Effect of organic additives on the intergranular conductivity of Al- doped ZnO

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Supplementary informations

1) Microscopy of the ZnO powder

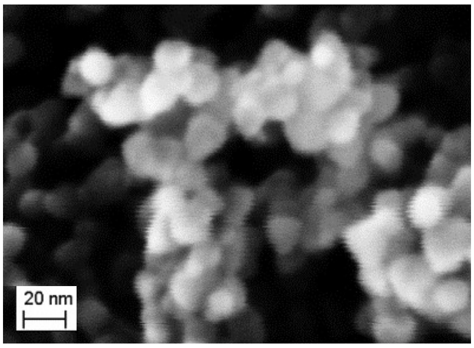

Fig. S0 Scanning electron microscopy of the ZnO powder

2) Study of the interaction between the organic molecule and the semiconductor thanks to infrared spectroscopy

The infrared spectroscopy was performed on a Nicolet 6700 FTIR in ATR mode using a ZnSe prims. 1 uL of a ZnO:Al suspension beforehand homogenized with ultrasonic waves for 5 min is deposited onto the ZnSe crystal of the spectrometer. The droplet is dried with an nitrogen flow and spectra are recorded while a flow of desired anchoring solution crosses the ZnO:Al powder. A drawing of the experimental set up is shown on Figure S1. Spectra are recorded after a background is made on the powder immersed in water. Three deprotonated acid solutions of SA, TA and DNBA at 5.10^{-4} M pH 7.5 were realized by dissolving the corresponding mass in water thanks to addition of successive amounts of 1 M NaOH solution in order to reach the desired pH. A 100 times diluted solution of the commercial PTS was made, which corresponds to an approximate concentration of 10^{-4} M.

At concentration lower than 10^{-3} M, the spectrometer is not sensitive enough to detect organic molecules in solution, therefore only those molecules adsorbed onto the surface of ZnO will be detected, whether the adsorption is covalent or electrostatic.

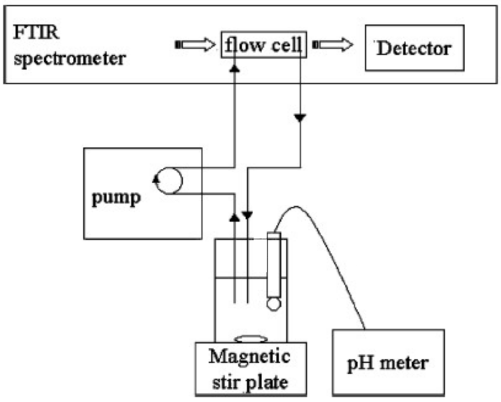

Fig. S1 Experimental apparatus for the infrared spectroscopy measurements. From ref. 39

Fig. S2.a shows the infrared spectra of the sodium succinate solution at the concentration of 10^{-2} mol.L^{-1}. One observes in particular the stretching modes of the CO_2^- carboxylate groups at 1562 cm^{-1} and 1396 cm^{-1}. When a solution of the succinate at the concentration of 7.10^{-5} mol.L^{-1} flows above the ZnSe prism, no signal can be observed (Fig S2.c) whereas, when ZnO powder is first deposited onto the surface of the prism, then an infrared signal of the carboxylate groups is observed indicating that the molecule have been concentrated on the ZnSe prims by adsorption onto ZnSe [1] (Fig S2.b). The stretching frequencies of the carboxylate functions are weakly shifted as compared to the SA- alone. This indicates that the carboxylate function probably remains symmetrical such as in the case of a bidentate chelating group onto Zn. Also the succinate anion contains two carboxylate functions and one of them remains free with unchanged vibrations when the other one is grafted onto the ZnO surface.

