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Comment on “In-situ synthesis of Co_3O_4 nanocrystal clusters on graphene as high-performance oxygen reduction reaction electrocatalysts” by Juanjuan Yin et al

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In their recently published article in this journal, Yin et al. [1] describe a promising nanomaterial based on cobalt oxide clusters supported on reduced graphene oxide (rGO), to be used as a catalyst in electrocatalytic oxygen reduction reaction (ORR). The in situ synthesised nanometre-sized particles are claimed to have Co_3O_4 composition with spinel crystallographic structure, exposing (111) crystal planes. The authors demonstrate that this catalytic material exhibits enhanced ORR activity as compared to commercial Pt/C catalysts and attribute it to a synergistic cooperation between the oxide and the support. Although both the topic and the approach, aiming at the replacement of noble metals in electrocatalysis, are timely and interesting, proposed interpretations of the experimental data and the related discussion are not adequately handled and contain a lot of serious errors.

In the following, we will mainly focus on the chemical analysis aspect of the above material. Electronic structure and chemical state of the near-surface region of the featured Co_3O_4 electrocatalyst was investigated by X-ray photoelectron spectroscopy (XPS). Several conclusions are made based on the XPS analysis; however, a series of misinterpretations renders them invalid or unsubstantiated.

Although no type of X-ray source (and thus the photon primary energy) has been specified in the Experimental section, it can be distinguished from the overall character of the wide survey spectrum in Fig. 6a (mainly from the positions of Auger transitions), concluding that Al K α was used in the measurements.

The two main features of the Co 2p region referred to as ‘asymmetric characteristic peaks’ are, indeed, components of the 2p level doublet due to spin-orbit splitting. As such, a mutual intensity ratio of all coupled components should follow the amount of degeneracy for each respective electronic sublevel. A theoretical value of 2 for a p-level can slightly vary in practice, but in the presented spectral decomposition, it is around 5 and 1.5 (roughly estimated from Fig. 6d in Yin et al. [1] since the actual numbers are not provided in the paper) for lower and higher EB component, respectively.

Each of the two branches of the doublet has been fitted into two contributions. No assignment of these individual contributions is given by authors except for the peak at 780.5 eV which is claimed to be composed of ‘at least two possible distributions, namely cobalt oxide and cobalt carbide’. It is further added that, based on the XRD and TEM results, this particular peak is likely associated with the latter, i.e. presence of Co–C bond.

In contrary to the above deductions, the peaks fitted at 779.1 and 780.5 eV represent two oxidation states of cobalt, namely Co^{3+} and Co^{2+} , exactly as one would expect for a Co_3O_4 spinel material [2–4]. Strictly speaking, the Co^{2+} -related spectral contribution should comprise two components at ~ 780.5 and 782.5 eV due to multiplet splitting caused by coupling of the final states with unpaired 3d electrons [3,5]. Alternatively, it can be fitted with a single feature, but provided it has a proper asymmetry to account for the final state multiplicity. Each oxidation state is naturally accompanied by a relatively wide shake-up satellite at ~ 785 – 786 and 789 – 790 eV for Co^{2+} and Co^{3+} , respectively [2–5], but in the spectral decomposition presented in the discussed paper, they have been completely omitted. In fact, a correct treatment of the satellite structure can substantially aid in the evaluation of the 0, 2+, and 3+ oxidation states of cobalt, owing to the larger separation and different relative magnitudes of the satellites with respect to their parent 2p photoelectron levels. Unfortunately, in the presented photoelectron spectra, the missing experimental points above 800 eV, where Co 2p $_{1/2}$ -related satellites are located, contribute to the overall inaccuracy of data elaboration.

Regarding the speculated cobalt carbide, it has been reported by other authors to exhibit the main 2p $_{3/2}$ peak at 780.2 eV for Co_2C , accompanied by a strong Co^{2+} satellite around 786 eV [6], or at binding energies (BEs) even lower than for metallic Co^0 in the case of non-stoichiometric CoC_x phases [7]. This is in a sharp contrast to the character of the Co 2p spectra provided by Juanjuan Yin et al. Another counterevidence is the absence of a corresponding carbidic peak in C 1s spectrum, expected at 282.8–283.3 eV [6,7].

