Supplementary Information for

A comprehensive adsorption and desorption study on the interaction of DNA oligonucleotides with TiO_2 nanolayer

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Table S1. pH values of 20 mM MES solution mixed with DNA oligonucleotides or metal ions

Solution	pH value
20 mM MES solution	3.93
20 mM MES solution with 10 nM Poly5A_Cy3	3.93
20 mM MES solution with 50 mM Na^{+}	3.84
20 mM MES solution with 200 mM Na^{+}	3.91
20 mM MES solution with 200 μM Ca^{2+}	3.99
20 mM MES solution with 20 mM Ca^{2+}	3.89
20 mM MES solution with 200 μM Mg^{2+}	3.94
20 mM MES solution with 20 mM Mg^{2+}	3.87
20 mM MES solution with 200 μM Zn^{2+}	3.99
20 mM MES solution with 1 mM Zn^{2+}	4.04
20 mM MES solution with 5 mM Zn^{2+}	4.39
20 mM MES solution with 20 mM Zn^{2+}	4.89
20 mM MES solution with 200 μM Ce^{3+}	3.95
20 mM MES solution with 500 μM Ce^{3+}	3.92
20 mM MES solution with 1 mM Ce^{3+}	3.89
20 mM MES solution with 2 mM Ce^{3+}	3.92
20 mM MES solution with 5 mM Ce^{3+}	3.89

The adsorption and desorption results in the citrate buffer are presented in **Fig. S1**, and the pH was set to 3.93 for direct comparison with the MES solution. **Fig. S1a** showed that Poly5A_Cy3 had similar adsorption kinetics for both acidic environments. The exception is that the initial adsorption rate of Poly5A_Cy3 in the citrate buffer was lower than that in the MES solution, which may be caused by the interruption of citrate adsorption. The desorption in the citrate buffer was carried out under pH = 3.93, 5.16, 7.22, and 10.12, as shown in **Fig. S1b**. Similar to the scenarios in the MES solution, the desorption is only 2.12 ± 0.42% at pH = 3.93. With the increase in pH, the desorption increases and reaches 37.73 ± 0.37% at pH = 10.5.

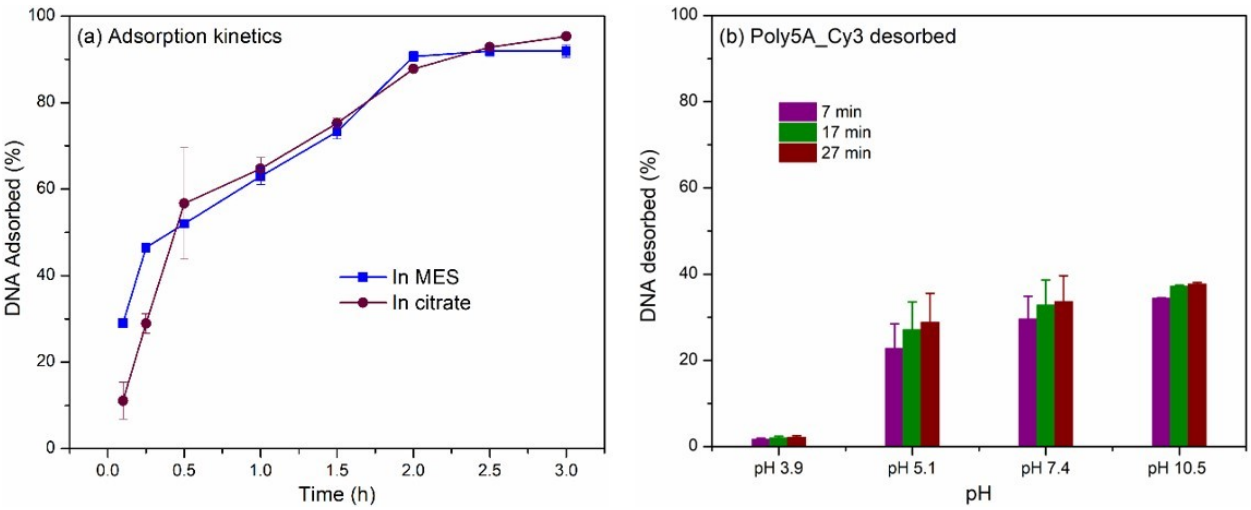

Fig. S1. (a) Adsorption kinetics of Poly5A_Cy3 in MES solution and citrate buffer to TiO_2 nanolayer. (b) Poly5A_Cy3 desorption percentage under different pH values.

