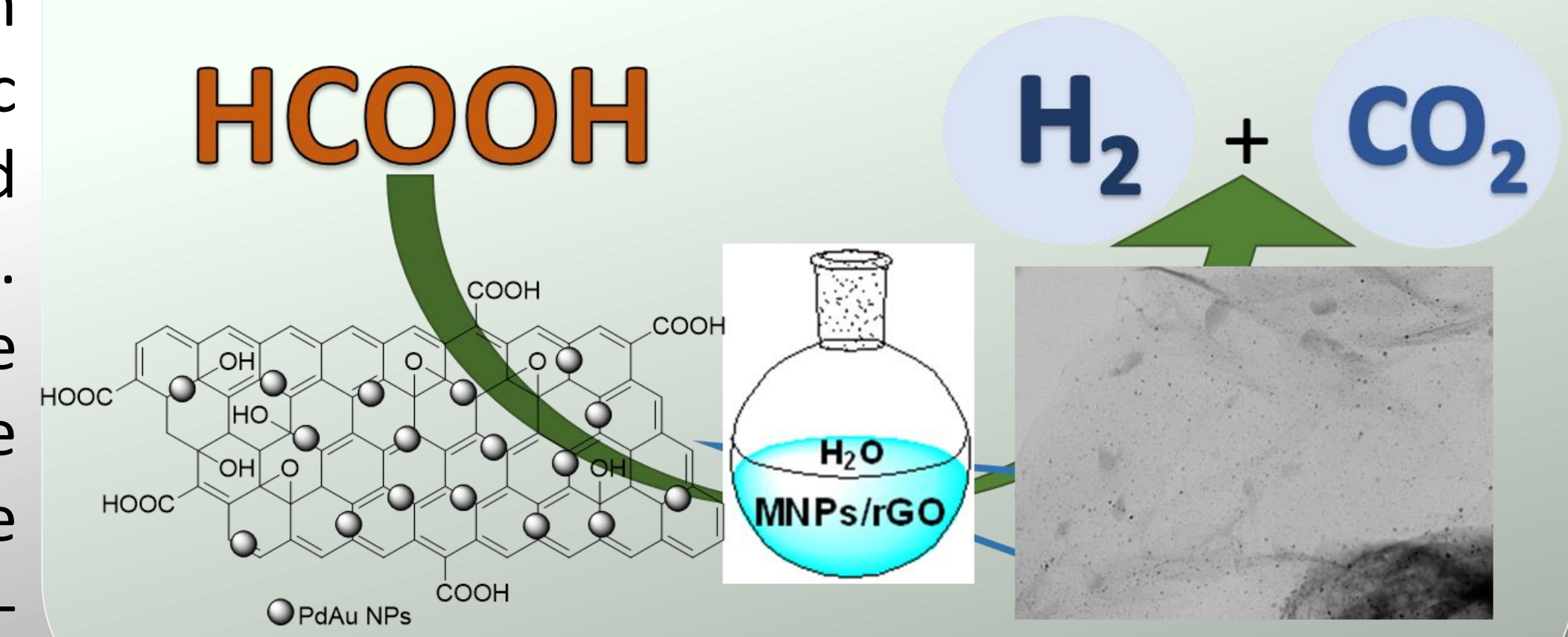


Introduction

Hydrogen (H₂) is considered a feasible and environmentally attractive energy carrier, although efficient and safe hydrogen storage technologies under mild conditions need to be developed. A feasible option is the storage of H₂ in an organic liquid medium (Liquid Organic Carriers, LOC) which can release H₂ in situ at ambient temperature for direct use in fuel cells. For the recent years, Formic Acid (FA, HCOOH) a major product of biomass processing, has been investigated as promising liquid storage material, capable to release hydrogen under mild condition via a catalytic decomposition. An important strategy to promote the development of hydrogen generation from formic acid is the use of new heterogeneous catalysts with high activity and relatively low cost, designed to replace the homogeneous catalysts with difficult synthesis, separating and recycling. In this study we present the facile synthesis of mono-metallic Pd(10wt%), Au(2.5wt%, 5 wt% and 10wt%) and bi-metallic Pd(7.5wt%)-Au(2.5wt%) alloy nanoparticles supported on reduced graphene oxide (rGO) by a new, simple, accessible and environmentally friendly method and investigation of their catalytic properties for FA decomposition in aqueous solution.



