Proceedings of the 7th International Conference of Recent Trends in Environmental Science and Engineering (RTESE'23)
Canada – June 04 - 06, 2023
Paper No. 119
DOI: 10.11159/rtese23.119

Efficient and Sustainable Room-Temperature CO_2 Conversion by Plasmonic Two-Dimensional Metal-Oxide Hybrid Nano-Interfaces

Mohammad Karbalaei Akbari[1, 2], Nasrin Siraj Lopa[1, 2], Serge Zhuiykov[1,2]
[1] Department of Solid State Sciences, Faculty of Science, Ghent University, 9000 Ghent, Belgium
[1] Centre for Environmental & Energy Research, Ghent University, Global Campus, Incheon, South Korea.
E-mail: Mohammad.akbari@ugent.be; Nasrin.Lopa@ghent.ac.kr; serge.zhuiykov@ugent.be

Abstract **-** The state-of-the-art nanotechnologies ensure the establishment of sustainable green systems for CO_2 conversion. Recently, plasmonic two-dimensional (2D) nanostructures are found as effective platforms for efficient visible light-assisted photocatalysis. The plasmonic nanodomains grown on the surface of advanced 2D semiconductor materials represent a new class of hybrid nanostructures. These 2D hybrid nanostructures activate supplementary mechanisms at material heterointerfaces enabling a wide range of solar-activated physic-chemical reactions. Here, the controlled growth of plasmonic crystalline silver (Ag) nanodomains on the 2D surface oxide films of liquid Ga-based nanoparticles enabled the efficient CO_2 conversion through combined photocatalysis and acoustic-activated technique. Driven by acoustic energy, the multiple contribution of Ga_2O_3-Ag semiconductor/plasmonic hybrid 2D heterointerfaces enabled the visible-light assisted hot-electron generation at 2D plasmonic hybridinterfaces and therefore rose the CO_2 conversion efficiency to values higher than 94.6%. The inherent plasmonic characteristics of developed 2D nanojunction assembly accompanied by the commercial availability of acoustic activated technologies depict promising future for efficient and sustainable CO_2 conversion in industrial levels.

Keywords**:** CO_2 Conversion, Two-Dimensional Materials, Plasmonic Photocatalysis, Nanotechnology and Environment.

1. Introduction

The solar-assisted photocatalysis conversion of greenhouse gases into value added byproducts is featured as one of the most promising approaches toward the energy-efficient conversion of environmentally hazardous gases [1]. Due to the high-thermal stability of C=O bonding, the activation thermal energy for the CO_2 conversion into intermediate species is considerably high (2000 ^oK) imposing a challenging burden for room-temperature catalytic conversion of CO_2 [2]. 2D metal-oxide semiconductors with their high-reactivity are promising catalyst materials for efficient CO_2 conversion. However, due to their intrinsic high bandgap, the solar-assisted photocatalytic functionalities of them are restricted [3]. Plasmonic nanodomains decorated on the 2D surface oxide films of room-temperature liquid metals enabled the establishment of novel class of hybrid nanostructures for environmental applications [4]. The visible-light assisted electron-hole generation at plasmonic interfaces of 2D metal-oxide semiconductors is the main mechanism of plasmonic photocatalysis [5]. Inspired by recent findings, it is believed that the plasmonic heterointerfaces can efficiently enhance the CO_2 conversion [6]. Theoretical studies aside, the controlled decoration of 2D semiconductors with plasmonic nanodomains is highly challenging. Furthermore, the design of new technologies for efficient CO_2 reduction is critically important for commercialization and sustainability targets. The present study has developed novel type of plasmonic 2D hybridinterfaces for efficient room-temperature synergistic CO_2 conversion. Accordingly, sonochemical functionalization enabled the growth of Ag nanodomains on the 2D Ga_2O_3 films of liquid Ga based nanoparticles. The triggering energy for CO_2 conversion was supplied from combined simulated solar light and acoustic sources. Consequently, the CO_2 conversion efficiency of 94.6% that was achieved accompanied by the generation of O_2 and H_2 gases. Therefore, this unique acoustic activated plasmonic photocatalysis system is expected to address various technical challenges and expectations toward sustainable conversion of CO_2 into value added environmentally friendly by-products.

