

Microwave-Assisted Solvothermal Synthesis and Mechanochemical Preparation of $[\text{Cu}_3(1,3,5\text{-benzenetricarboxylate})_2]$

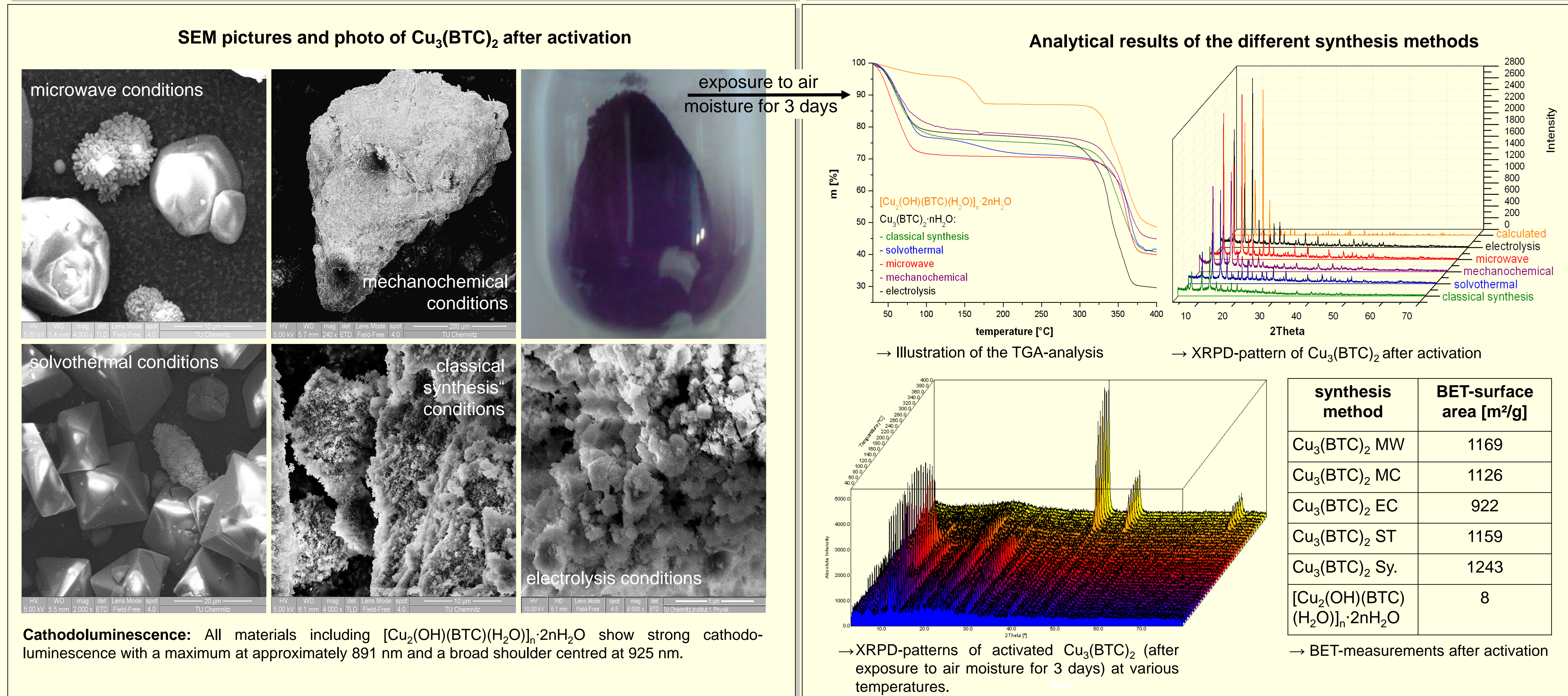
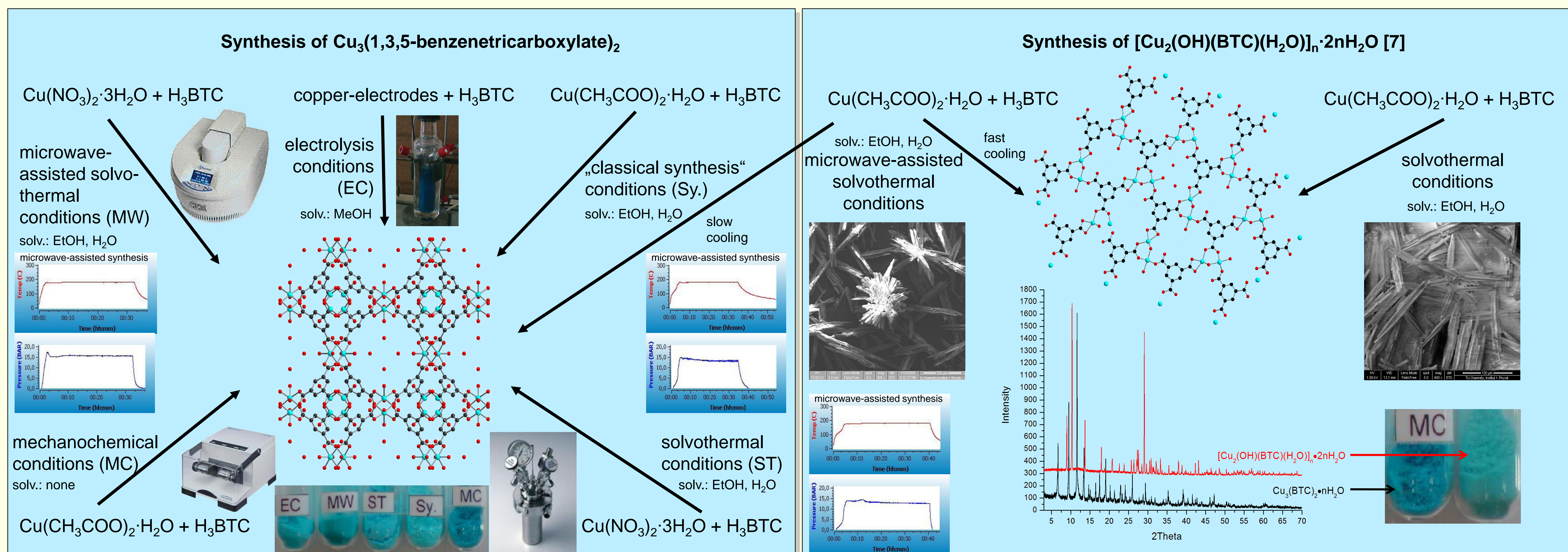


