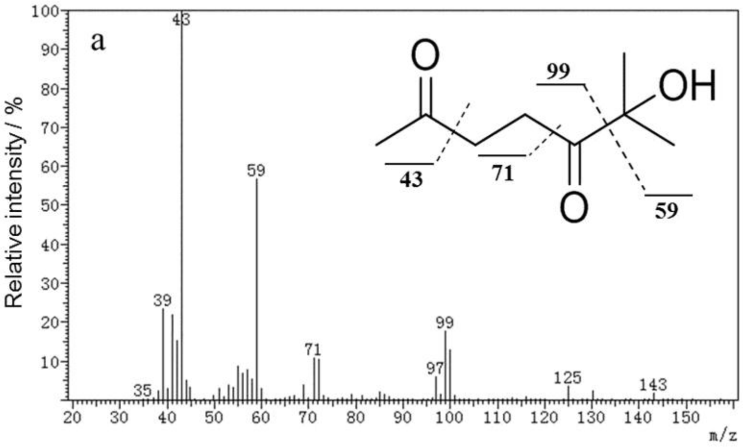
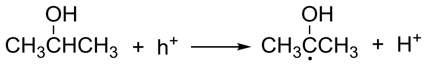


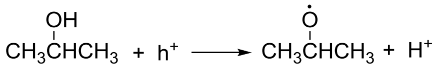
Figure S3. Mass spectrum of product located at 17.61min retention time in GC and schematic diagram of related ion fragments.

Quantitative analysis HMHD: Because HMHD is a new compound, we cannot buy it directly. Its concentration was estimated from peak-area analysis of GC and LA peak-area was used as reference.

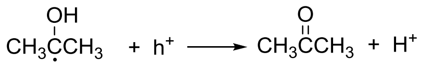
Mechanism of isopropanol oxidation and pinacol formation: As indicated by the EPR analysis, both $(CH_3)_2COH$ and $(CH_3)_2CHO$ radicals are first produced from hole-induced isopropanol oxidation, derived from the cleavage of O-H and α-C-H bond, respectively (equations 1 and 2). The two radicals can be further oxidized by holes to produce acetone (equations 3 and 4). Alternatively, the $(CH3)_2COH$ radicals can behave a C-C coupling reaction to produce pinacol (equation 5).



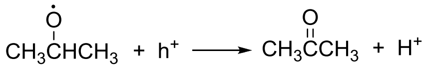
$$CH_3\overset{OH}{C}HCH_3 + h^+ \longrightarrow CH_3\underset{\bullet}{\overset{OH}{C}}CH_3 + H^+ \qquad (1)$$



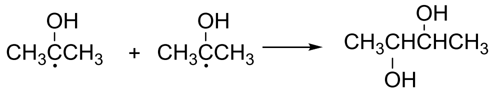
$$CH_3\overset{OH}{C}HCH_3 + h^+ \longrightarrow CH_3\overset{\dot{O}}{C}HCH_3 + H^+ \qquad (2)$$



$$CH_3\underset{\bullet}{\overset{OH}{C}}CH_3 + h^+ \longrightarrow CH_3\overset{O}{\overset{\|}{C}}CH_3 + H^+ \qquad (3)$$

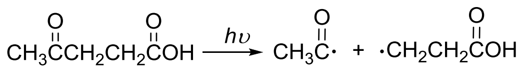


$$CH_3\overset{\dot{O}}{C}HCH_3 + h^+ \longrightarrow CH_3\overset{O}{\overset{\|}{C}}CH_3 + H^+ \qquad (4)$$

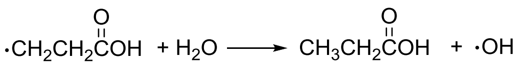


$$CH_3\underset{\bullet}{\overset{OH}{C}}CH_3 + CH_3\underset{\bullet}{\overset{OH}{C}}CH_3 \longrightarrow CH_3\underset{OH}{C}H\overset{OH}{C}HCH_3 \qquad (5)$$

