

Study of 4-nitrophenol reduction over graphene oxide modified with Ag and CeO₂ nanoparticles by *in situ* UV-vis spectroscopy

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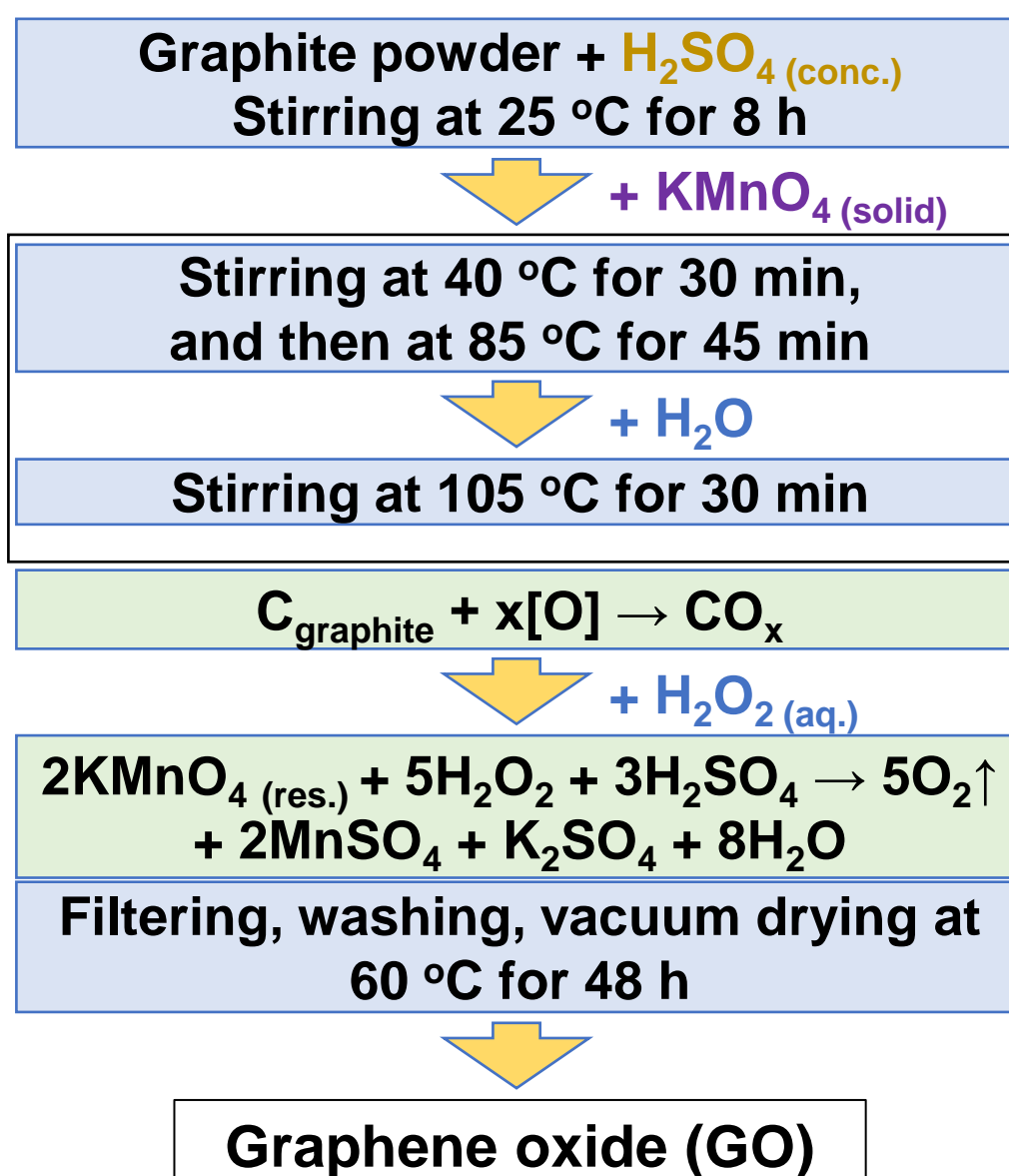
Introduction