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Metal-Organic frameworks are currently focus of intense research because a large number of them have porous structures and offer a variety of potential applications such as gas sorption, hydrogen storage, sensing and catalysis.[1] A prominent compound that has attracted considerable interest because of its stability and interesting framework structure is presented by $[\text{Cu}_3(\text{benzene-1,3,5-tricarboxylate})_2]$, so-called $\text{Cu}_3(\text{BTC})_2$. [2] The most striking structural feature of $\text{Cu}_3(\text{BTC})_2$ is that the coordination sites of the metal ions are occupied by weakly bound water molecules and not by strongly coordinated multifunctional organic ligands. The water can easily be removed from the characteristic „paddle-wheel“ $\text{Cu}_2(\text{OOCR})_4$ unit upon heating without collapse of the framework structure to give coordinatively unsaturated Cu-Ions. So far, several synthetic strategies for $\text{Cu}_3(\text{BTC})_2$ have been reported including solvothermal [3] as well as pressure-free „classical“ synthesis,[4,5] electrochemical production [1] and oriented growth on functionalized self-assembled monolayers.[6] Here we present our results on different synthetic procedures with special focus on the microwave-assisted solvothermal synthesis and mechanochemical preparation of $\text{Cu}_3(\text{BTC})_2$. Especially, the question whether microwave-assisted solvothermal synthesis is simply the most rapid production process or does offer other advantages, e.g. with respect to phase purity, surface area and morphology, is discussed. Additionally, the materials obtained were analyzed with respect to cathodoluminescence.



Conclusion

- For the first time environmentally benign **mechanochemical preparation** of $\text{Cu}_3(\text{BTC})_2$ with high BET-surface area is reported.
- Solvothermal synthesis** starting from $\text{Cu}(\text{CH}_3\text{COO})_2$ in water/ethanol or $\text{Cu}(\text{NO}_3)_2$ [7] in water gave two-dimensional $[\text{Cu}_2(\text{OH})(\text{BTC})(\text{H}_2\text{O})]_n$, whereas three-dimensional $\text{Cu}_3(\text{BTC})_2$ is observed from water/ethanol starting from $\text{Cu}(\text{NO}_3)_2$. [2]
- Studies on the **microwave-assisted solvothermal synthesis** revealed some interesting details: i) This synthesis strategy allows for the control of product formation by the choice of the cooling rate (fast cooling: $\text{Cu}_3(\text{BTC})_2$ vs. slow cooling: $[\text{Cu}_2(\text{OH})(\text{BTC})(\text{H}_2\text{O})]_n$); ii) Starting from both $\text{Cu}(\text{NO}_3)_2$ and $\text{Cu}(\text{CH}_3\text{COO})_2$ we did obtain $\text{Cu}_3(\text{BTC})_2$; iii) In contrast to solvothermal synthesis formation of Cu_2O as byproduct was not observed; iv) Finally, microwave-assisted solvothermal synthesis is the most rapid and most convenient synthetic method for the preparation of $\text{Cu}_3(\text{BTC})_2$.
- Electrochemical synthesis** of $\text{Cu}_3(\text{BTC})_2$ gave the lowest BET-surface area.
- The **morphology** of the materials strongly depends on the synthesis method, but the BET-surface areas of the different $\text{Cu}_3(\text{BTC})_2$ samples are comparable with an exception being observed for the material prepared by electrochemical synthesis.

References

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