2. Results and Discussions

2.1. Acoustic-activated CO_2 plasmonic photocatalysis

The efficient acoustic-activated CO_2 reduction technique was recently developed by using Ga-based nanocatalyst system [7]. In our setup, the suspension of 2D Ga_2O_3-Ag films (50 gr /lit) was agitated continuously by ultrasonic waves in a quartz

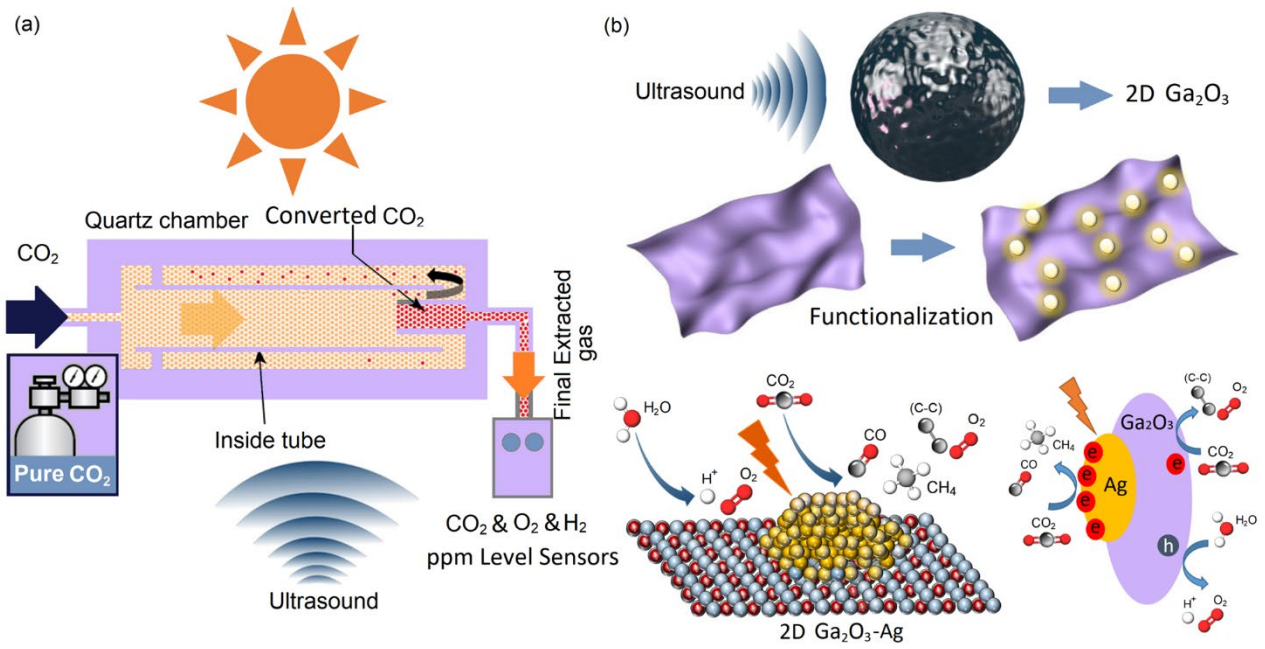

Fig. 1: (a) The Schematic illustration of ultrasonic-assisted CO_2 photocatalysis setup. (b) The image shows the functionalization and synthesis of 2D Ga_2O_3-Ag films accompanied by the mechanism of plasmonic photocatalytic conversion of CO_2.

chamber containing deionized water (Fig. 1a). The Xenon-lamp (DY. TCH, 500 W) was used to simulate the solar radiation during reactions. The high-purity CO_2 (99%) was introduced into 30 mm reactor with input rate of ~ 5 sccm at 20°C. The exhaust gases were analysed by ppm level CO_2, O_2 and H_2 sensors. To synthesize 2D Ga_2O_3, the liquid Ga-In alloy was sonicated in a reactor containing 0.1 µmol/l Ag solution at 20°C. The Ag content was adjusted to prevent the progressive Ga/Ag alloying. The by-products of sonication process were later sorted by centrifugation, where the synthesized Ga_2O_3-Ag nanosheets were separated from nanoparticles. Accordingly, Ag nanodomains nucleated on the surface of 2D Ga_2O_3 by sonochemical synthesis technique (Fig. 1b) [4]. This Ag nanodomains act as plasmonic nanoantennas for reception of visible and infrared lights. The developed 2D Ga_2O_3-Ag plasmonic nanosheets actively convert CO_2 into CO, O_2 and C in reaction chamber. The photogenerated hot electrons and holes are transferred to the adjacent 2D Ga_2O_3 film or directly interact with CO_2 on the surface of Ag nanodomains. The following electron transfer through localized surface plasmon resonance accompanied by acoustic energy enabled the C=O debonding. The strong near electric field enhancement in the vicinity of Ag plasmonic nanodomains can further intensify the charge separation process in adjacent 2D Ga_2O_3 films (Fig. 1b). The enhanced electron-hole separation not only intensifies the rate of CO_2 reduction, but also it enables the H_2 and O_2 generation through the water splitting reactions (Fig. 1b). Furthermore, acoustic waves act as strong supplementary energy source that enhance both CO_2 conversion and water splitting at plasmonic 2D metal oxide hybridinterfaces.