With 10 mM citrate buffer (pH is around 3.93) incubated on the surface of the TiO_2 nanolayer for 1 h, the XPS data showed significant Na^+ adsorption on the TiO_2 nanolayer (**Fig. S2a**), which suggested that Na^+ would be enriched to screen the charges on the surface. For the carbon element, the chemical state of O-C=O was also significantly increased compared with the fresh TiO_2 chip, from 9.51% to 35.09% in the total carbon element (**Fig. S2b**). Considering that one citrate molecule has three carboxyl groups, this suggested that TiO_2 nanolayer could also strongly adsorb citrate molecules.

Moreover, Zhang et al.[1] reported that TiO_2 nanoparticles would adsorb citrate to the surface and the Zeta potential was significantly changed compared to bare nanoparticles. During the interaction, TiO_2 would transform to TiOH at a lower pH. We infer that citrate could interact with the TiO_2 nanolayer through a hydrogen bond between the carboxyl group and hydroxide group.[2]

Furthermore, the citrate adsorption can also be verified by pre-adsorption experiments. As the pre-adsorption of citrate would disturb the adsorption of DNA oligonucleotides by rendering a

negatively charged surface, we incubated the small TiO_2 chips with 10 mM citrate buffer and 20 mM MES solution (both pH = 3.93) for 15 min, then incubated 20 nM Poly5A_Cy3 in MES solution for another 15 min. **Fig. S2c** shows that the pre-adsorption of citrate buffer (21.73 ± 4.96%) results in much less DNA adsorption than MES (40.72 ± 4.98%), while DNA adsorption in MES solution and citrate buffer are higher than the pre-adsorbed assay, suggesting that both MES and citrate molecules disturb DNA adsorption, and the disturbing effect of citrate is stronger.

