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Photocatalytic reduction of CO_2 with H_2O into C_2H_6 mediated by dual metalation strategy

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Artificial solar-energy-driven CO_2 reduction into value-added fuels under mild conditions provides a promising strategy to mitigate energy crisis and alleviate environmental issues around the world. Among diverse products of CO_2 reduction reaction, C_{2+} compounds are more desirable in terms of their high energy density and commercial value [1]. Thus far, various photocatalysts have been constructed for CO_2 reduction. Nevertheless, the conventional photocatalytic systems, even the most advanced ones, primarily produce C_1 products, bearing with the shortcomings of low activity, low efficiency, and also, demanding sacrificial agents [2]. Thereby, the development of practical photocatalytic devices for converting CO_2 into C_{2+} products without any applied bias or sacrificial agents is of enormous scientific significance [3,4]. However, the exploration of efficient photocatalysts incorporated with suitable semiconductors to facilitate C–C coupling remains a huge challenge [5].

Very recently, reporting in *Nature Catalysis*, Mi, Song, Zhou and co-workers fabricated a state-of-the-art artificial photosynthesis-integrated device (APID), namely, the AuIr dual-metalated composite accurately photodeposited on the III-nitride semiconductor of InGaN NWs/Si, noted as, AuIr@InGaN NWs/Si [6]. By employing CO_2, water and light as the only inputs, it can realize highly efficient photocatalytic CO_2 reduction to C_2H_6 in water with no bias or sacrificial agents (Figure 1a). Specifically, under concentrated light irradiation of 3.5 W cm^{-2}, the designed device of $Au_{0.44}Ir_{0.56}$@InGaN NWs/Si can reduce CO_2 towards C_2H_6 with the activity up to 58.8 mmol g^{-1} h^{-1} (Figure 1b), achieving a turnover number of 54,595 and a selectivity of 5.6% (Figure 1c), exhibiting no significant decrease for the performance within 60 h. Meanwhile, the generation rate of CH_4 is 125.4 mmol g^{-1} h^{-1}, which is several orders of magnitude higher than that of the reported catalytic systems to date, leading to a total selectivity of 17.6% for hydrocarbons (Figure 1c). Moreover, considering the useful by-products of syngas (CO and H_2), the designed device possesses a great light-to-fuel (LTF) efficiency of approximate 0.59%. These above results demonstrate a tremendous superiority for the optimized AuIr dual metalation strategy in the sphere of photocatalytic CO_2 reduction [7]. Of note, H_2O_2 was simultaneously formed from water oxidation by photoexcited holes, making this process more commercially promising.

The authors found that due to the epitaxial growth of 1D InGaN NWs on 3-inch silicon wafers, the pre-synthesized semiconductor displayed outstanding optical absorption and charge transfer efficiency for promoting charge separation, which offered an ideal platform to support the bimetallic AuIr alloy for promoting CO_2 reduction towards C_{2+} product. Additionally, the authors validated that it was iridium but not gold in the AuIr alloy responsible for the C–C bond generation. Meanwhile, the existence of electronic interactions between gold and iridium was also verified, which can extremely enhance C–C coupling during the catalytic process.

According to the control experiments, it is found that while

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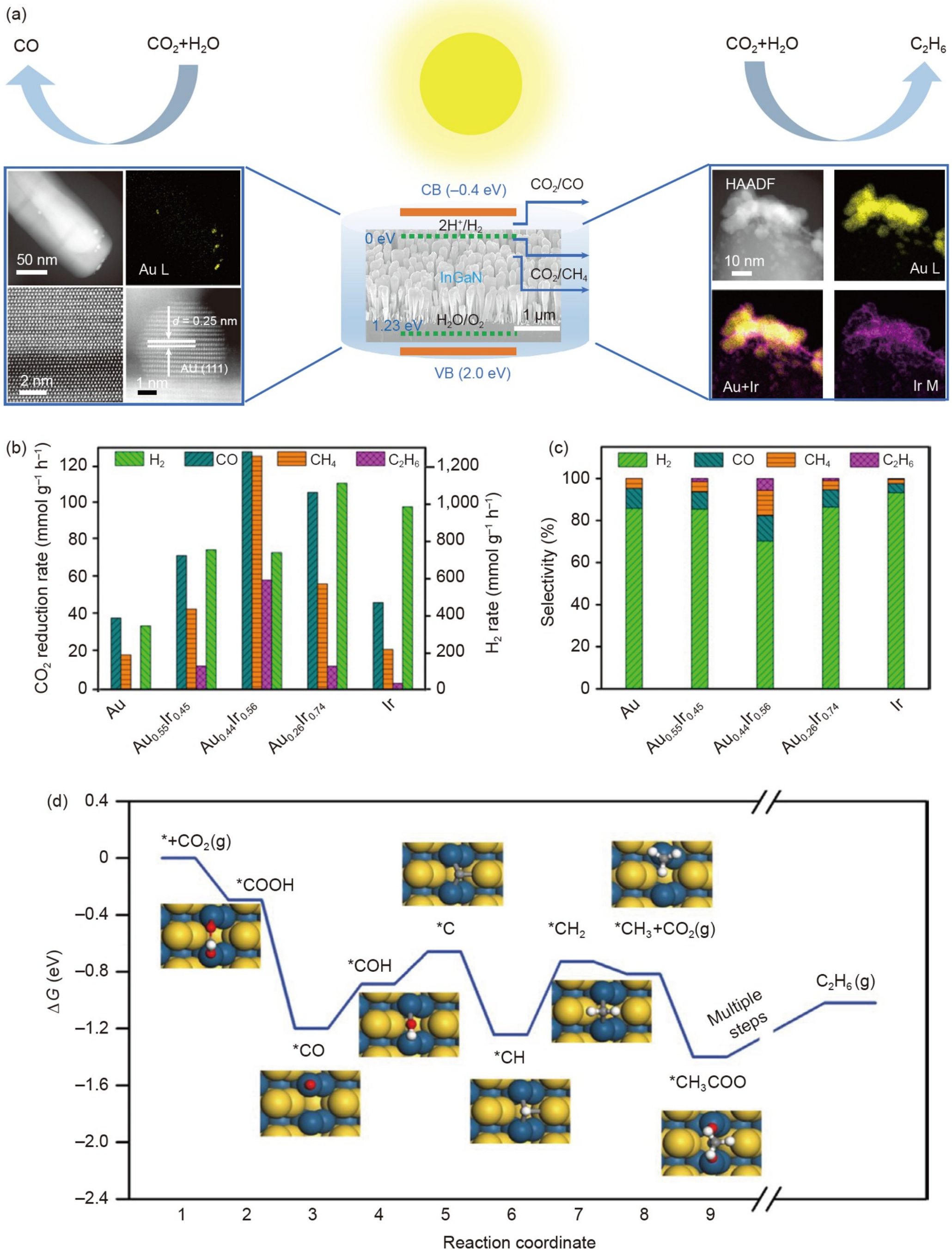

