Communication

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Matters Arising: Weak (if at All) Experimental Evidence for Structure Model and Superior Performance Claims of a 2D Polyaniline

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Abstract: Arising from Zhang et al. *Nature* https://doi.org/10.1038/s41586-024-08387-9. The authors present a multi-layer-stacked crystalline 2D Polyaniline (PAni) structure with metallic out-of-plane electrical conductivity. [1] They claim this out-of-plane metallic conductivity (15 S/cm) to be the highest conductivity of this type ever published. The PAni structure presented would in fact be unique and a new structure principle for conductive polymers as their model involves single chains as network strings in a 2D layer. While this publication offers some interesting prospects, there are too many unsupported statements, hence having found a new principle may be least premature.

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1. A µXPS elemental analysis in Supplementary Table S1 shows a relation

a) of Cl2p to N1s = 2.5 to 8 which is not in line with the composition shown in Figure 1d (which shows be 1:2 or 4:8), and 1:2 would be an optimal composition for maximum conductivity;

b) of C1s and N1s (72.2:8.0 = 9:1) which does not represent a normal PAni composition, this should be about 6:1 if it were a linear PAni chain, or 7.5:1 when looking at the paper's Figure 1d and Supplementary Figure S1 (TDQ intermediate);

c) and shows O1s which is not an element in PAni*HCl; it is not clear (and the authors did not comment about) why the flakes contain so much oxygen.

The elemental analysis based on XPS does not support the presented structure model.

2. The synthesis procedure (Aniline + APS in a HCl solution containing a surface active agent, reaction at 1 °C) is not much different from standard procedures as published in countless papers – nevertheless, their structure model (showing a linear PAni chain with TDQ units) is very different from what was ever published; but their µXPS elemental analysis does not support the structure model containing TDQ units.

- The colour shown (Figure 2A) is not typical for doped Polyaniline; during a communication with the authors, the colour was called „a mixture of amaranth and blue" [8], which resembles the colour of Pernigraniline [2], not protonated PAni (which is green).

3. There is no information about the polymerisation degree, but the structure model suggests quite a long and straight chain with rectangular branches. Such isolated single chains are not possible from a thermodynamical standpoint of view [3] considering unbalanced charge distribution with „naked" positive and negative charges. As such single chains are claimed to be a valid structure model, the thermodynamical considerations in [3] would need to be soundly refuted.

4. In spite of these questionable structural details, the interlayer distance of 3.59 Å determined by x-ray is interesting as already in 2010 we have published an interlayer distance of 3.6 Å while having prepared macroscopic samples [4], but via a completely different process series: Controlled polymerisation at 2 °C followed by a dispersion step, followed by extraction of the dispersion matrix

and finally deposition of the dispersion based film [5]. The PAni morphology had changed from an originally globular shape (after polymerisation) to an ellipsoidal form (original publication in patents [6]). The chain formation was hypothetically assumed to be helical. [5].

A further similarity can be seen in a 2.2 nm changing to 2.5 nm plane distance [5] (interpreted as helix turn plane) which corresponds to a monomolecular layer thickness of 2.6 nm previously reported by Zhang et al. [7] It is striking that these values are of the same size as the network building blocks, for which the authors claim the bright network string to represent the PAni chain, however giving no evidence for it.

As this was state of the scientific knowledge since years, it should have been cited and would have been appropriate to show how (and why) a similar polymerisation procedure would lead to not only a completely different PAni structure (as claimed), but also to the same interlayer distance, the key for metallic conductivity. And this after the process leading to the results published in [4,5] involves short PAni chains (about 12 monomer units) and dispersion, while the process described in [1] directly formed the samples during synthesis and allegedly created long straight chains (a claim which however, as mentioned above, is not supported by experimental data).

5. In addition, there is no information about what could be the structure of the materials within the holes of the rectangular network (allegedly surrounded by PAni single straight chains). This only leaves room for speculation considering that the reaction yield is „very low“[8] and obviously no cleaning steps (after polymerisation) had been applied.

6. A publication [5] showing metallic conductivity of >200 S/cm metallic was not cited; Zhang et al.‘s claiming highest out-of-plane conductivity ever published is inappropriate for 2 reasons:

$\sigma_{\parallel}/\sigma_{\perp}$

a) with the reported 7.1 +/- 3.4 (= max. 10.5) S/cm in-plane, and 14,9 +/- 4.6 (= min. 10.3) S/cm out-of-plane, an anistropy can not be justified, it could in both directions well be „10“;

b) anisotropy was shown in [9] to decrease from a factor of 60 to 1.2 with increasing sample dimension,

i. e. the much earlier publication [5] shows higher values by a factor of 10.

7. While their previous publication [8] reports a 160 S/cm conductivity upon post-doping with HCl, this was – for unknown reasons – not mentioned in the actual paper.

8. The conductivity / temperature dependence shown by Zhang et al. [1] in Supplementary Figure S34 is extremely similar to the behaviour shown in Figure 3. In [9]; i. e. in spite of completely different sample generation, crystallinity and (unclear) structure, the (nano)metallic character is basically the same, which asks for discussion or explanation, especially considering the unsupported structure model.

9. The authors promote the belief according to which charge transfer mainly occurs along the conjugated chains, with a secondary contribution by interchain hopping citing [10] (ref. 5 in [1], the granular metal concept with metallic islands, similar to Figure A.3.3 in [11]). The chains sketched therein connecting the „islands“ have never been experimentally supported, they are a result of pure speculation. During dispersion, they would have been torn apart if they existed. In contrast to this but in line with experimental data, metallic 3D charge transfer has been shown within primary particles including tunneling between the particles after dispersion [12].

10. The structural features detected by HRTEM are extremely interesting, but not understandable, because we don’t know what the different structural elements are chemically. It is not helpful to declare „The 2DPANI network appears bright on a dark background“ (Figure 2) without giving any evidence. It would be helpful especially for the understanding the nanometallic characteristics mentioned in par. 8. above to see the surface morphology by SEM and AFM.

To summarize: With the experimental data given so far, it is still unclear whether the presented approach can fulfill hopes to prepare metallic cores (irrespective whether 2D or 3D) in size significantly bigger than 10 nm (preferably beyond 1 µm) so to overcome the mesoscopic conductivity limitations which would allow to get macroscopic conductivity in the range of values so far seen only as intrinsic conductivities in the range of 10^3 to 10^4 S/cm [9].

Supplementary Materials:

Competing interest: B. W. has no financial competing interest in fundamental research on Polyaniline; he is currently a technical consultant to Ormecon Pvt. Ltd. (Navi Mumbai, India) with no remuneration and a small (<5%) minority share in this very small company which – so far with no success – tries to reanimate Polyaniline use in corrosion protection (passivation) for which the previous patents filed by B. W. on behalf of the former Zipperling Kessler and Ormecon GmbH, resp. (both Germany, the companies are sold), have expired. The Indian startup is not involved in fundamental research nor in development of potential applications of technologies in any way connected with the topics under discussion here and has no plans (and no financial resources) to extend its activities beyond corrosion protection. B. W. is an active author of popular science books for Springer Nature.

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