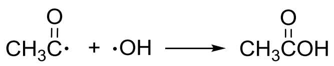
Mechanism of LA photolysis: Based on the fact that the hydrogenative cyclization of LA can by-produce water stoichiometrically, the photolysis of LA into PA and HOAc likely following a water-facilitated mechanism:



$$CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}OH \xrightarrow{h\upsilon} CH_3\overset{O}{\overset{\|}{C}}\cdot + \cdot CH_2CH_2\overset{O}{\overset{\|}{C}}OH \qquad (6)$$



$$\cdot CH_2CH_2\overset{O}{\overset{\|}{C}}OH + H_2O \longrightarrow CH_3CH_2\overset{O}{\overset{\|}{C}}OH + \cdot OH \qquad (7)$$



$$CH_3\overset{O}{\overset{\|}{C}}\cdot + \cdot OH \longrightarrow CH_3\overset{O}{\overset{\|}{C}}OH \qquad (8)$$

Table S1. A comparison with previous reported H_2-fed thermocatalysis in reaction efficiency and catalyst-utilization efficiency.

Catalyst	Active Metal(wt%)	LA feeding (mmol)	P H_2 (MPa)	T(^oC)	time(h)	LA Conv.(%)	GVL Sel.(%)	Rate I [a] (mmol $h^{-1}g^{-1}$)	Rate II[b] (mmol $h^{-1}g^{-1}$)	Ref.
Cu/ZrO_2 (0.5g)	35	43.1	3.45	200	5	100	100	17.2	49.3	15
Ru/C (0.6g)	5	108	1.2	130	2.7	99	92	60.72	1214.4	18
Ru/C (0.025g)	5	4.31	1.2	130	2.7	98.8	97.7	61.6	1231.7	19
Au/RA-TiO_2 (0.05g)	0.5	20	No need	RT(light)	9	79	85.3	29.8	5968.9	Our work

[a] Rate I: Specific rate of GVL formation on the basis of the total amount of catalyst including support and active metal.

[b] Rate II: Specific rate of GVL formation on the basis of the amount of active metal.

