

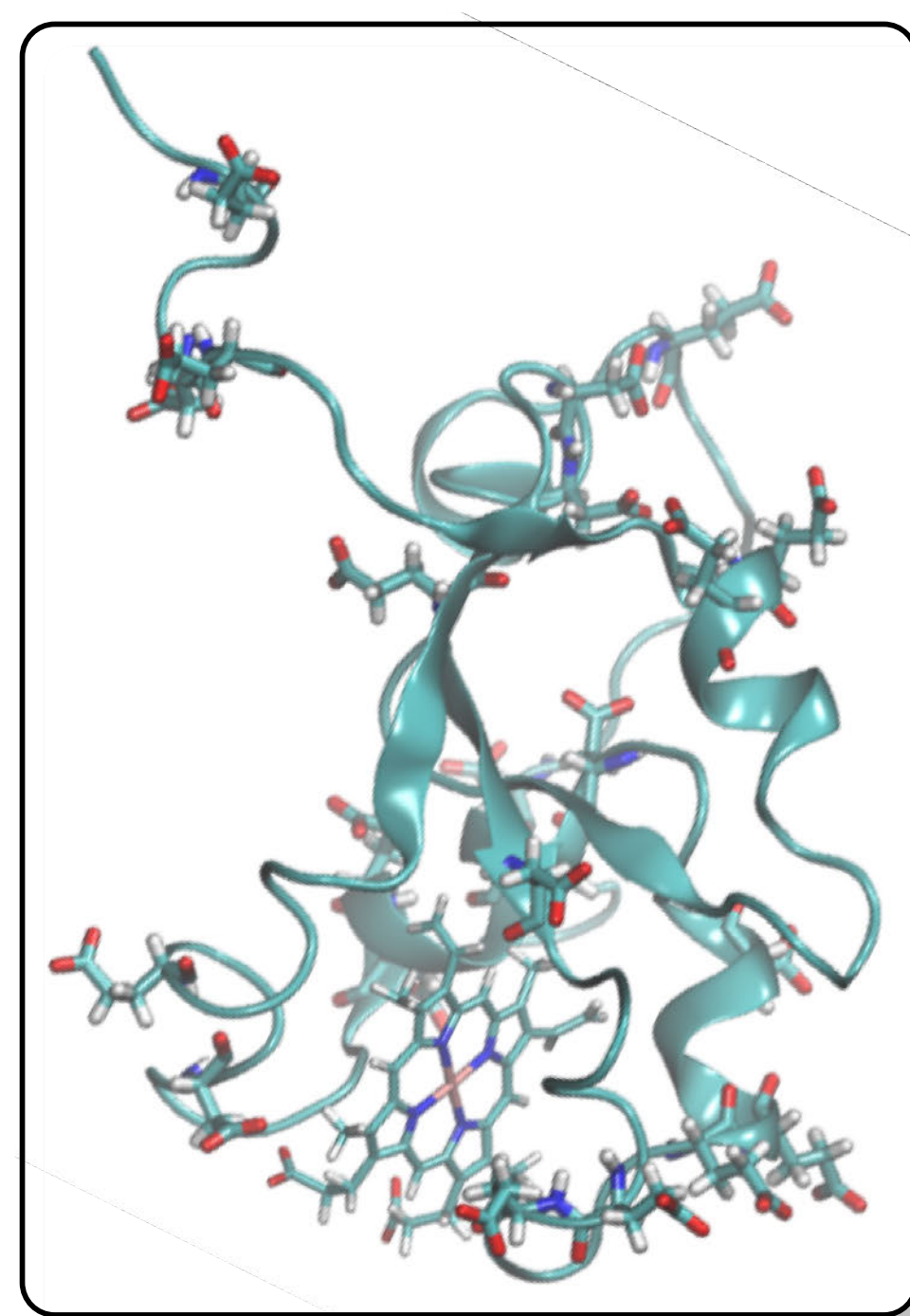
# TiO<sub>2</sub> nanotube electrodes for surface enhanced Raman spectro-electrochemistry

Ibrahim Halil Öner<sup>a</sup>, Christine Querebillo<sup>b</sup>, Christin David<sup>c</sup>, Khoa H. Ly<sup>a,\*</sup>, and Inez M. Weidinger<sup>a,\*</sup>