The catalytic hydrogenation of nitroarenes under mild conditions addresses two challenges: efficient manufacturing of aromatic amines, valuable industrial intermediate compounds, and feasible removal of nitroarenes from wastewater followed by recycling. The Ag-containing catalysts are in the focus of green chemistry as advantageous systems due to relatively low cost, low-temperature activity, nontoxicity, and facile preparation and modification procedures [1]. Graphene, a two-dimensional carbon nanomaterial, and its derivatives (e.g., graphene oxide (GO)),

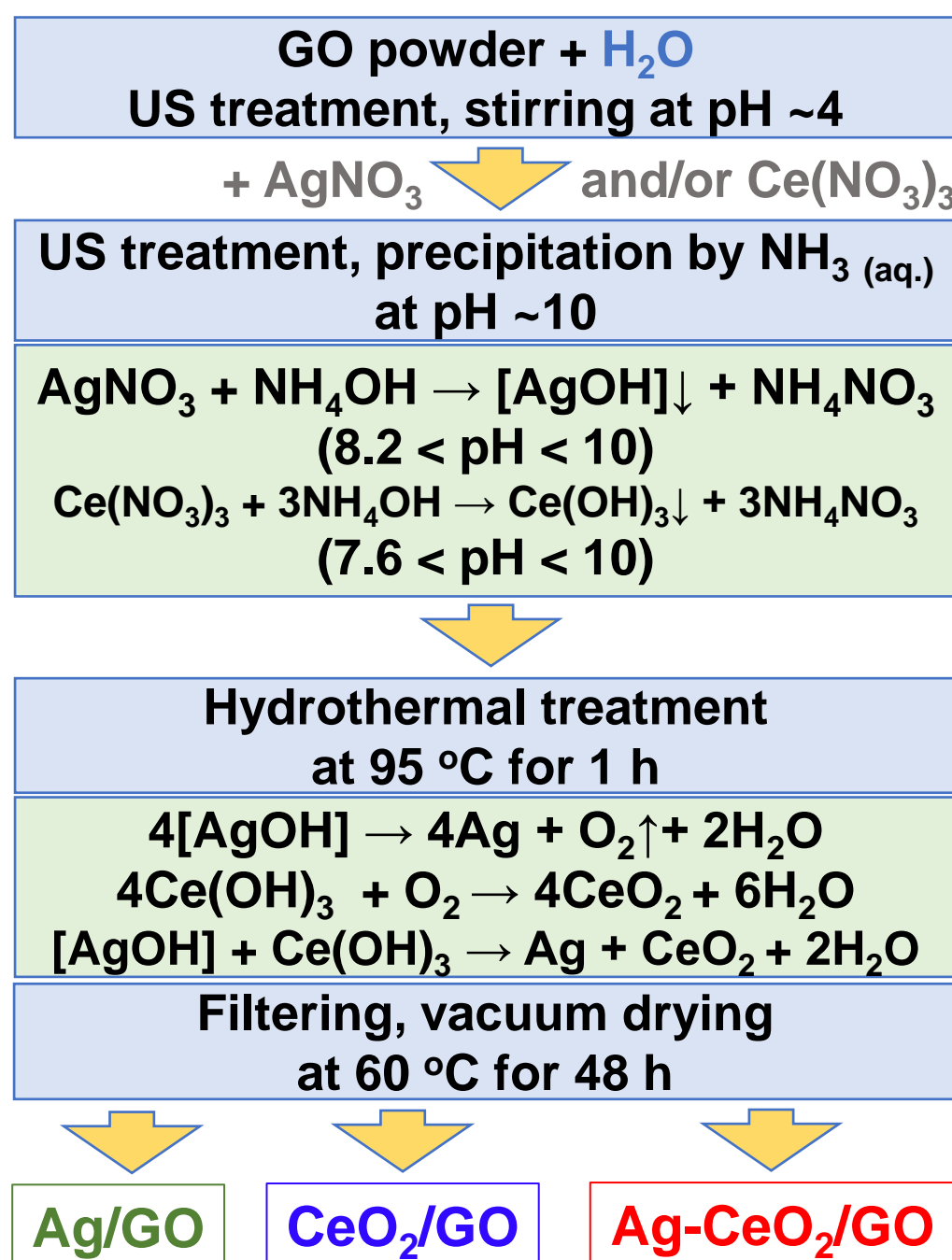
reduced graphene oxide (RGO) are considered promising environmentally benign adsorbents and catalyst supports [2].