Catalysts preparation & Characterization

The catalysts were prepared by impregnation of GO with an aqueous solution of metal salts followed by the simultaneous thermal/H₂ reduction of GO and metal ions.

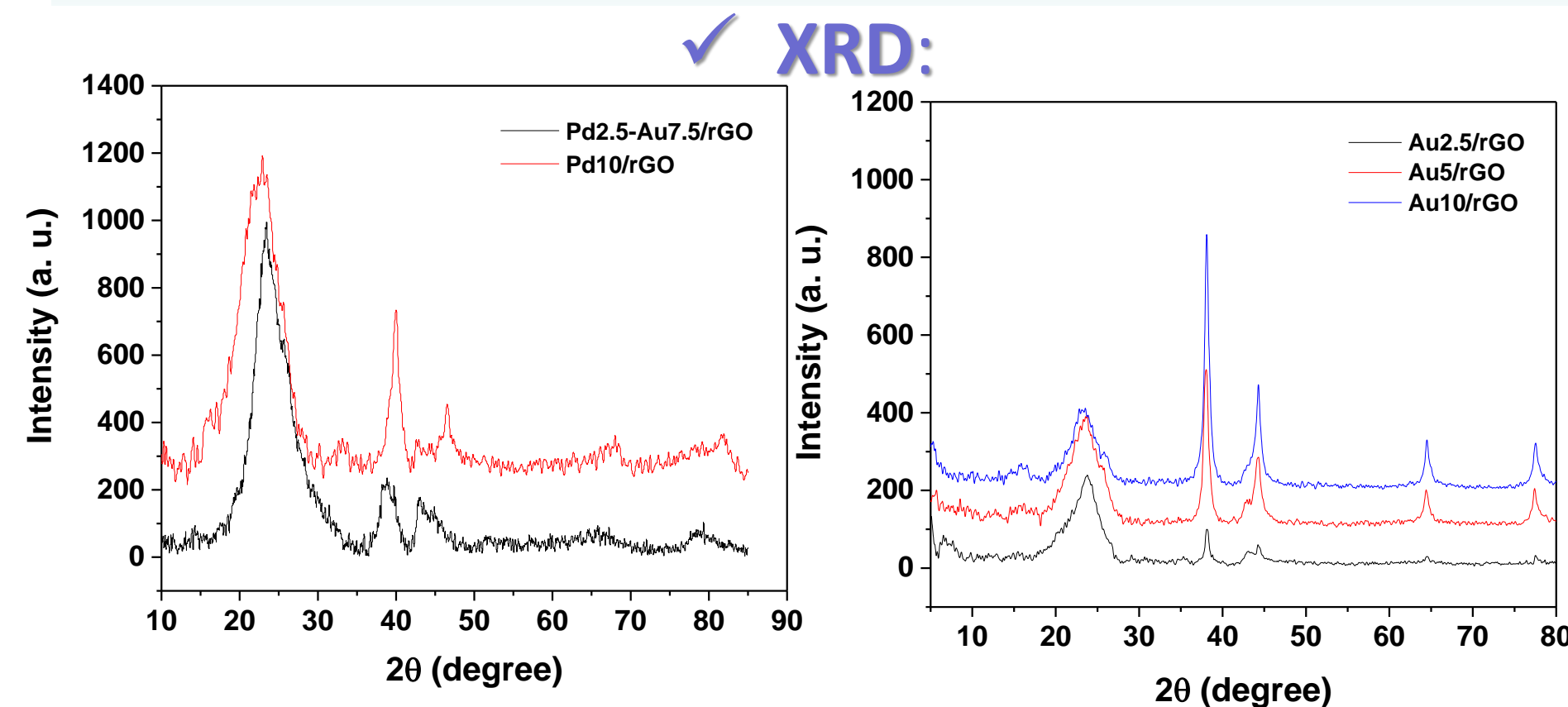


Figure 1. XRD profiles of GO supported palladium, gold and gold-palladium catalysts

- The XRD patterns indicate the good crystallinity of the carbon and also the formation of few layers' graphene material.
- The specific rGO XRD reflection is situated at 23° for Pd/rGO and at 23.7° for Au/rGO composites and Pd-Au bimetallic one.