2.2. Characterization of Ga_2O_3-Ag plasmonic 2D structures

The high-resolution transmission electron microscopy (HRTEM) images of 2D Ga_2O_3 and functionalized 2D Ga_2O_3-Ag films are shown in Fig. 2a and b. The uniform growth of Ag crystalline nanodomains is observed on the surface of 2D Ga_2O_3 films (Fig. 2b). The following SAED patterns show the vivid signature of (111), (200) and (220) crystalline plane of Ag (Fig. 2c). The complementary XRD result in Fig. 2d shows the characteristic peaks of (111), (200) and (220) crystalline plane of Ag, confirming the polycrystalline nature of grown Ag nanodomains. The Raman spectra of 2D Ga_2O_3-Ag films respectively depict the characteristic peaks of A_g^1, A_g^2 and A_g^3 of Ga_2O_3 at 143, 172, and

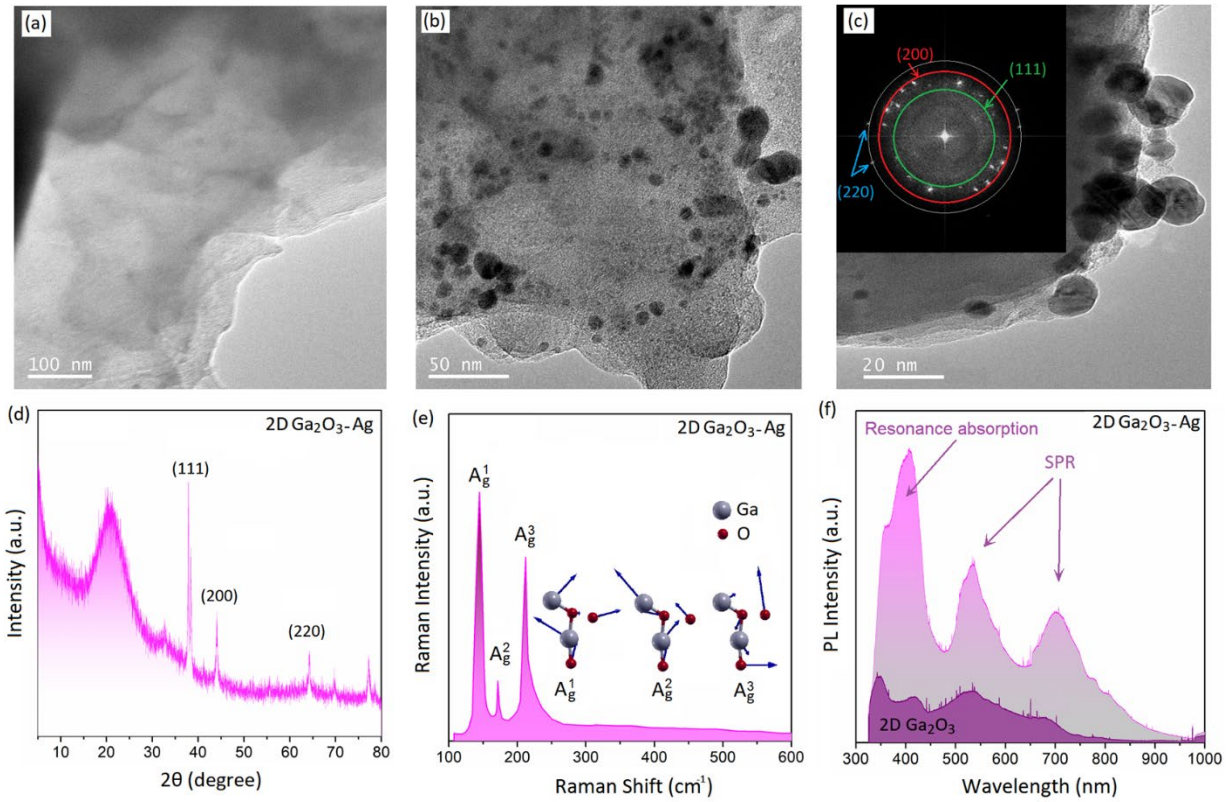

Fig. 2. The HRTEM images of (a) 2D Ga_2O_3 and (b) 2D Ga_2O_3-Ag nanosheets. (c) The Ag nanodomains on 2D Ga_2O_3 and their corresponding SAED patterns. (d) The XRD, (e) Raman and (f) PL spectra of 2D Ga_2O_3-Ag nanosheets.

215 cm^{-1}. The PL spectra of 2D Ga_2O_3-Ag films demonstrate an evident peak at λ= 360 nm attributed to the Ga_2O_3 (Fig. 2f). 2f). The characteristic peak at λ=410~430 nm is assigned to the resonance absorption wavelength of Ag nanodomains. The The broad peaks at λ=550 nm and λ=700 nm are associated to the plasmonic characteristics of Ag nanodomains. To be specific these PL peaks are originated from the photonic local field enhancement and surface plasmon resonance (SPR) interactions of Ag nanodomains [3]. Therefore, the evidence of plasmonic characteristics of 2D Ga_2O_3-Ag nanosheets were observed and confirmed.