This work aims to synthesize the Ag-CeO₂/GO systems and study their catalytic activity in the 4-nitrophenol (4-NP) reduction into 4-aminophenol (4-AP) at room temperature and ambient pressure. Special attention is given to the effect of co-deposition of Ag and CeO₂ onto GO and catalyst pretreatment on catalytic activity. The series of Ag- and/or CeO₂-containing catalysts are investigated by XRD, TGA, UV-vis spectroscopy.

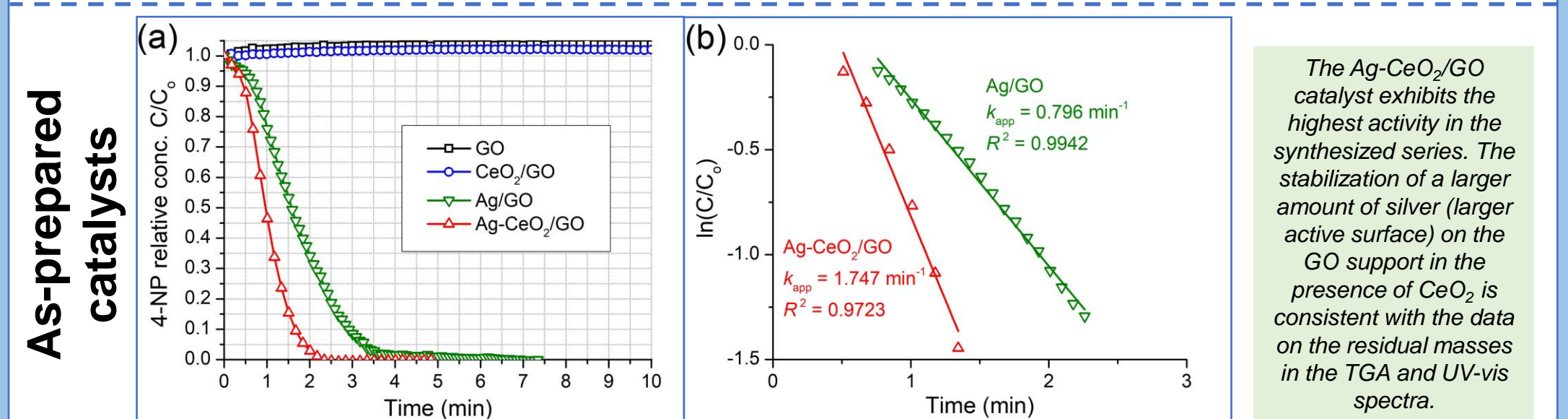
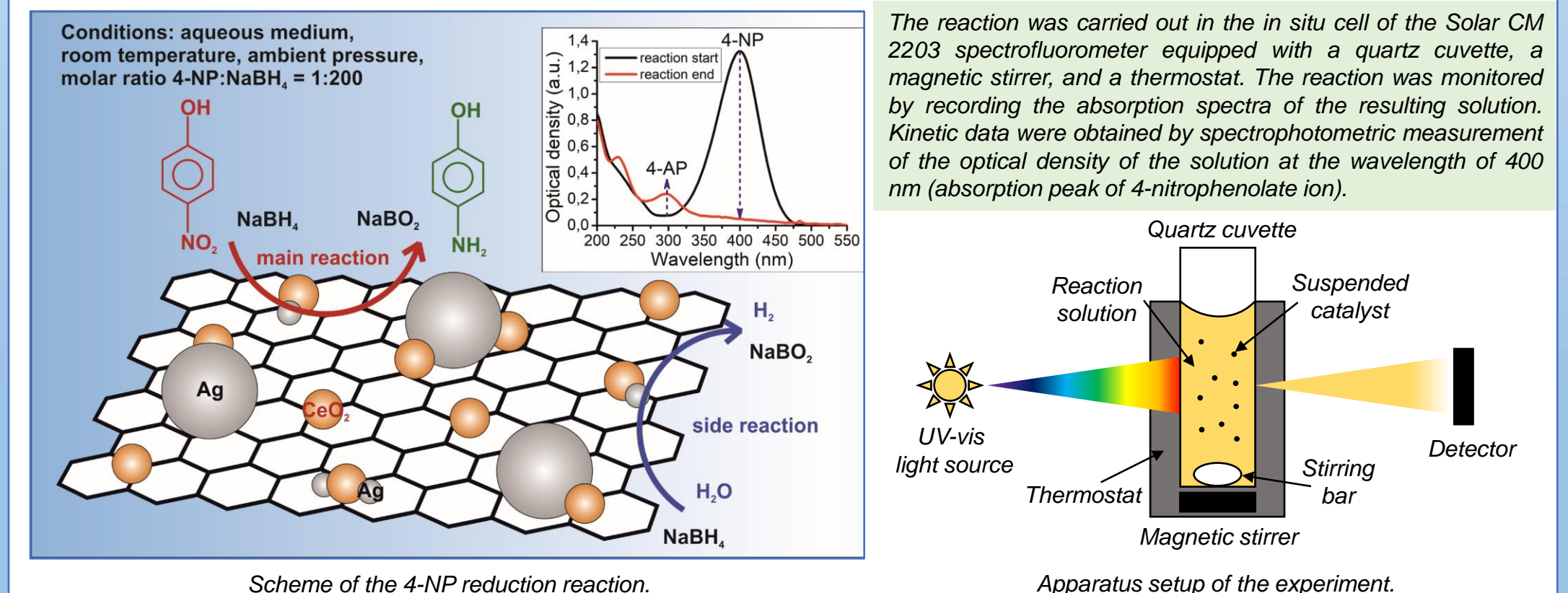
Synthesis of support