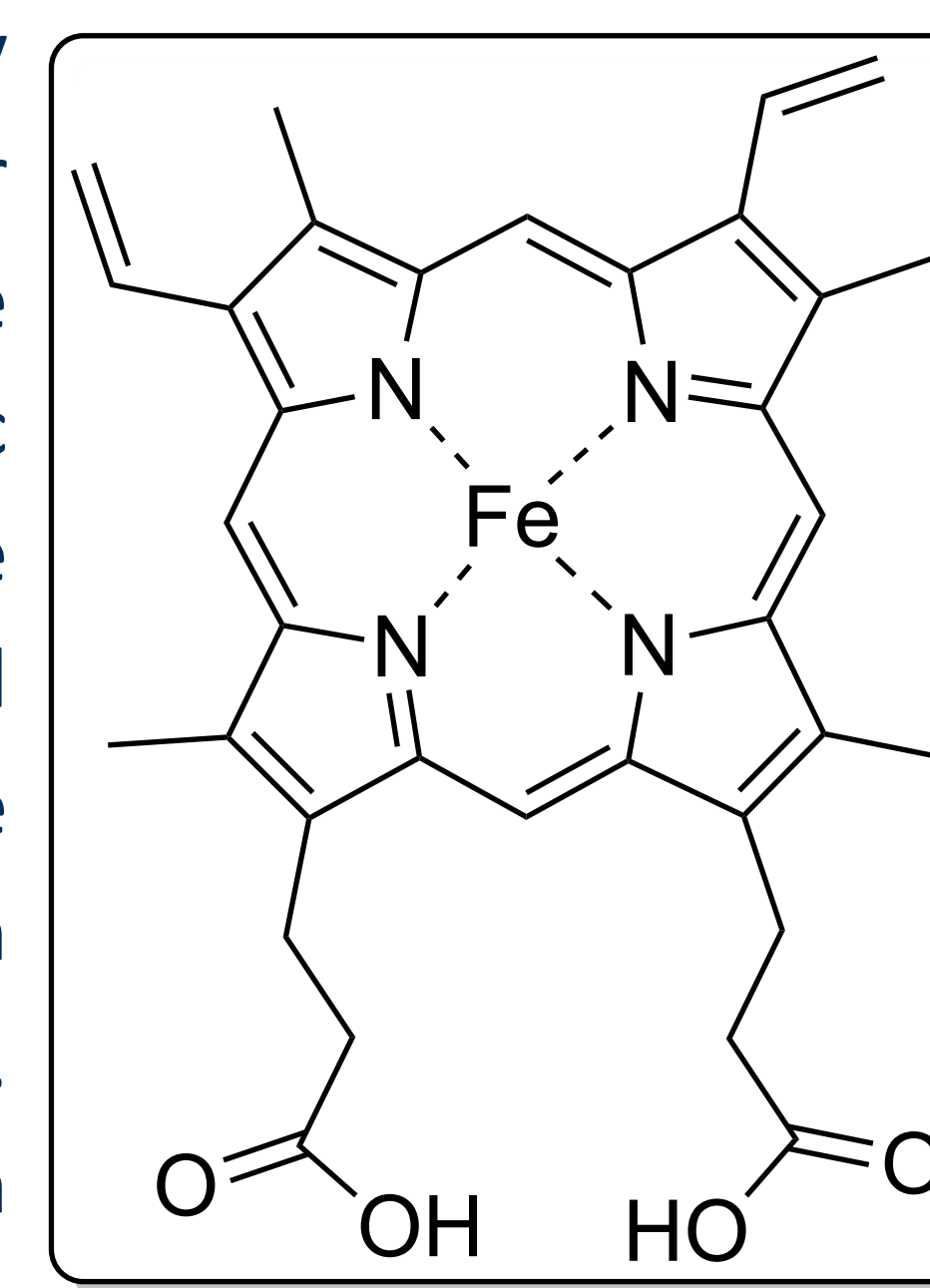
<sup>a</sup> Professur für Elektrochemie, Technische Universität Dresden, 01062 Dresden, Germany, <sup>b</sup> Institut für Chemie, Technische Universität Berlin, 10623 Berlin, Germany,