Figure 1 (a) SEM image and energy band structure of InGaN NWs/Si, HAADF-STEM and elemental mapping images of Au NPs@InGaN NWs and AuIr@InGa NWs/Si. (b) Evolution rate (c) selectivity of diverse products from photocatalytic CO_2 reduction by AuIr@InGaN NWs/Si with various Au/Ir ratios. (d) Free energy diagram of the reaction pathway on the Au_2Ir_2 (111) facet. Yellow, blue, red, grey and white spheres represent gold, iridium, oxygen, carbon and hydrogen atoms, respectively [6] (color online).

utilizing CH_3COOH and $CH_4 + CO_2$ as feedstock, the TOFs of C_2H_6 are greatly high compared with that of using CO_2, CO and HCOOH as feedstock, respectively. Meanwhile, the *in-situ* diffuse reflectance infrared Fourier-transform (DRIFT) spectroscopy reveals the main intermediate for producing C_2H_6 consisting of $–CH_x$ and C=O groups. These results preliminary suggest that the CO_2 insertion into $–CH_3$ should be the determining step for C–C coupling. Furthermore, the results of density functional theory (DFT) calculations on the Au_2Ir_2 (111) facet demonstrate that the reaction pathway would go through the hydrogenation of CO_2 to *COH and then to *C→*CH→$*CH_2$→$*CH_3$, subsequently, the insertion of $*CO_2$ into $*CH_3$, forming the main $*CH_3COO$ intermediate (Figure 1d). Finally, established on the above investigations, the authors proposed that C–C coupling can be efficiently accomplished by inserting CO_2 into $*CH_3$ due to Ir modulating Au with the best Au:Ir ratio of around 1:1 in AuIr@InGaN NWs/Si.

In this work, taking advantage of the synergistic effect of gold and iridium, as well as the one-dimensional InGaN nanowire semiconductor with unique optical and electronic properties, the well-designed photocatalytic device exhibits a break-through performance for generating C_2H_6 derived from CO_2 reduction, which reveals an inspiring strategy for designing novel robust photocatalysts for C–C coupling *via* benign and environmentally-friendly approach. The finding of this study opens a door for the production of C_{2+} compounds from sunlight, CO_2 and water without any other energy input, which paves the way for realizing CO_2 resource utilization through photocatalysis. Of note, apart from C_{2+} fuels yielded from photocatalytic CO_2 reduction, the concurrent formation of H_2O_2 from photocatalytic water oxidation over AuIr@InGaN NWs/Si makes such an artificial photosynthesis process more commercially promising.

Conflict of interest The authors declare no conflict of interest.

1 Shen Y, Ren C, Zheng L, Xu X, Long R, Zhang W, Yang Y, Zhang Y, Yao Y, Chi H, Wang J, Shen Q, Xiong Y, Zou Z, Zhou Y. *Nat Commun*, 2023, 14: 1117
2 Li X, Sun Y, Xu J, Shao Y, Wu J, Xu X, Pan Y, Ju H, Zhu J, Xie Y. *Nat Energy*, 2019, 4: 690–699
3 Fang S, Rahaman M, Bharti J, Reisner E, Robert M, Ozin GA, Hu YH. *Nat Rev Methods Primers*, 2023, 3: 61
4 Bonchio M, Bonin J, Ishitani O, Lu TB, Morikawa T, Morris AJ, Reisner E, Sarkar D, Toma FM, Robert M. *Nat Catal*, 2023, 6: 657–665
5 Yang W, Wang HJ, Liu RR, Wang JW, Zhang C, Li C, Zhong DC, Lu TB. *Angew Chem Int Ed*, 2021, 60: 409–414
6 Zhou B, Ma Y, Ou P, Ye Z, Li XY, Vanka S, Ma T, Sun H, Wang P, Zhou P, Cooper JK, Xiao Y, Navid IA, Pan J, Song J, Mi Z. *Nat Catal*, 2023, 6: 987–995
7 Ou H, Li G, Ren W, Pan B, Luo G, Hu Z, Wang D, Li Y. *J Am Chem Soc*, 2022, 144: 22075–22082