Synthesis of catalysts

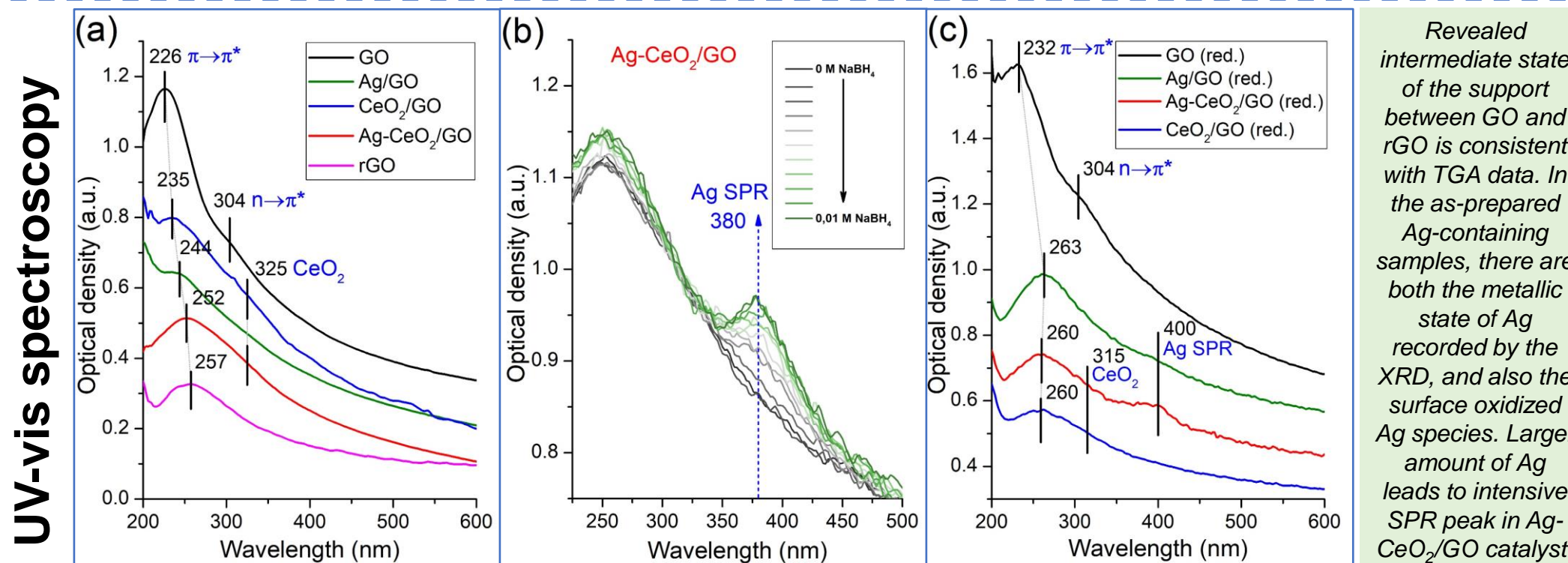