<sup>c</sup> Madrid Institute for Advanced Studies in Nanoscience (IMDEA), 28049 Madrid, Spain, E-Mail: [halil.oener@tu-dresden.de](mailto:halil.oener@tu-dresden.de), [khoa.ly@tu-dresden.de](mailto:khoa.ly@tu-dresden.de), [inez.weidinger@tu-dresden.de](mailto:inez.weidinger@tu-dresden.de)\*

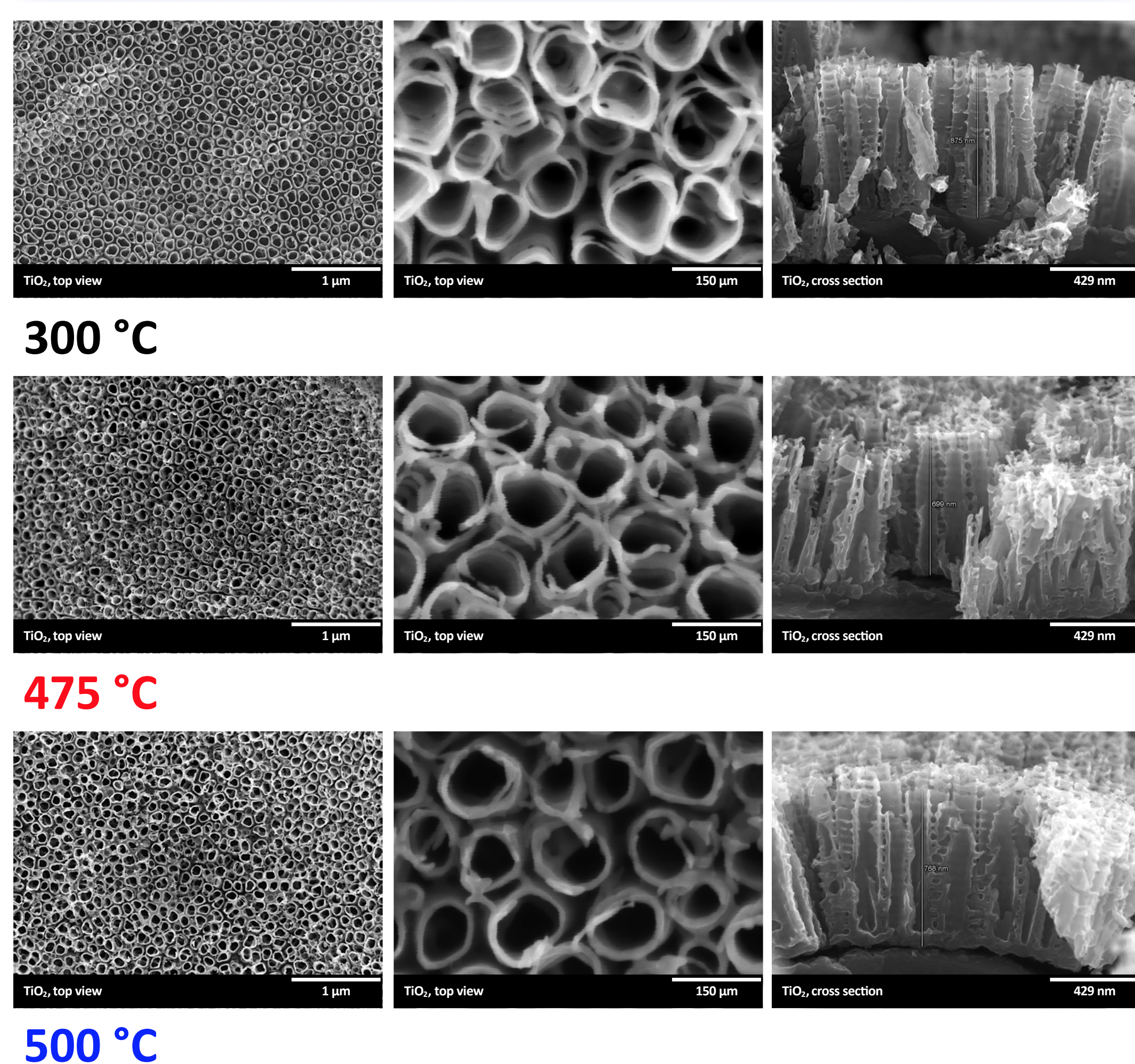
**Fabrication of TiO<sub>2</sub> nanotube electrodes with high biocompatibility and extraordinary spectroscopic properties due to enhanced localized electric fields as can be seen with SERR spectroscopy.<sup>[1]</sup>**