2.3. CO_2 conversion

The statistical data on CO_2 reduction is provided in Fig. 3. The measurements of exhaust compositions confirmed the presence of CO_2, O_2 and H_2 gasses in by-products of CO_2 conversion. We determined the CO_2 conversion efficiently through the measurement of the CO_2 content of exhaust gases, since it is estimated that O_2 gas is originated from both CO_2 conversion and water splitting processes. It was found that the CO_2 content reduced to less than 10 percent within 15 min (Fig.3a). The CO_2 conversion efficiency reached to the value of 94.6 %, and then remained constant after 30 min cyclic reaction (Inset in Fig.3a). These high CO_2 conversion efficiency is achieved through the combined effects of plasmonic photocatalysis of highly active 2D Ga_2O_3-Ag nanosheets and also the acoustic activated CO_2 conversion mechanism. We further collect the carbon-rich by-products of reactions and analysed them. After stabilization of CO_2 conversion, the amount of ~180 μmol of solid carbon was extracted after 30 min of catalysis reaction which is equal to the carbon production rate of ~360 μmol h^{-1} (Fig. 3b). Our following investigation on the thermal dependence of carbon production rate confirmed that the calculated rate constant (k) correlated with reaction time through the Arrhenius model. The calculation showed that the activation energy for conversion of CO_2 on the surface of 2D Ga_2O_3-Ag nanosheets at room temperature was 8.8 kJ mol^{-1} (Fig. 3c).