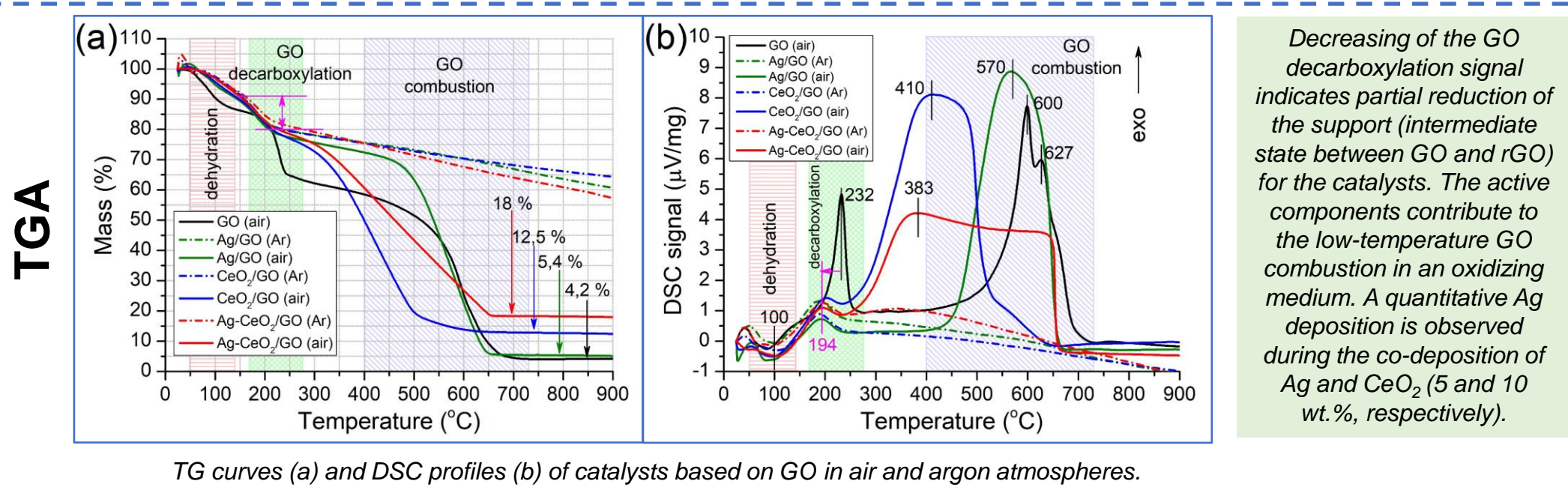
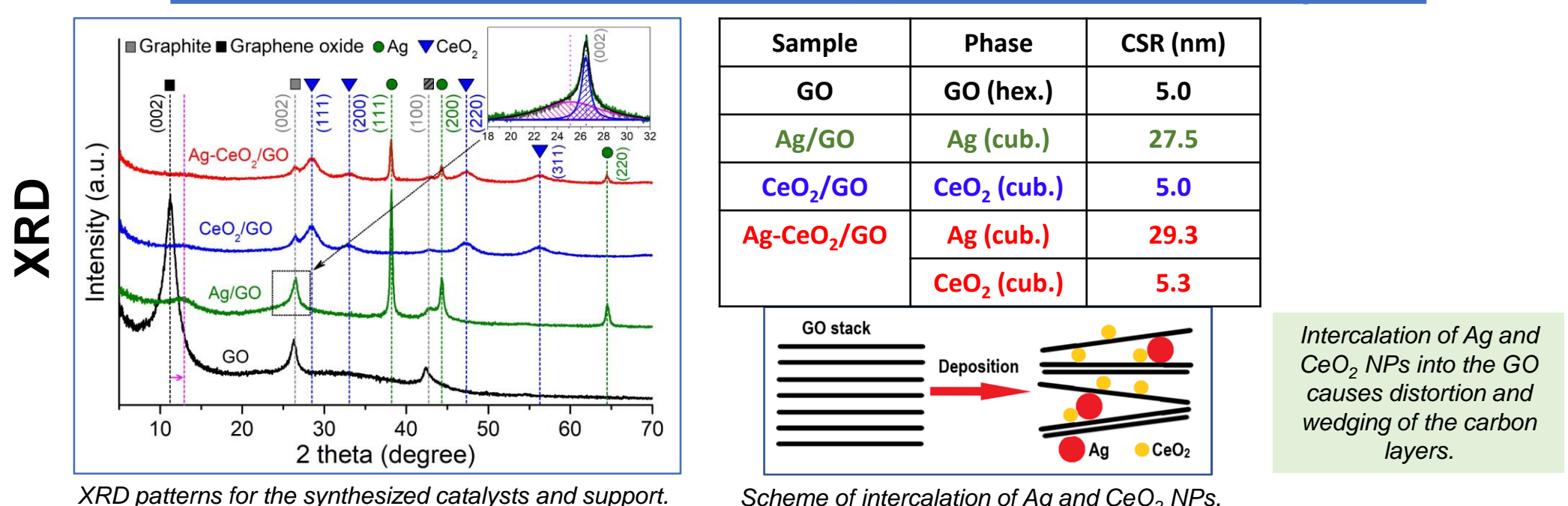