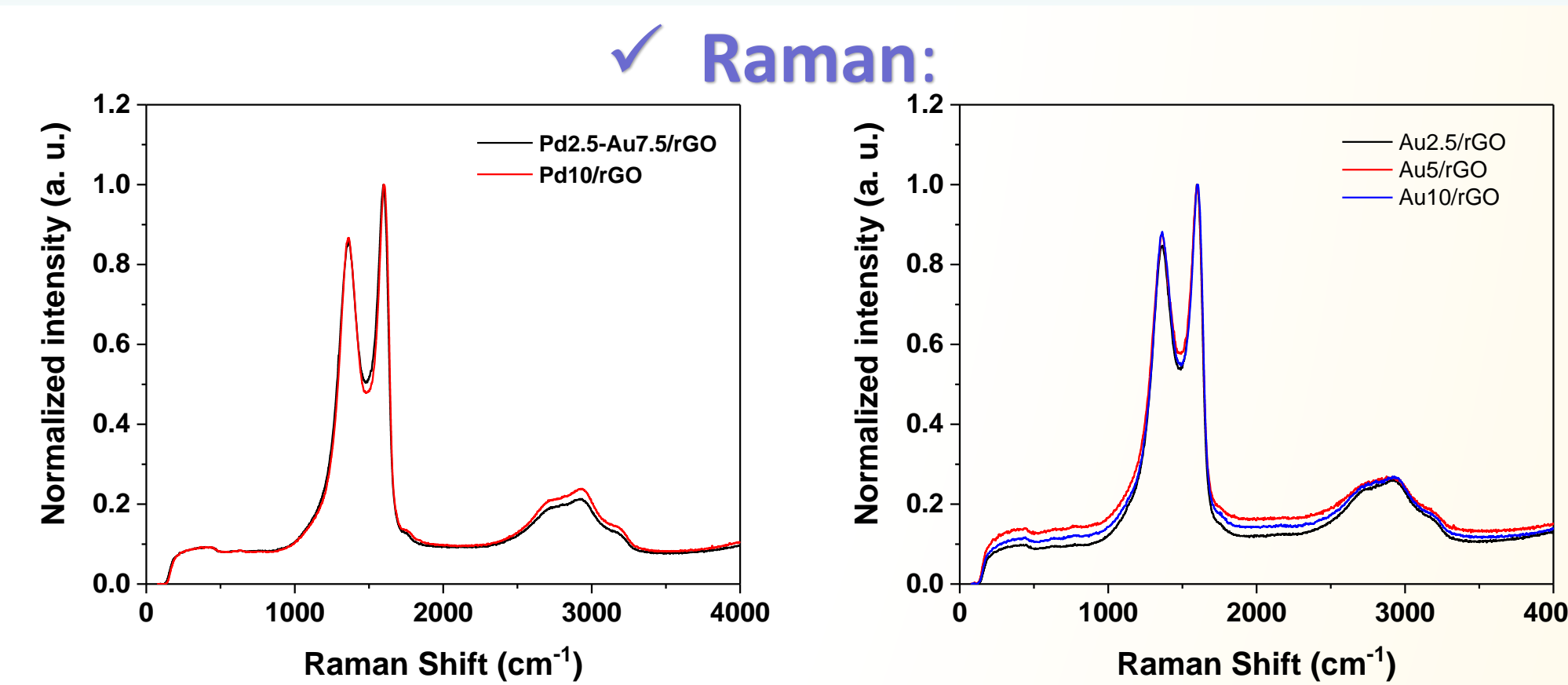


Figure 3. Raman spectra (1000-4000 cm⁻¹, 500 nm, 1.5 mV) of GO supported palladium, gold and gold-palladium catalysts