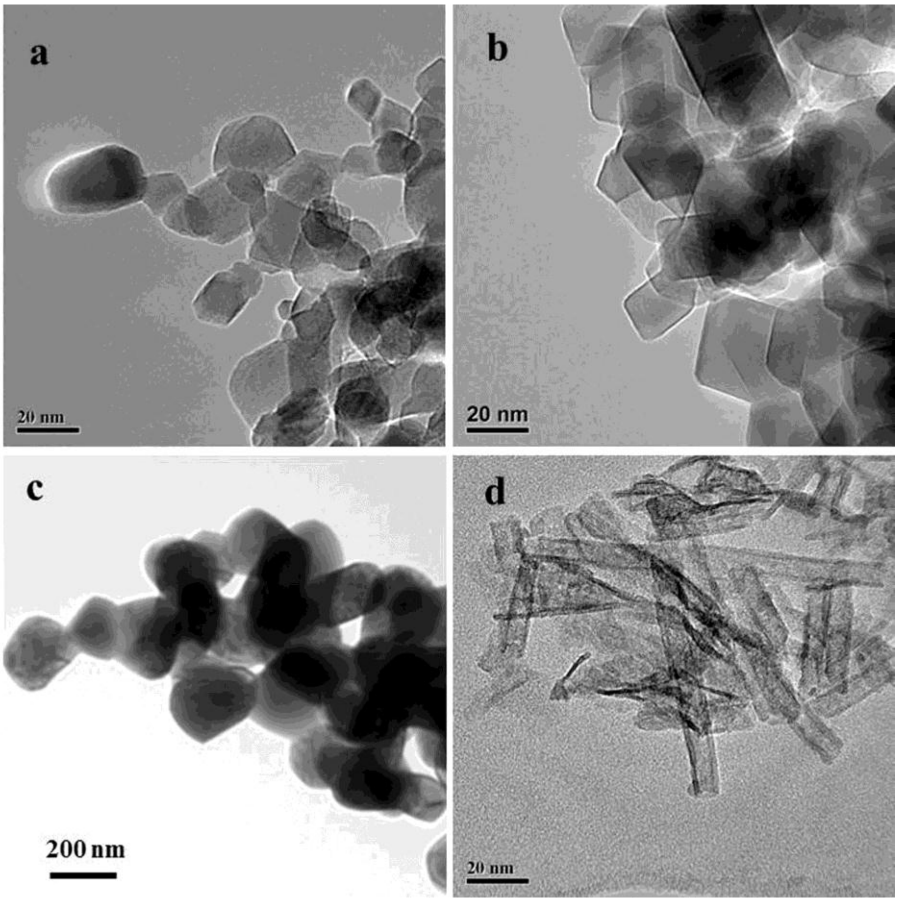


Figure S4. TEM images of the photocatalysts a) P25-TiO_2; b) RA-TiO_2; c) R-TiO_2; d) NT-TiO_2.

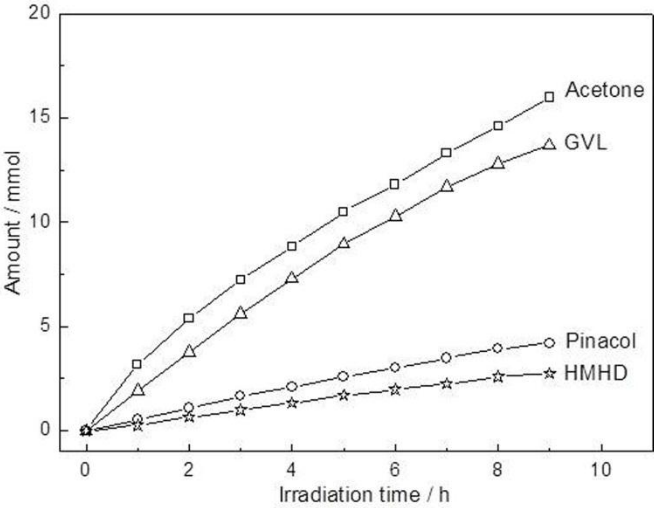


Figure S5. Products generation during photocatalytic process in ethyl levulinate/isopropanol mixture. Reaction conditions: solution, 20 ml 1 M ethyl levulinate in isopropanol; catalyst, 0.05 g RA-TiO_2 loaded 0.5 wt% gold; atmosphere, argon; temperature, 20 ^oC; Light source, 300 W high-pressure Hg-lamp.

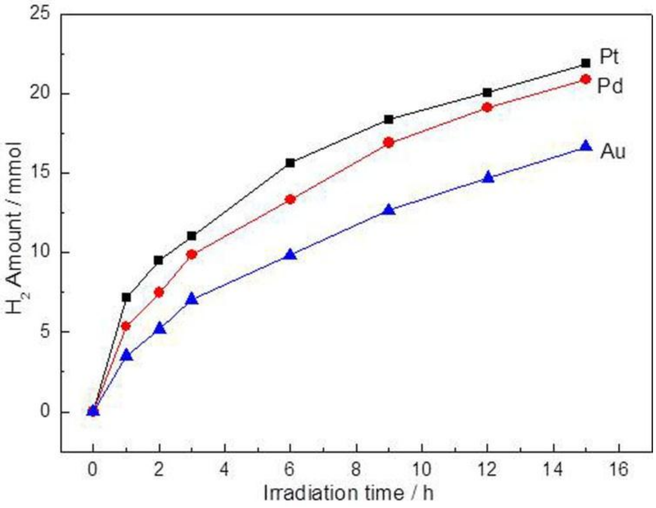


Figure S6. The evolution profiles of H_2 during photocatalytic hydrogen production in neat isopropanol. Reaction conditions: 20 ml isopropanol; catalyst, RA-TiO_2 loaded 0.5 wt% cocatalyst; atmosphere, argon; temperature, 20 ^oC; Light source, 300 W high-pressure Hg-lamp.