Catalytic experiment

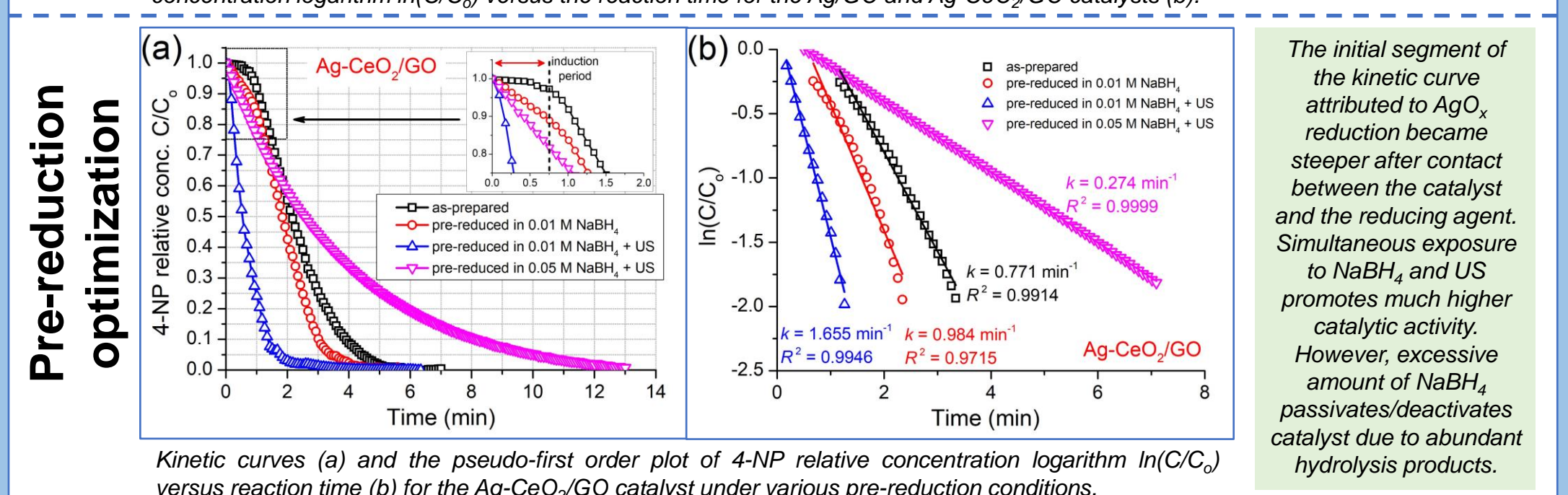


The Ag-CeO₂/GO catalyst exhibits the highest activity in the synthesized series. The stabilization of a larger amount of silver (larger active surface) on the GO support in the presence of CeO₂ is consistent with the data on the residual masses in the TGA and UV-vis spectra.