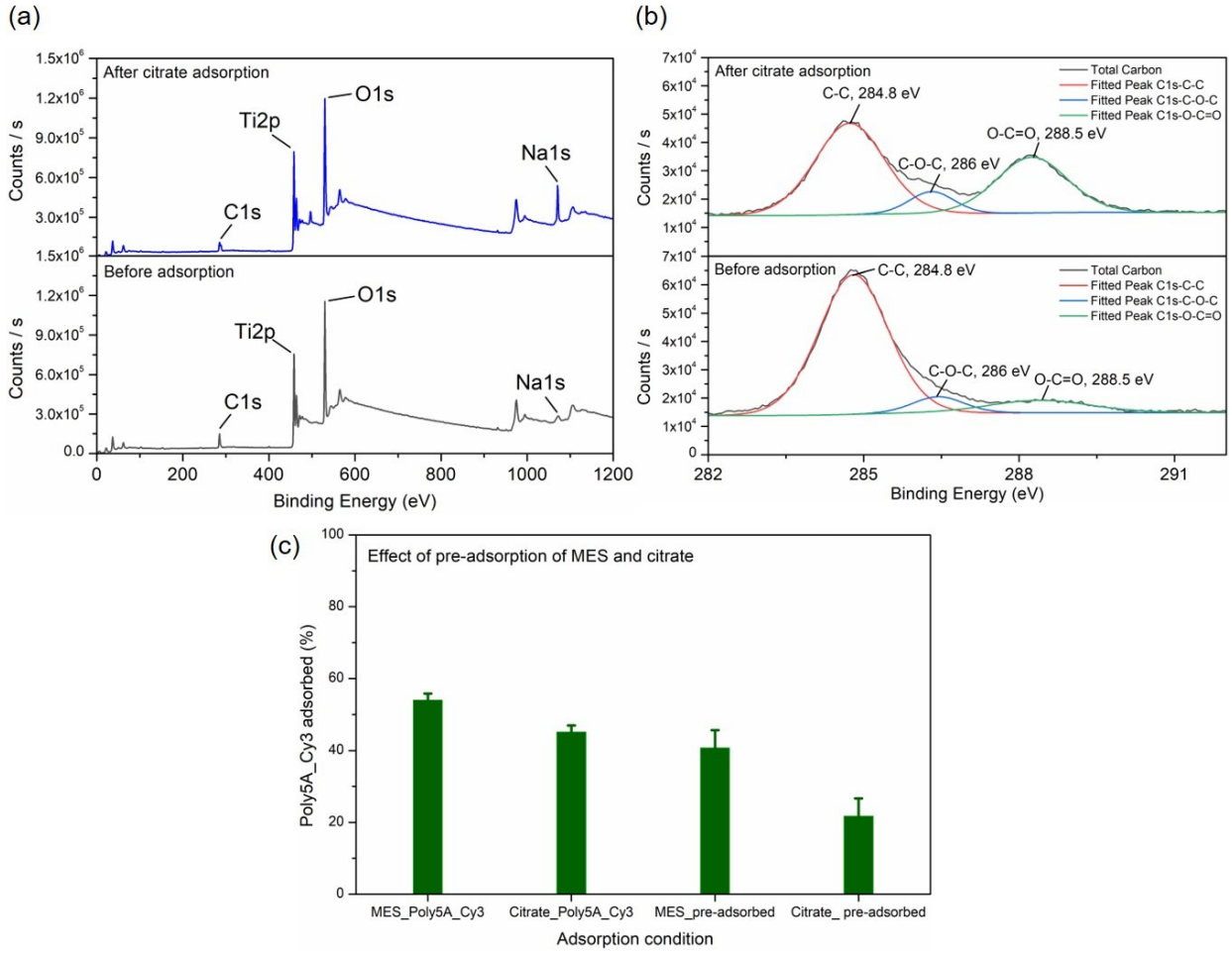

Figure S2. (a) XPS survey and (b) fine spectrum of carbon element chemical states before (bottom) and after (top) citrate adsorption. (c) Effect of pre-adsorption of MES solution and citrate buffer

on DNA adsorption, the first two bars represent Poly5A_Cy3 adsorption in MES solution and citrate buffer without pre-adsorption, respectively.

Some white precipitates were observed when adding a relatively high concentration of Zn^{2+} into the HEPES buffer. The precipitates first appeared for 2 mM Zn^{2+} and as the Zn^{2+} concentration increased to 5, 10, and 20 mM, the precipitates increased as well, as shown in **Fig. S3** below. This observation is consistent with previous studies that reported increased formation of ZnO or $Zn(OH)_2$ with the increase of Zn^{2+} concentration.[3-5]

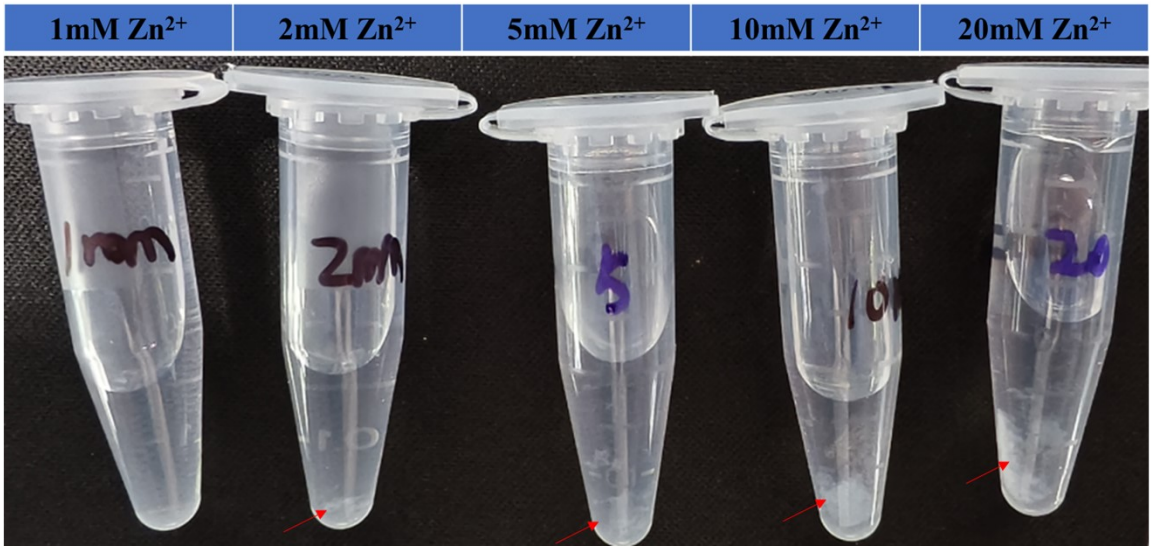

Fig. S3. White precipitates pointed by a red arrow after adding different concentrations of Zn^{2+} into the HEPES buffer.

References

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