What has also been completely neglected is the absence of $L_3M_{4,5}M_{4,5}$ Auger line of cobalt, which partially overlaps with the Co 2p photoelectrons in $\sim 765\text{--}783$ eV range when probed by Al K α X-ray source [2–4]. In the presented truncated data, shown only for $EB > 774$ eV, at least a single wide component between ~ 775 and 780 eV should have been allowed to be fitted as an Auger LMM representation.

Despite the above negligence, the composite fitted curve seems to follow the experimental points relatively well. This is, however, a misleading impression. The mathematically satisfactory fit is in part due to the excessive data truncation, in part because the background subtraction (not specified by authors, presumably Shirley-type) was not done correctly. Exaggerated background intensity leads to virtual elimination of both Auger peaks and all satellite contributions.

In the discussion of the XP spectra, a few papers are cited (refs. 60–64 in Yin et al. [1]), of which three are totally irrelevant, i.e. not featuring XPS measurements or dealing with different materials than those related to Co. Ironically, the only relevant reference (ref. 64), although not flawless, is merely mentioned but not used as a guide; in fact, the fitting recipe applied in Yin et al. [1] is severely contradicting it. Wang et al. [8], which is also not followed by Juanjuan Yin et al. in his analysis, albeit cited therein as ref. 63, attempts to decompose spectra of cobalt oxides. However, this is yet another bad example of XPS data treatment; the authors of this study refer to another problematic fitting routine suggested in Li et al. [9], although they used a different X-ray excitation source (Mg K α in Li et al. [9]). It is somewhat incomprehensible why such literature sources are followed, since there are numerous published works available, dealing with this particular topic much more correctly, elaborately, and on more fundamental level (e.g. [2–4]).

Indeed, researchers frequently prefer to employ simplified fitting procedures, sometimes even involving only the Co 2p $_{3/2}$ branch of the photoemission line, with a background often cut into the Auger LMM section (in the case of the Al K α primary source), virtually eliminating it. This may be a justifiable approach in many cases, for instance in identifying qualitative trends in Co oxidation state variation, as long as the fitting is performed consistently within the whole experimental series. However, one has to be aware of the fact that such simplification can also contribute to systematic quantitative errors up to a few tens of per cent [2] and may cause difficulties when compared to other literature data, theoretical calculations, or photoelectron spectra acquired with different excitation sources. Hence, such facilitative approaches, commonly seen in literature (not only for cobalt, but also for some other transition metal elements, especially those of the first row, namely Fe, Ni, Cu, etc.), ought to be used with extra vigilance and

should not go beyond a certain point of simplification of physical reality.

If we now take a broader perspective, the spectral interpretation of photoelectron lines of mutually binding or interacting elements should provide a consistent picture. Specifically in this case, if C–O is claimed to be seen in O 1s, why does not it have its counterpart in C 1s? In fact, the peak at 287.6 eV interpreted by authors as C=O is more likely (or mainly) C–O within C–O–C of rGO [10,11], especially since the fitted contribution at 286.1 eV has been attributed to C–OH (although the plot legend in Fig. 6b does not match the designations used in the text, so it is not exactly clear what authors meant here). Accordingly, what is considered in Yin et al. [1] to be C=O at 529.5 eV in the O 1s spectra actually originates from the lattice oxygen of Co $_3$ O $_4$ particles, whereas C–O probably forms the main contribution at 530.8 eV, replacing the original assignment to hydroxyls, which can be found near 532.9 eV.

In general, what one would find particularly astonishing is to have the lattice oxygen excluded from an interpretation of an oxide material, as well as to disregard different oxidation states of cobalt (Co $^{2+}$, Co $^{3+}$) while presenting the investigated compound as being Co $_3$ O $_4$ spinel.

Last but not least, the omitted peak near 400 eV, clearly visible in the wide spectrum (Fig. 6a), most likely belongs to N 1s. The origin and potential influence of this element in the samples is, however, left without any discussion.