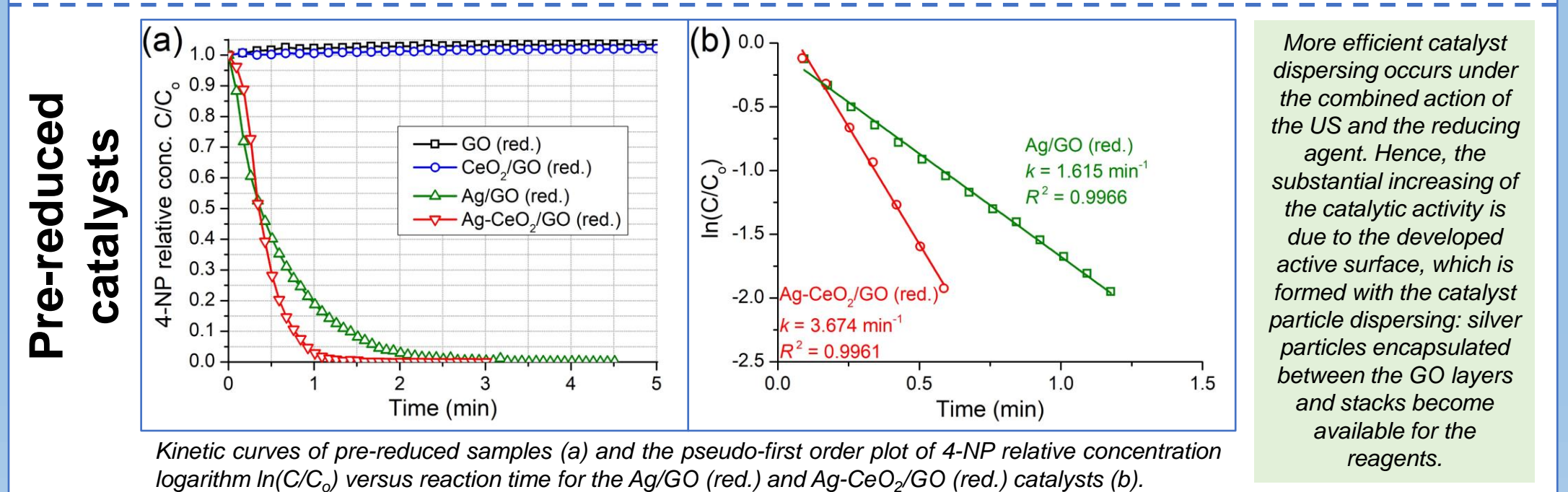
Characterization of support and catalysts



Revealed intermediate state of the support between GO and rGO is consistent with TGA data. In the as-prepared Ag-containing samples, there are both the metallic state of Ag recorded by the XRD, and also the surface oxidized Ag species. Larger amount of Ag leads to intensive SPR peak in Ag-CeO₂/GO catalyst.



The initial segment of the kinetic curve attributed to AgO_x reduction became steeper after contact between the catalyst and the reducing agent. Simultaneous exposure to NaBH₄ and US promotes much higher catalytic activity. However, excessive amount of NaBH₄ passivates/deactivates catalyst due to abundant hydrolysis products.



More efficient catalyst dispersing occurs under the combined action of the US and the reducing agent. Hence, the substantial increasing of the catalytic activity is due to the developed active surface, which is formed with the catalyst particle dispersing; silver particles encapsulated between the GO layers and stacks become available for the reagents.

Conclusions

- Graphene oxide (GO) is a promising matrix to stabilize small Ag and CeO₂ NPs.
- The co-deposition of Ag and CeO₂ ensures developed active surface of Ag-CeO₂/GO.
- The reaction is catalyzed by Ag NPs featuring a metallic surface state. NaBH₄ reduces both the surface AgO_x species and 4-NP.
- High catalytic activity and stability of Ag-CeO₂/GO in 4-NP reduction by NaBH₄ into 4-AP at room temperature and atmospheric pressure was revealed.
- The catalytic activity of the pre-reduced catalysts increases upon simultaneous exposure to NaBH₄ and US.