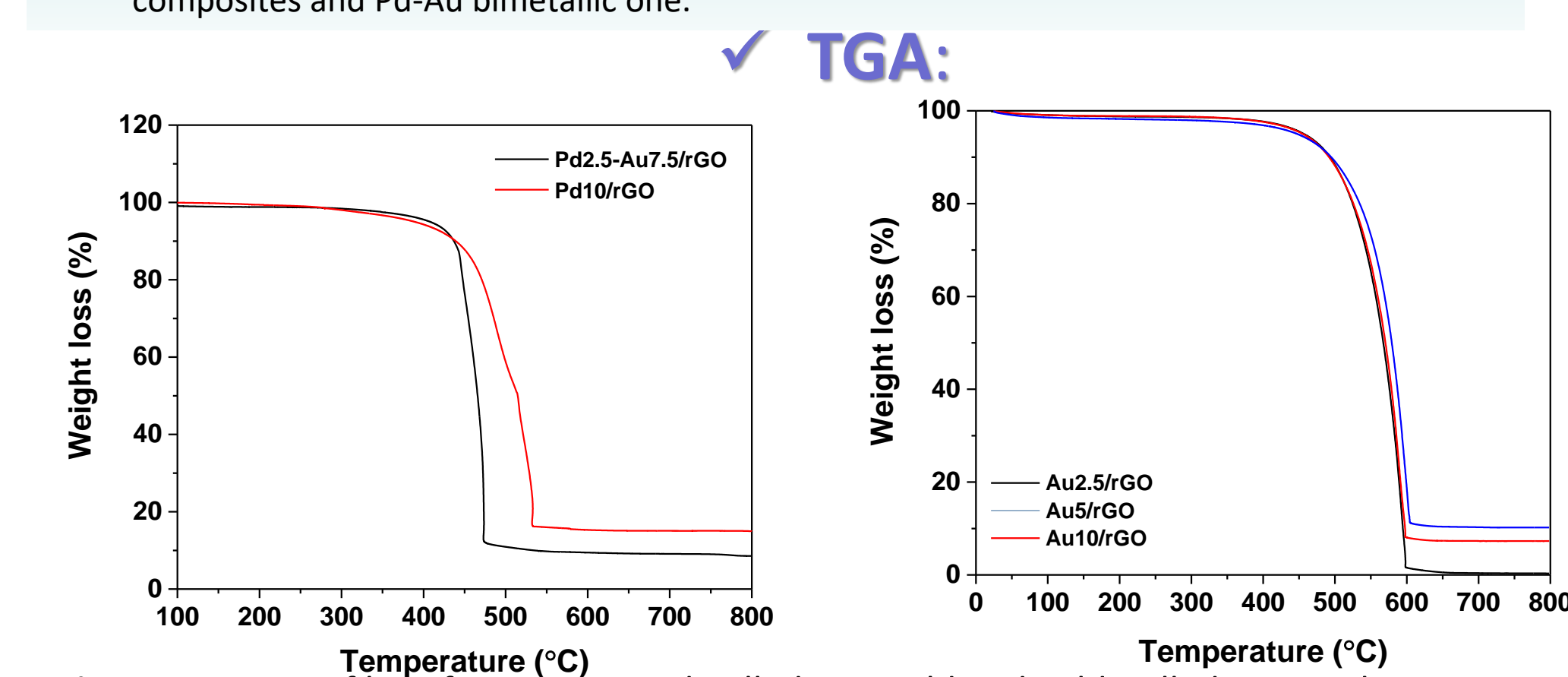


Figure 2. TGA profiles of GO supported palladium, gold and gold-palladium catalysts

- All catalyst present very similar thermal behaviour, only one mass loss profile being observed, indicating the existence of only one type of carbonaceous material in their structure.
- The values of the burning temperature of gold containing materials, are very close to 600°C, indicate high crystalline carbon, in good agreement with the XRD data. For the palladium containing materials is observed only one mass loss profile at 517 °C for palladium catalyst and 447 °C for Pd-Au bimetallic one.

