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To Prof. Dr. Hab. Maciej Kubicki

The PhD manuscript of M. Szewczyk is presented in the form of a short introduction describing the challenges to be overcome to improve photocatalytic materials. This introduction is followed by a description of the possible role of polydopamine, produced through the oxydation of dopamine or other catechol amines in this field. Finally, the different aims of the thesis are explained before the presentation of the obtained results in the form of 6 articles for which Jakub Szewczyk is the first author. The last article is the result of an important collaboration with the European Institute for Membranes in Montpellier. The work has been performed under the supervision of Dr. Emerson Coy and Mikhael Bechelany.

Article 1, published in *Catalysis Today* (2022) reviews the applications of PDA based nanocomposites as photocatalysts, which fixed the state of the art of this PhD project.

Article 2, published in *European Polymer Journal* (2022), is a review describing the deposition of PDA films through electrochemical methods: cyclic voltammetry, pulsed voltammetry, and galvanostatic methods. The characterization of those coatings through electrochemical impedance spectroscopy is also described, this description is important for the data interpretation in the following articles. The article finishes with an overview of sensing applications of electrodeposited PDA containing films

Article 3, published in *Mater. Today Chem*. 2022) is an interesting experimental paper dealing with the characterization of polydopamine films grown at the water-air interface and their transfer on Si(100) substrates. Jakub Szewczyk contribued, among others, in the construction and calibration of the spectroscopic reflectometry technique which was the main tool of this investigation. The pH of the solution, the dopamine concentration and the stirring speed used in the preparation vessel were found to be critical parameters in the polydopamine membrane thickness and homogeneity. Interestingly, the polydopamine membranes present some molecular order as confirmed by X-ray diffractometry.

Article 4, published in *ACS Applied Materials and Interfaces* (2023) deals mostly with the impact of boric acid (making strong hydrogen bonds with catechols) and Cu^{2+} cations (able to coordinate with vicinal OH groups) on the properties of polydopamine films formed at the water-air interface. The mechanical properties of those membranes were characterized using nanoindentation and Brillouin light scattering, which is a very original approach in this case.

Article 5, published in *European Polymer Journal* (2024) takes advantage of all the knowledge acquired in articles 3 and 4 to transfer polydopamine membranes produced at the water-air interface to the surface of semiconductors : TiO_2 and ZnO. Both sides of the membranes are put in contact with the semiconductor using the scooping and the stamping transfer methods. Both sides were characterized by X ray diffraction, contact angle measuements, Raman and infra-red spectroscopy. The side of the polydopamine film in contact with water was found to be more hydrophilic. In addition the thickness of the membranes was controlled by changing the deposition time at the water-air interface (10 or 24 h). Finally, the membranes were found to reduce the gap of both TiO_2 and ZnO by about 0.1 eV and to change their photoluminescence. Reasonable tentative explanations, related to a change in the oxygen vacancy sites, for those findings have been provided in the manuscript. Finally, the electrochemical behavior of the composite layers was investigated in the absence and presence of light : the real part of the impedance is drastically reduced when the semi conductors are coated with polydopamine. At the end of the manuscript some improved and accelerated photocatalytical decomposition of methylene blue is demonstrated.

The last article was published in *ACS Applied Materials and Interfaces* (2024) and combines all the knowledge developped in the preceeding papers to produce multilayers alternating polydopamine and TiO_2. Polydopamine was synthesized at the water-air interface and transfered on TiO_2 produced by atomic layer deposition at pretty low temperature (200 °C, yielding amorphous titanium dioxide). The different layers present a very reproducible thickness (about 25 nm for polydopamine and 40 nm for TiO_2) with a remarkable N gradient in the TiO_2 layers as nicely demonstrated by a combination of TOF-SIMS and XPS spectroscopies.

This property allowed for an important decrease in the band gap by 0.63 eV for the material made from 3 TiO_2-polydopamine strata and an important increase in the photocurrent.

Overall this work is of *excellent quality* with *impressive result*s both from a qualitative and quantitave point of view. The manuscript is presented in coherent manner. As a consequence, I give an excellent support for M. Szewczyk to defend his manuscript in front of his PhD commitee.

Sincerely yours.

Vincent BALL