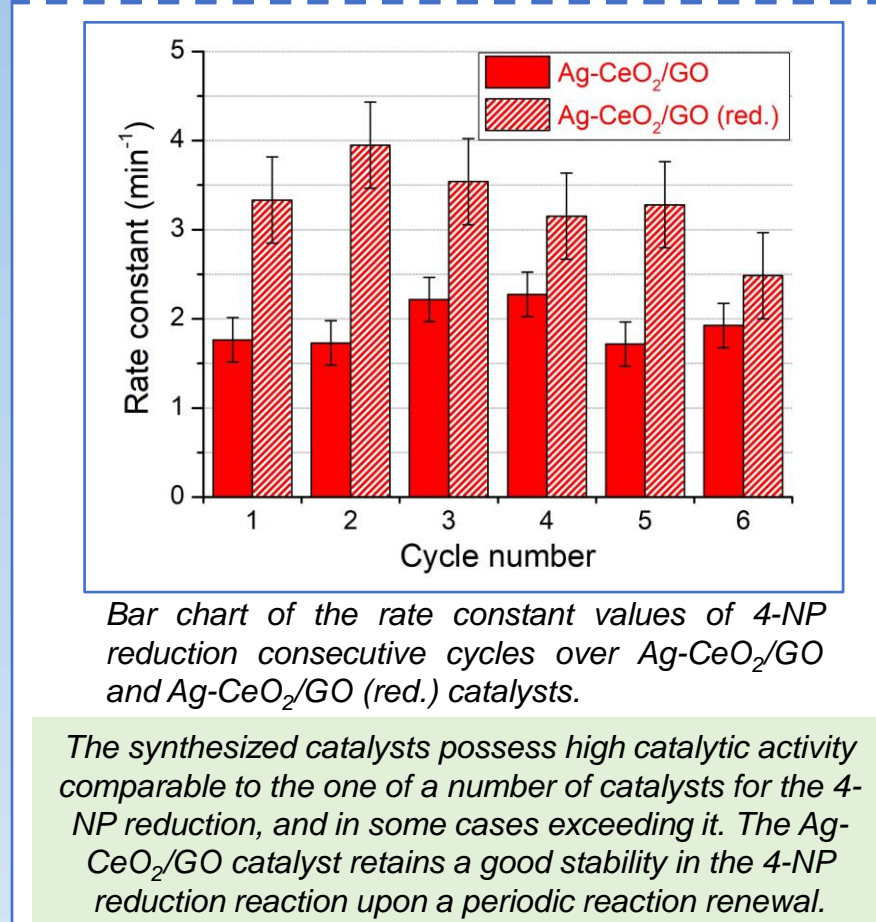
References

- C. Wen, A. Yin, W.-L. Dai, Appl. Catal. B: Environ. 160-161 (2014) 730-741.
- M. Yusuf et al., Adv. Colloid Interface Sci. 273 (2019) 102036.
- Z. Ji et al., Appl. Catal. B: Environ. 144 (2014) 454-461.
- A. Taratayko et al., Catal. Today 375 (2021) 576-584.
- Y. Shi et al., RSC Adv. 6 (2016) 47966-47973.
- M. Kohantorabi et al., New J. Chem. 41 (2017) 10948-10958.
- G. Lei et al., Ind. Nanomaterials 8 (2018) 877-884.
- J. Qu et al., Chem. Eng. J. 211-212 (2012) 412-420.
- S. Varshney et al., ChemCatChem 12 (2020) 4680-4688.
- W. Li et al., Inorg. Chem. Front. 3 (2016) 663-670.

Acknowledgements

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Sample	C _{catalyst} (mg/L)	Concentration		k _{app} (min ⁻¹)	Ref.
		NaBH ₄ (mM)	4-NP (mM)		
Ag-CeO ₂ /GO	30	15	0.075	1.747	This work
Ag/GO	30	15	0.075	0.796	This work
Ag-CeO ₂ /GO (red.)	30	15	0.075	3.674	This work
Ag/GO (red.)	30	15	0.075	1.615	This work
RGO/Ag/CeO ₂	-	15	0.075	0.269	[3]
Ag-CeO ₂ /SBA-15	60	30	0.15	0.960	[4]
Ag@CeO ₂	10	20	0.13	1.920	[5]
Ag ₈₀ Ni ₂₀ @CeO ₂	10	0.08	400	6.231	[6]
GO/Ag-Fe ₃ O ₄	6.7	0.1	33	1.602	[8]
Ag-Pt (9:1)	0.6	0.1	1.4	3.540	[9]
Ag@hm-SiO ₂	2	0.016	10	1.080	[10]



The synthesized catalysts possess high catalytic activity comparable to the one of a number of catalysts for the 4-NP reduction, and in some cases exceeding it. The Ag-CeO₂/GO catalyst retains a good stability in the 4-NP reduction reaction upon a periodic reaction renewal.