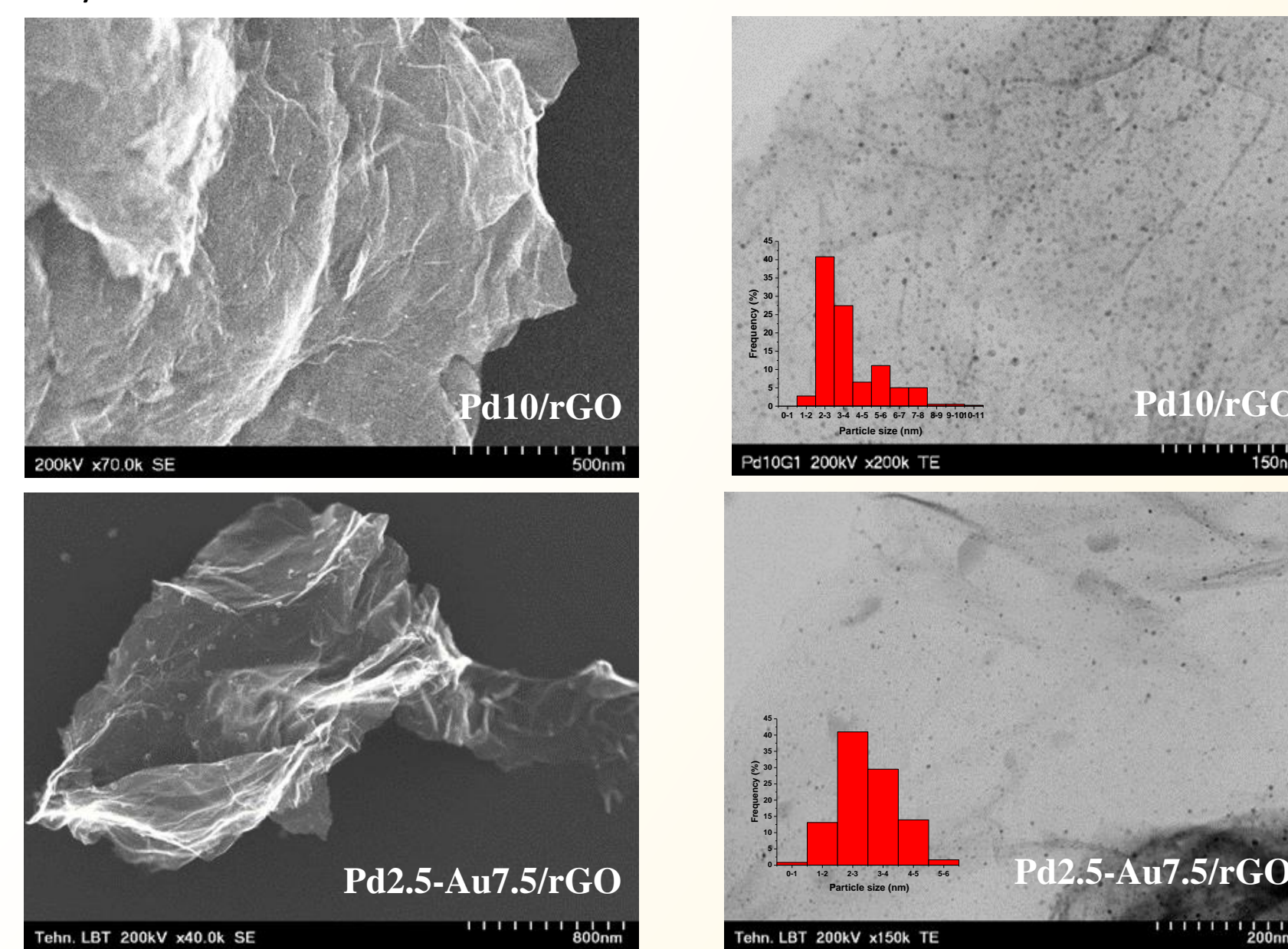