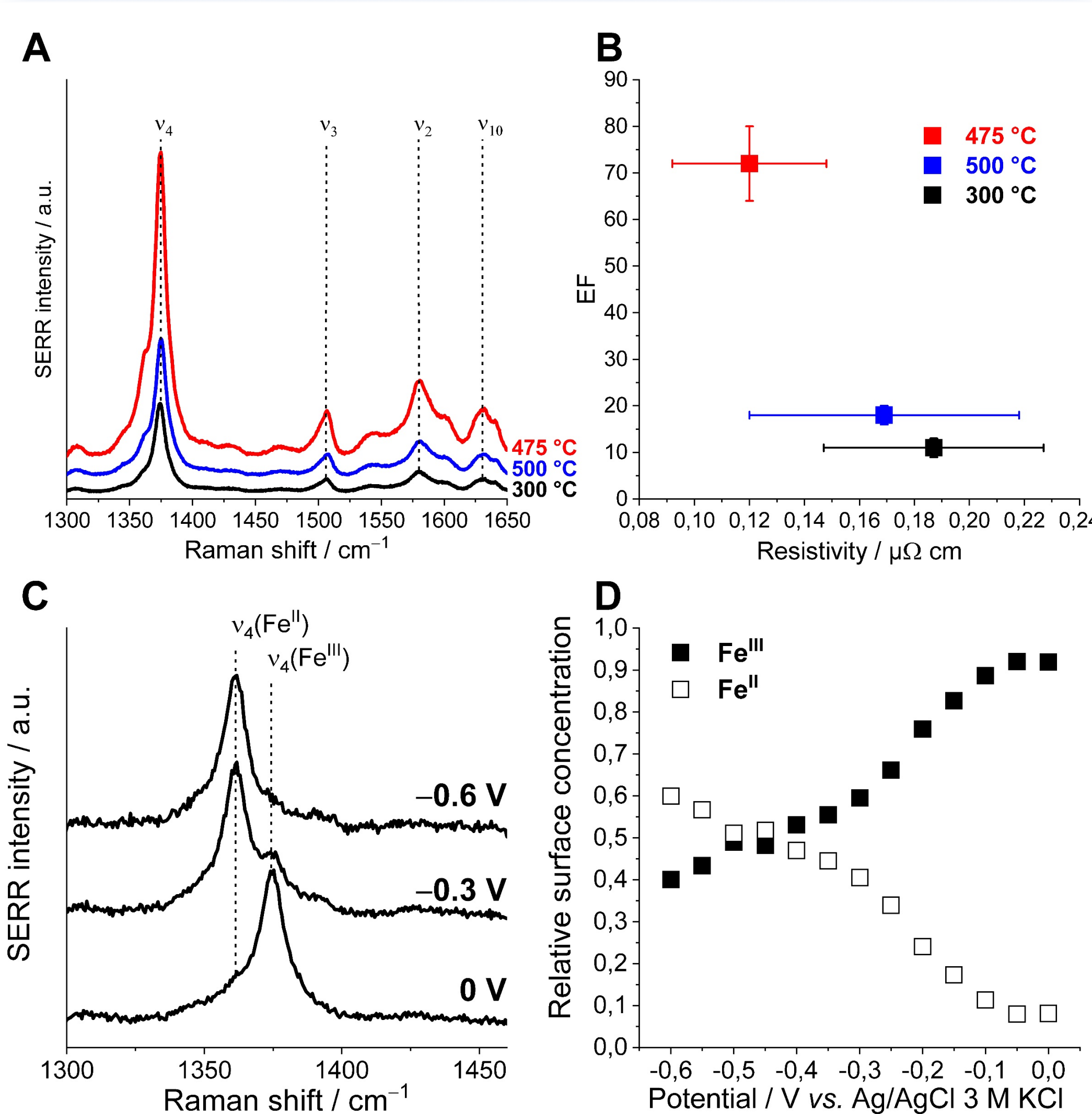
Nanostructured TiO<sub>2</sub> is a stable and low cost material with numerous applications in medicine, photocatalysis and energy storage.<sup>[2]</sup> Applicability of this material for surface enhanced Raman (SER) spectroscopy, however, has been limited so far mostly to directly interacting probe molecules exhibiting at least a partial chemical surface enhancement.<sup>[3]</sup> In our work, we present the fabrication of TiO<sub>2</sub> nanotube (NT) electrodes with high biocompatibility and extraordinary spectroscopic properties. Intense surface enhanced resonance Raman (SERR) signals of the heme unit (right) of the redox enzyme Cytochrome b<sub>5</sub> (left) were observed upon covalent immobilization of the protein matrix to the TiO<sub>2</sub> surface reflecting overall preserved structural integrity and redox behavior.<sup>[4]</sup> The enhancement factor could be rationally controlled by varying the electrode annealing temperature with a record maximum value of over 70 at 475 °C. Due to the separation of the Raman probe from the TiO<sub>2</sub> we can exclude an involvement of charge-transfer processes to be responsible for the signal amplification. The origin of the surface enhancement is therefore exclusively attributed to enhanced localized electric fields resulting from the specific optical properties of the nanotubular geometry.