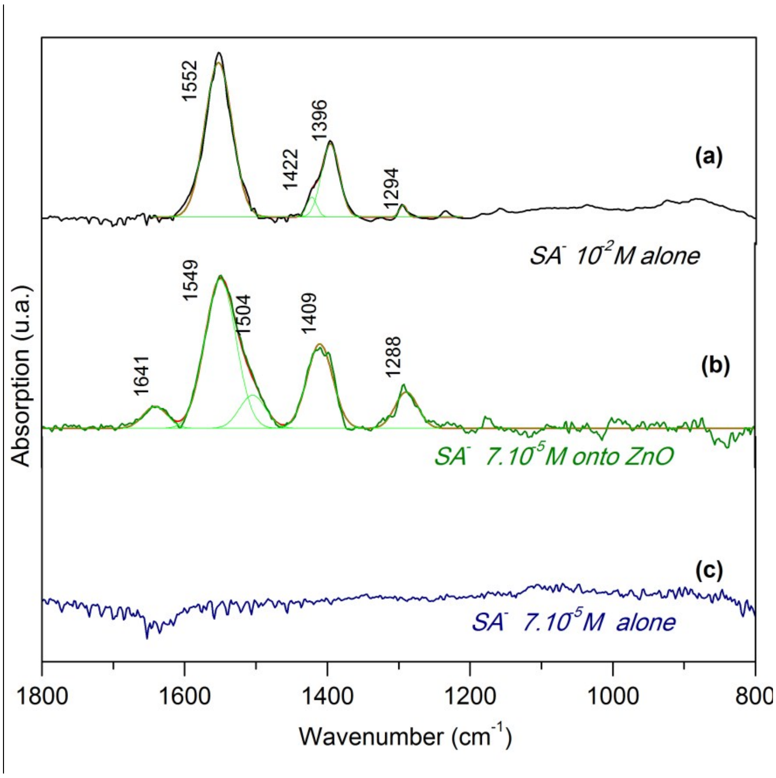

Fig. S2 IR spectra of (a) SA^- at 10^{-2} M alone in an aqueous solution at pH 7 ; (b) of SA^- at 7.10^{-5} M pH 7 flowing through ZnO ; and (c) of SA^- et 7.10^{-5} M in an aqueous solution at pH 7.

The recorded spectra after flowing of the different anchoring solutions are presented on Fig. S3. The signal observed for each molecule is the signature of the adsorption. When the powder is washed with circulating water, the signal is maintained only for PTS and SA adsorption, which proves that a persistent link, probably covalent due to the shift in wavenumber compared to the free species, is created during adsorption. For TA and DNBA, the infrared signal is lost after washing of the ZnO suspension, which highlights the labile nature of the link. It is however difficult to assess whether the interaction is electrostatic of if a covalent bond is created.

In all cases, adsorption onto ZnO was therefore validated for all four molecules and similar results were assumed for the analogue molecules DHTA and NTA. However no washing of the powders will be done in the next experiments to prevent desorption.