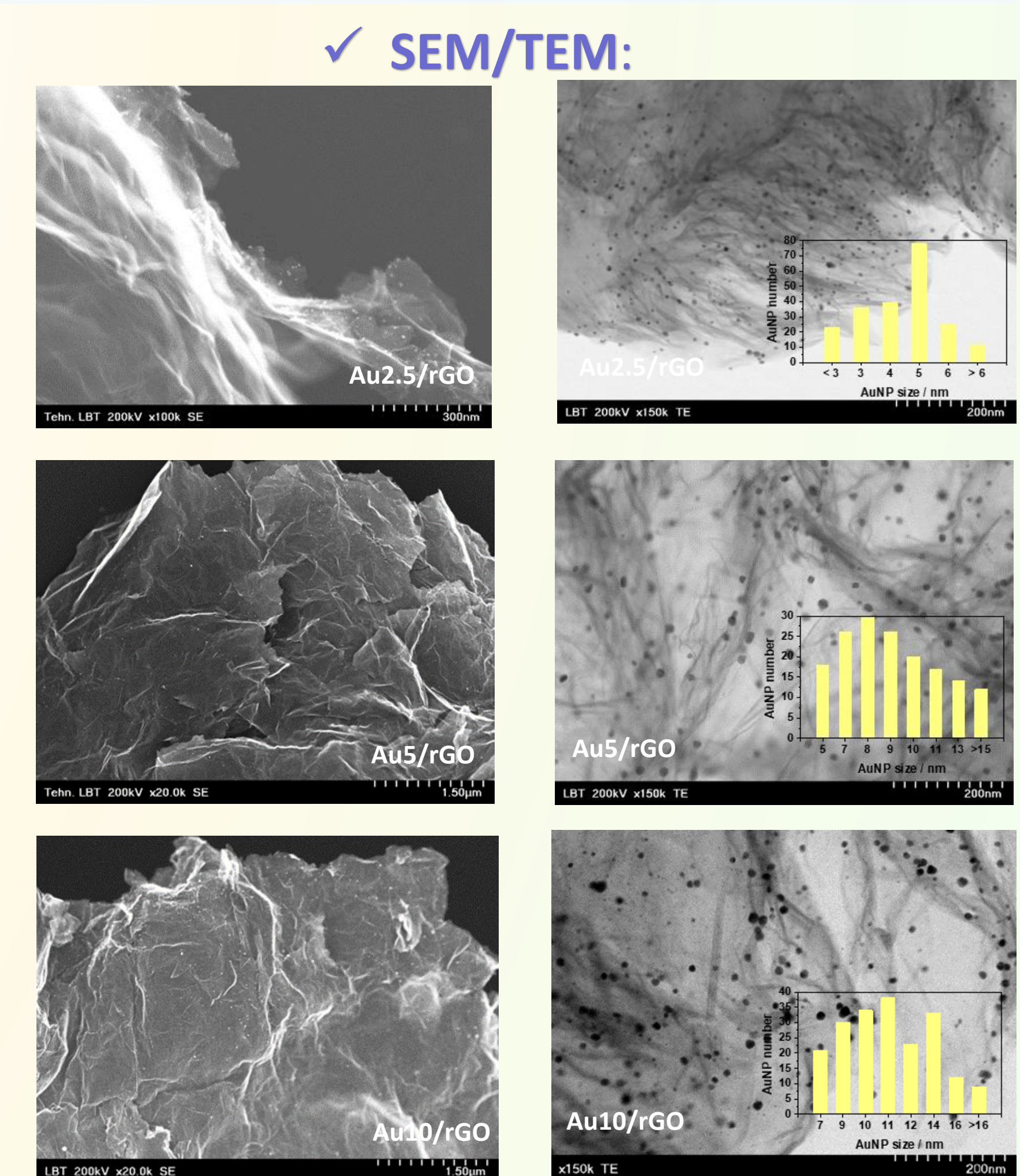