## Fabrication



## Experimental



## Calculation

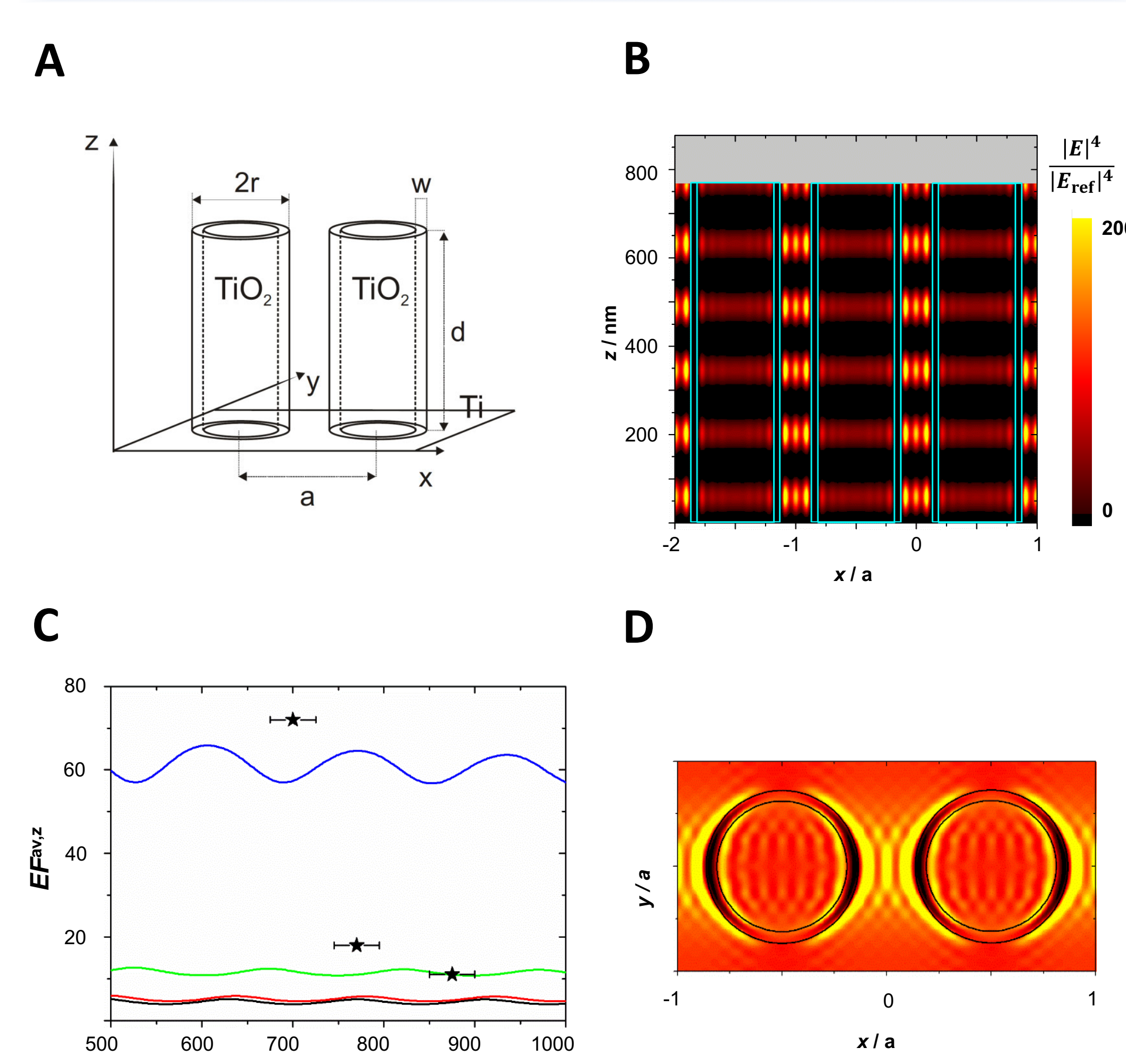


Figure 1. SEM images of anodized TiO<sub>2</sub> NT electrodes annealed at 300 °C, 475 °C and 500 °C. Nanotubular geometry in top view does not change either before or after annealing. A tube diameter with (70 ± 10) nm and a wall thickness of (10 ± 2) nm was determined in average for all annealing temperatures. However, the tube length varied at these temperatures; that is, (875 ± 25) nm for 300 °C, (700 ± 25) nm for 475 °C and (770 ± 25) nm for 500 °C.

Figure 2A: SERR spectra of Cyt b<sub>5</sub> on TiO<sub>2</sub> NT electrodes as a function of annealing temperature with a maximum absolute intensity for electrodes annealed at 475 °C. This trend is inversely proportional to the resistivity which is lowest for these electrodes. By the same trend, the highest EF is at lowest resistivity; that is, EF = (72 ± 8) for 0.12 μΩcm (2B). Relative intensities of the redox transition Fe<sup>II</sup> ↔ Fe<sup>III</sup> at applied potential (2C) was noted for determining E<sub>redox</sub> = (-0.25 ± 0.02) V (2D).

Figure 3. Electromagnetic field calculations using Rigorous Coupled Wave Analysis (RCWA). 3A: Scheme of TiO<sub>2</sub> NT. Periodically occurring enhanced localized electric fields between NTs (3B: vertically cut through three NTs, 3D: top view of two NTs). Experimental EFs (2B) are in 3C well presented when varied carrier densities were considered that account for the different specific resistivities. Furthermore, a sine-like dependence of EF<sup>av,z</sup> on the tube length was found.