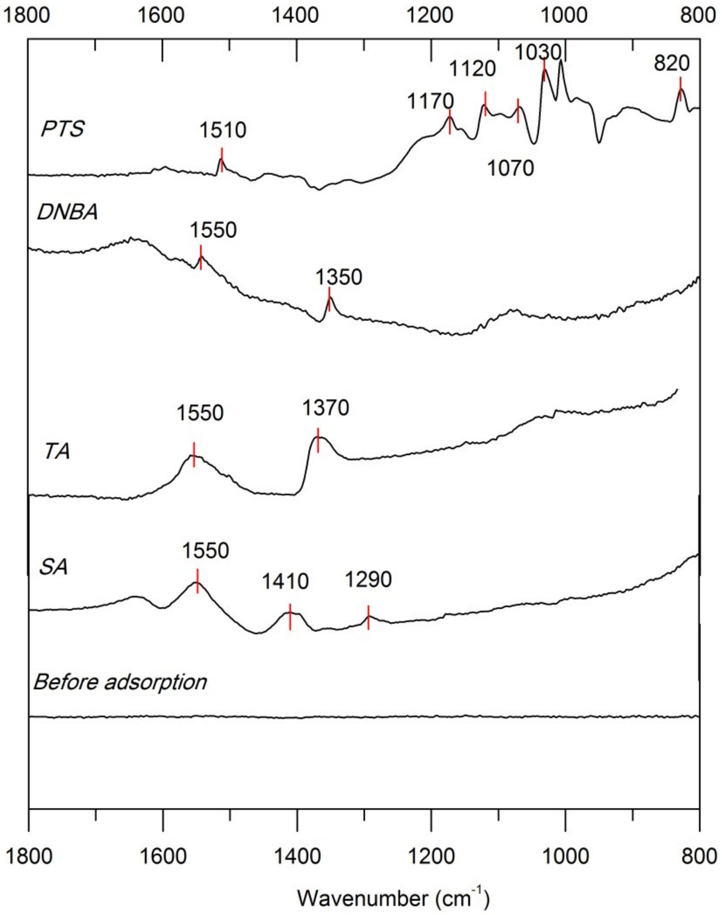

Fig. S3 IR spectra of SA- (a) at 10-2 M pH 7 alone in solution ; of SA- (b) à 7.10-5 M pH 7 circulating above a ZnO powder; (c) of SA- à 7.10-5 M pH 7 alone in solution.

3) Relative density of the powders

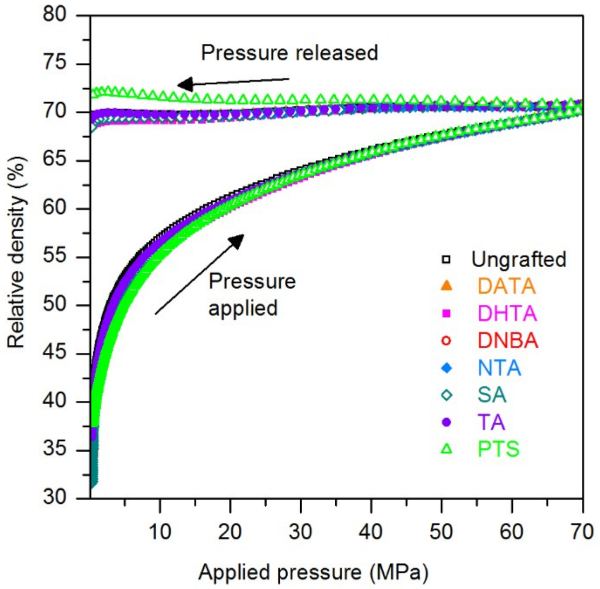

Fig. S4 Relative density versus applied pressure on grafted and ungrafted ZnO:Al powders (anchoring molecules in legend).

4) Energy level alignment after assuming Fermi level pinning

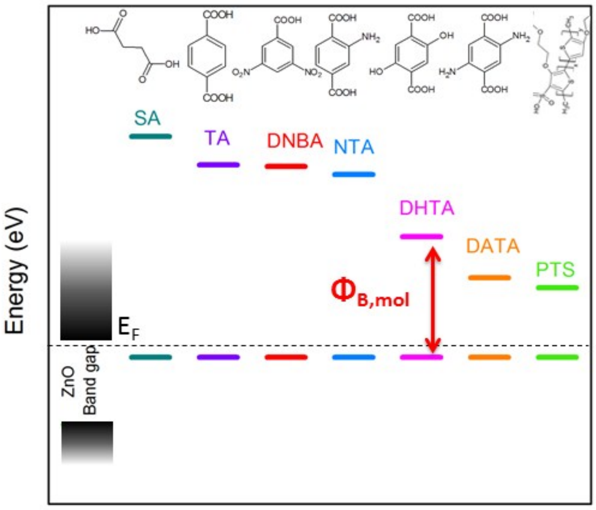

Fig. S5 Position of the LUMO and HOMO of organic molecules following alignment of the HOMO with the Fermi level of ZnO. E_F is the Fermi level of ZnO ; $\Phi_{B,mol}$ is the energy barrier for electron transfer from the semiconductor to the molecule.

References

1. G. Lefevre, *Adv Colloid Interface Sci*, 2004, **107**, 109-123.