Figure 4. SEM/TEM images of GO supported palladium, gold and gold-palladium catalysts



By applying the same preparation method, but varying the gold target concentrations small Au nanoparticles with narrow size distribution and medium diameter of 5 nm were formed for Au2.5/rGO, while for Au5/rGO the majority of AuNPs size is around 5-10 nm and for Au10/rGO a broad AuNPs size distribution of 7-14 nm is observed. The palladium composites presents small Pd and Pd-Au nanoparticles with medium size smaller than 5 nm.

HCOOH's decomposition & The performance of the catalysts

H₂ stored in FA can be released through a *catalytic dehydrogenation* way Eq. (1). However, from the perspective of hydrogen storage application, the dehydration way Eq. (2) should be avoided because CO is toxic to the fuel cell catalysts.

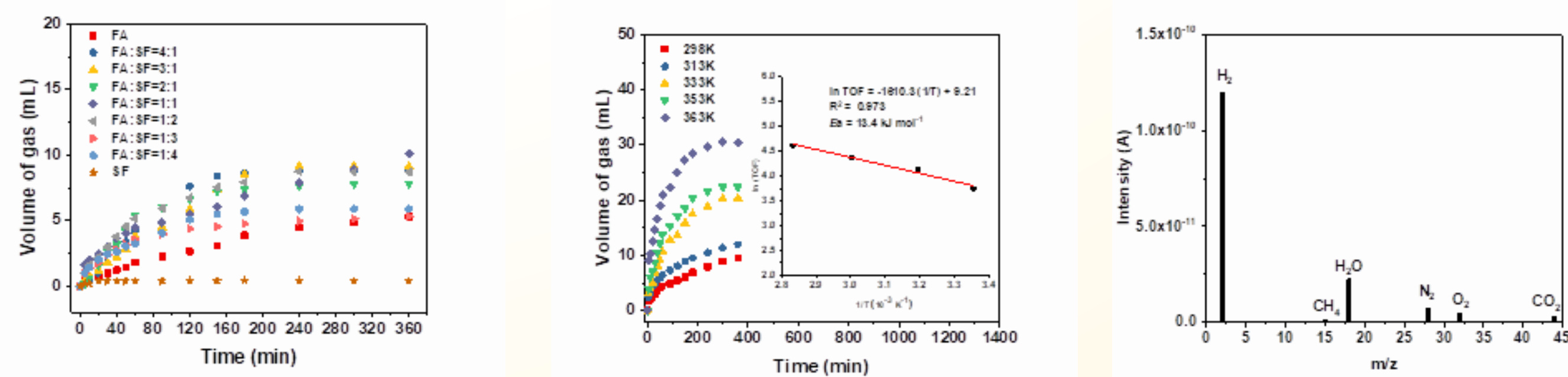


Figure 5. (a) The plots of generated gas (CO₂ + H₂) versus time; (b) The plots of generated gas (H₂+CO₂) versus time and Arrhenius plot (ln(TOF) vs 1/T) at different temperatures at the molar ratio of FA/SF = 1:1; (c) MS spectrum for the evolved gas from aqueous solution of SF and FA at the molar ratio of FA/SF = 1:1 over Pd-Au/rGO under Ar atmosphere (n_{Pd}-Au/n_{FA} = 0.015) at 298 K, (reaction conditions: 5 mL solution FA/SF, c_{FA} + c_{SF} = 0.25 M, in the presence of 11.25 mg of PdAu/rGO)

- The effect of SF on the performance of the PdAu/rGO catalyst for decomposition of FA was investigated (Fig. 5a). In this case it can be seen that the highest volume of gas released was achieved with an FA-SF ratio of 1:1.
- The apparent activation energy for the generation of hydrogen from FA/SF 1:1 system at different temperatures, ranging from 298 to 353 K, was calculated. The apparent activation energy (E_a) for this reaction is 13.4 kJ·mol⁻¹ (inset of Fig. 5b), which is lower than most of the previously reported values for Pd-based catalysts.
- The results presented in Figure 5 (c) show that the only species resulted from FA decomposition reaction are H₂ and CO₂, no CO being detected in the effluent gases.