Juanjuan Yin et al. also attempted to complement and support the physico-chemical characterisation of their samples by elemental analyses provided by energy-dispersive X-ray spectroscopy mapping in scanning electron microscope and high-angle annular dark field–scanning transmission electron microscopy instruments, respectively. They declare: ‘... the mapping image of Co $_3$ O $_4$ /rGO shows the presence of Co, C, and O, which further proves that Co $_3$ O $_4$ nanocrystals are generated’. Although potentially useful for many systems, one has to realise, that these methods are barely indicative in the presented case and do not allow to determine reliably the actual stoichiometry. Hence, no valuable conclusions can be drawn in order to support the proclaimed Co $_3$ O $_4$ crystalline structure of the rGO-supported nanoparticles. Nor any spatially related considerations can be done for average 5-nm particles, with regards to the EDS image pixel size of ~ 300 nm and the high level of noise as in Fig. 2d–f.

Due to the above mentioned numerous discrepancies and negligences, no reasonable and valid conclusions can be reached such as ‘rGO provides electron transfer channel for the catalytic reaction’, or ‘... synergistic coupling between Co $_3$ O $_4$ particles and

rGO sheets'. This is because both electronic structure of the material and the microscopic nature of the interactions between rGO substrate and the supported cobalt oxide are not adequately addressed in the presented study. If done properly, some relationships could be rendered between the chemical state of cobalt, oxide morphology and its electrocatalytic performance, to shed some light on the origin of the otherwise promising electrochemical properties of the $\text{Co}_3\text{O}_4/\text{rGO}$ system. At more general level, the presented analysis by Yin et al. can mislead or confuse other researchers in their own processing and interpretation of experimental data.

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References

- [1] Yin JJ, Guo YY, Liu ZW, et al. In-situ synthesis of Co_3O_4 nanocrystal clusters on graphene as high-performance oxygen reduction reaction electrocatalysts. *Mater Technol.* 2022;37(12):2106–2115. doi:10.1080/10667857.2021.1934359 .
- [2] Cabrera-German D, Gomez-Sosa G, Herrera-Gomez A. Accurate peak fitting and subsequent quantitative composition analysis of the spectrum of Co 2p obtained with Al K α radiation: I: cobalt spinel. *Surf Interface Anal.* 2016;48:252–256.

- [3] Lykhach Y, Piccinin S, Skala T, et al. Quantitative analysis of the oxidation state of cobalt oxides by resonant photoemission spectroscopy. *J Phys Chem Lett.* 2019;10(20):6129–6136.
- [4] Biesinger MC, Payne BP, Grosvenor AP, et al. Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Cr, Mn, Fe, Co and Ni. *Appl Surf Sci.* 2011;257(7):2717–2730.
- [5] Yang J, Liu HW, Martens WN, et al. Synthesis and characterization of cobalt hydroxide, cobalt oxyhydroxide, and cobalt oxide nanodiscs. *J Phys Chem C.* 2010;114(1):111–119.
- [6] Zhang TF, Wu JS, Xu YQ, et al. Cobalt and cobalt carbide on alumina/NiAl(110) as model catalysts. *Catal Sci Technol.* 2017;7(24):5893–5899.
- [7] Rodriguez-Gomez A, Holgado JP, Caballero A. Cobalt carbide identified as catalytic site for the dehydrogenation of ethanol to acetaldehyde. *ACS Catal.* 2017;7(8):5243–5247.
- [8] Wang LM, Liu QF, Ta N, et al. Multi-functional cerium modification to accelerate the oxygen reduction reaction of spinel Co_3O_4 . *Chemistryselect.* 2021;6:3512–3518.
- [9] Li K, Chen C, Bian XC, et al. Electrolytic nitrate reduction using Co_3O_4 rod-like and sheet-like cathodes with the control of (220) facet exposure and $\text{Co}^{2+}/\text{Co}^{3+}$ ratio. *Electrochim Acta.* 2020;362:137121.
- [10] Al-Gaashani R, Najjar A, Zakaria Y, et al. XPS and structural studies of high quality graphene oxide and reduced graphene oxide prepared by different chemical oxidation methods. *Ceram Int.* 2019;45(11):14439–14448.
- [11] Wei GD, Yu J, Gu M, et al. Dielectric relaxation and hopping conduction in reduced graphite oxide. *J Appl Phys.* 2016;119:224102.

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