## Conclusion

Here we demonstrate the fabrication of highly biocompatible TiO<sub>2</sub> NT electrodes.

Upon direct adsorption of Cytochrome b<sub>5</sub>, an enhancement factor > 70 is achieved for electrodes annealed at 475 °C.

Based on electromagnetic field calculations the high enhancement was attributed to the unique geometry of the nanotubes with photonic crystal properties.

## References

- [1] I. H. Öner, C. J. Querebillo, C. David, U. Gernert, C. Walter, M. Driess, S. Leimkühler, K. H. Ly, I. M. Weidinger, *Angew. Chem. Int. Ed.* 2018, 57, 7225-7229.
- [2] P. Roy, S. Berger, P. Schmuki, *Angew. Chem. Int. Ed.* 2011, 50, 2904-2939. [3] X. X. Han, J. Wei, B. Zhao, Y. Ozaki, *Nanoscale*, 2017, 9, 4847-4861.
- [4] X. X. Han, C. Köhler, J. Kozuch, U. Kuhlmann, L. Paasche, A. Sivanesan, I. M. Weidinger, P. Hildebrandt, *Small*, 2013, 9, 4175-4181.

## Acknowledgement

We thank Peter Hildebrandt for technical support and helpful discussions. Financial support from the DFG (SALSA Excellence Initiative, WE 5278/2-1 and EXC 314 UniCat) and of the European Union via the Horizon 2020 program (Marie Curie Grant GAN 701192-‘VSHER’ for K. H. Ly) is gratefully acknowledged. C.D. thanks the Spanish Ministry of Economy, Industry and Competition (MINECO) for funding of the Centers of Excellence Severo Ochoa (Ref. SEV-2016-0686). Financial support is further provided by the Comunidad de Madrid (Ref. 2017 T2/IND-6092).