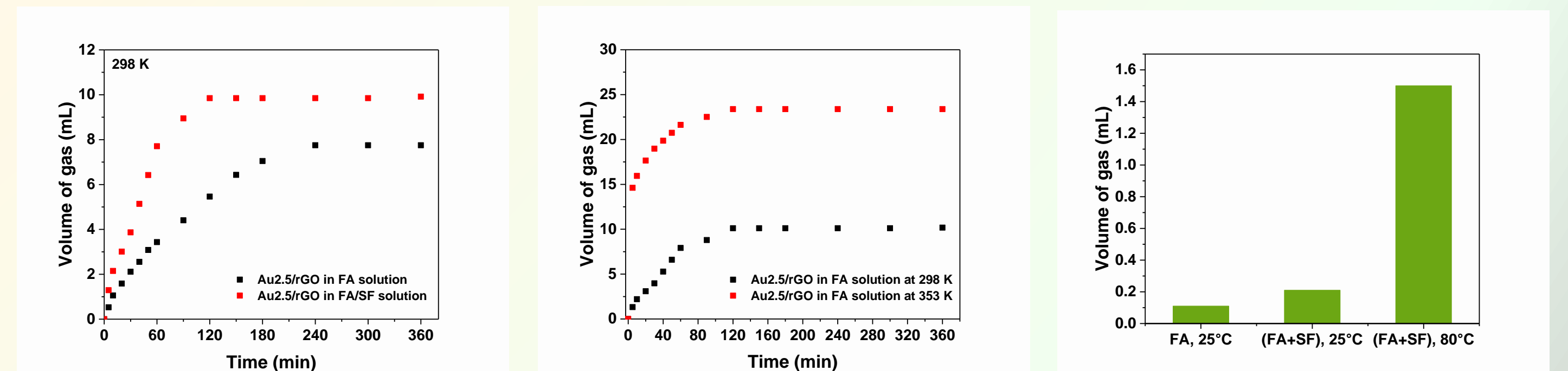


Figure 6. (a) The plots of generated gas (CO₂ + H₂) versus time in the presence of SF (5 mL solution; FA=0.25 mmol; SF=1 mmol) and in the absence of SF (5 mL solution; FA=1.25 mmol) for FA dehydrogenation catalysed by Au2.5/rGO at 298K; (b) Temperature dependent gas generation by the decomposition of FA; (c) Initial rate (after 10 minutes of reaction) the presence and in the absence of sodium formate

- Taking into account the poor catalytic results for Au5/rGO and Au10/rGO, the experiments involving the FA/SF were performed only for Au2.5/rGO catalyst.
- The addition of sodium formate at room temperature (298K) increases both the reaction rate and the volume of gases generated per mole of FA (Fig. 6a). Approximately 25% more (H₂+CO₂) was released, indicating a better FA activation and decomposition in the presence of SF. The FA decomposition practically reaches its terminus point in the presence of SF in half of the time necessary to reach it in its absence.

Conclusion

- We have developed a strategy using reduced graphene oxide (rGO) as support for preparing mono-metallic Pd(10wt%), Au(2.5wt%, 5 wt% and 10 wt%) and bi-metallic Pd(7.5wt%)-Au(2.5wt%) alloy NPs catalysts which were tested for the decomposition of FA into H₂ and CO₂ in FA or FA/SF aqueous solution.
- Compared to Pd/rGO, PdAu/rGO bi-metallic composite exhibited a slightly higher catalytic activity, which results in higher conversions and activation energy of 13.4% which is half from the activation energy value performed with Pd NPs. This improved catalytic performance originates from the smaller particles, good dispersion and the synergistic effect with the reduced graphene oxide. In the case of gold-graphene composites, the Au/rGO composites with low gold content (2.5wt%) and low dimension of AuNPs present better results for FA decomposition in aqueous solution compared to Au/rGO composites with 5 and 10 wt%.

Acknowledgments

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