3. Conclusion

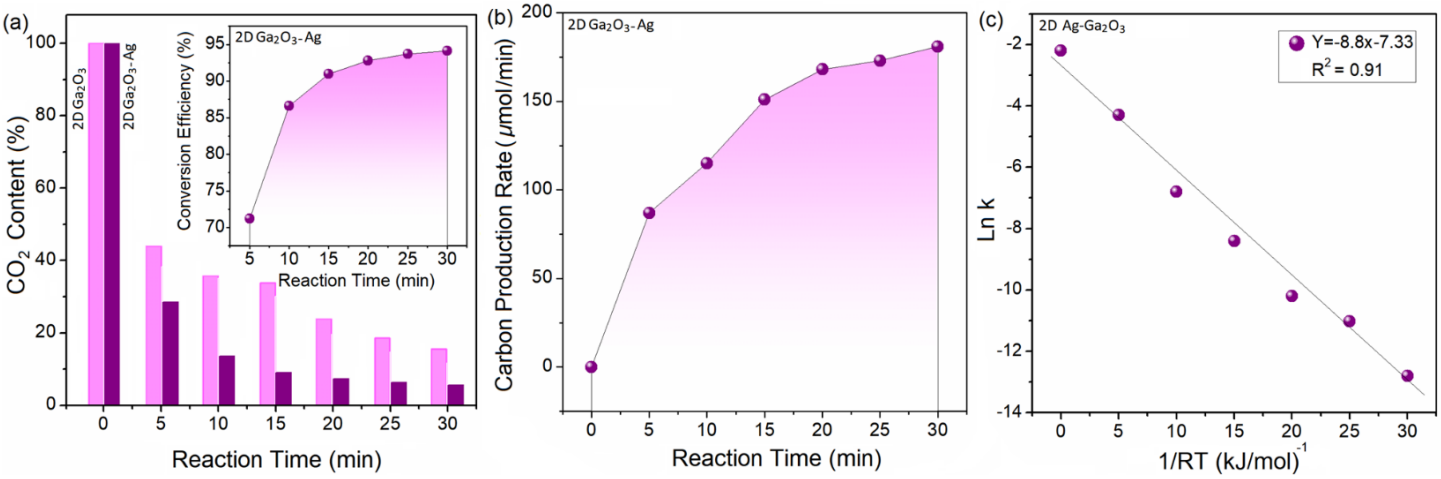

Fig. 3. (a) The CO_2 percentage and conversion efficiency (inset) during catalysis process. (b) The carbon production rate vs. reaction time. (c) The changes of logarithmic rate constant vs. reaction time.

In summary, Ag plasmonic polycrystalline nanodomains were grown on the surface of 2D Ga_2O_3 catalyst. These heterointerfaces were found highly efficient platform for plasmonic CO_2 photocatalysis. It was observed that the sonomechanical energy, accompanied by the plasmonic photocatalysis co-contributed to enhance the CO_2 conversion efficiency to values higher than 94.6%. The challenging growth of Ag nanodomains was crucially dependent on the selection as well as synthesis process. The extracted data from materials characterization including PL spectroscopy confirmed the local field enhancement and surface plasmon resonance (SPR) interactions of Ag nanodomains on 2D Ga_2O_3. The enhanced CO_2 conversion capabilities of these nanostructures originated from the following factors: the plasmonic photocatalysis at Ga_2O_3-Ag heterointerfaces, the plasmonic hot-electron transfer at catalyst interfaces, and finally the acoustic-activated CO_2 debonding and conversion. Consequently, this principally developed novel technique for solar-activated photocatalysis of CO_2 into value-added by-products provide excellent opportunities for establishment of technological platforms for generation of clean fuels similar to O_2 and H_2 from CO_2. photocatalytic conversion.

Acknowledgements

The study was supported by research and development program of Ghent University Global Campus, South Korea.

References

[1] D. Gao, R. M. Arán-Ais, H.S. Jeon, and B. R. Cuenya, "Rational catalyst and electrolyte design for CO_2 electroreduction towards multicarbon products," *Nat. Catal.,* vol. 2, pp. 198-210, 2019.

[2] S. Ackermann, L. Sauvin, R. Castiglioni, J. L. M. Rupp, J. R. Scheffe, and A. Steinfeld, "Kinetics of CO_2 reduction over nonstoichiometric ceria", *J. Phys. Chem. C.,* vol. 119, pp. 16452-16461, 2015.

[3] M. Karbalaei Akbari, F. Verpoort, and S. Zhuiykov, "State-of-the-art surface oxide semiconductors of liquid metals: an emerging platform for development of multifunctional two-dimensional materials", *J. Mater. Chem., A*, vol. 9, pp. 34-73, 2021.

[4] M. Karbalaei Akbari, Z. Hai, Z. Wei, R. K., Ramachandran, C. Detavernier, M. Patel, and S. Zhuiykov, "Sonochemical functionalization of the low dimensional surface oxide of galinstan for heterostructured optoelectronic applications" *J. Mater. Chem. C*, vol.**7**, pp. 5584-5595, 2019.

[5] M. Karbalaei Akbari, Z Hai, and S. Zhuiykov, "Wafer-scale two-dimensional Au-TiO_2 bilayer films for photocatalytic degradation of Palmitic acid under UV and visible light illumination" *Mater. Res. Bull.* vol. 95, pp. 380-391, 2017.

[6] R. Verma, R. Belgamwar, and V. Polshettiwar, “Plasmonic photocatalysis for CO_2 conversion to chemicals and fuels” *ACS Materials Lett*., vol. 3, pp. 574-598, 2021.
[7] J. Tang, M. Mayyas, M. B., Ghasemian, and K. Kalantar-Zade, “Liquid-metal-enabled mechanical-energy-induced CO_2 conversion” *Adv. Matter.* vol. 34, 2105789, 2022.