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Tuning of Surface Protein Adsorption by Spherical Mixed Charged Silica Brushes (MCB) with Zwitterionic Carboxybetaine Component

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^{1}H NMR

The ^{1}H NMR was used to verify the QD of MCB. PCBMA and Poly(DMAEMA-*co*-CBMA) were both cleaved by etching the silica core with HF solution. After cleavage and dialyzed against pure water, the obtained free polymer solutions were lyophilized and then used for ^{1}H NMR measurement. By comparing Figure S1(a) and Figure S1(b), the successful quaternization was confirmed and the exact QD of DMAEMA was calculated from equation 1, in which I_e and $I_{e'}$ denote the ^{1}H NMR signal integrations of methyl signals at 3.18 and 2.92 ppm, respectively.

$$\mathrm{QD} = \frac{I_{e'}}{\left(I_{e'} + I_e\right)} \times 100\% \tag{1}$$

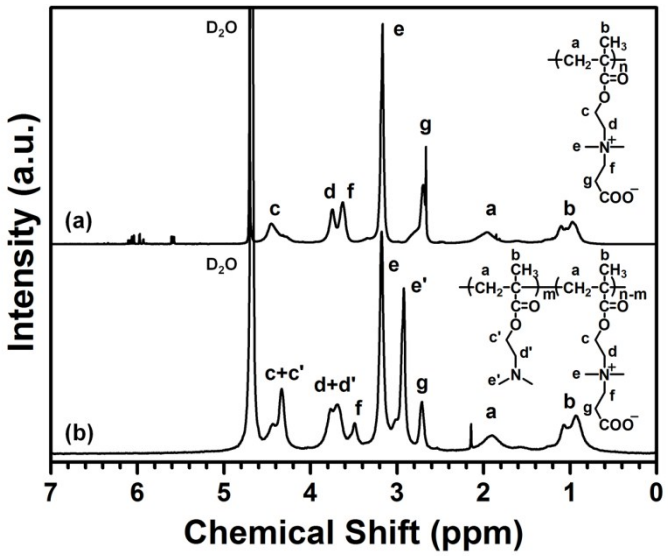

Fig. S1 ^{1}H NMR spectra of (a) PCBMA and (b) Poly(DMAEMA-*co*-CBMA) cleaved from silica core by HF.

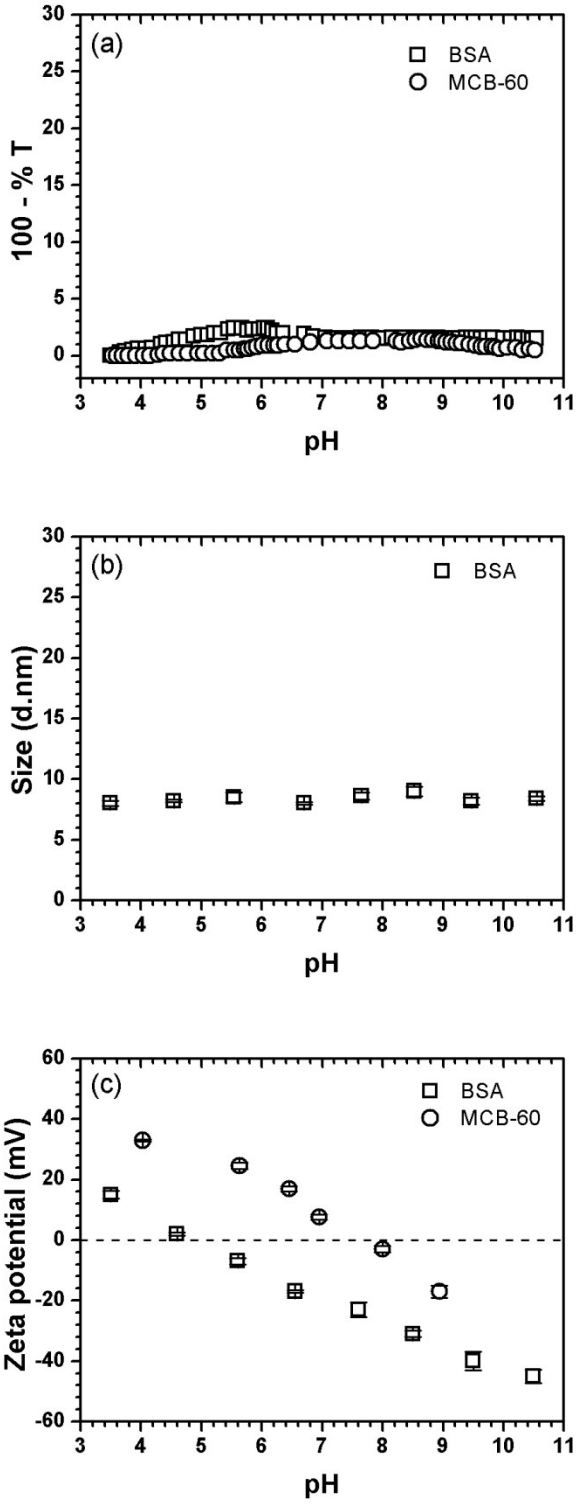

Figure S2. (a) Turbidimetric titration of BSA and MCB-60, (b) size of BSA, and (c) zeta potential of BSA and MCB-60 with pH. The ionic strength was set as 5 mM.

Isothermal Titration Calorimetry (ITC)

The binding constant, K_b, and binding number, n, of lysozyme to silica brush were determined by ITC (MicroCal iTC_{200}, GE Healthcare). Lysozyme and silica brush solutions were made in 5 mM CHES at pH 9.0 with concentrations of 5.2×10^{-6} mM and 0.20 mM, respectively. After instrument stabilization at 25℃, 40 μL of lysozyme solution in the syringe was titrated with 16 successive injections of silica brush solution in the sample cell with volume of 200 μL. The interval between injections was 180 s. The stirring speed in the sample cell was set to 1000 rpm during the whole titration. All parameters are model-dependent, and one-site binding model was used to fit the integration data from ITC in our work.

Isothermal titration calorimetry (ITC) was known as a useful tool to study the interactions in a host-guest system, which was based on the microcal level of energy variation during the interaction. Here, we also use ITC to investigate the thermodynamics for the Entry 2 in Table 2. Fitted by a one-site binding model of the integrated heat data, it was shown that the binding amount was ~635 (N = 635), which was estimated at 0.43wt.-% in mass. Such a low value of protein adsorption could not be detected by depletion method as shown in Table 2. We also converted this stoichiometry to generally used adsorption unit and the value was 200 ng cm^{-2}, which was less than monolayer adsorption on silica core if treating Lyz as 4-nm nanoparticles[1]. It was known that PCBMA own excellent antifouling property as brush structure and the adsorption amount was less than 5 ng cm^{-}

[22]. We then turned to see the binding constant during the titration, and it was 1.66×10^6 M^{-1}, which is relatively high when compared to other protein-brush like nanoparticle systems[3]. The high binding constant should not from the protein-brush chain interaction, and most possibly attributed to protein adsorption on surface of silica core.

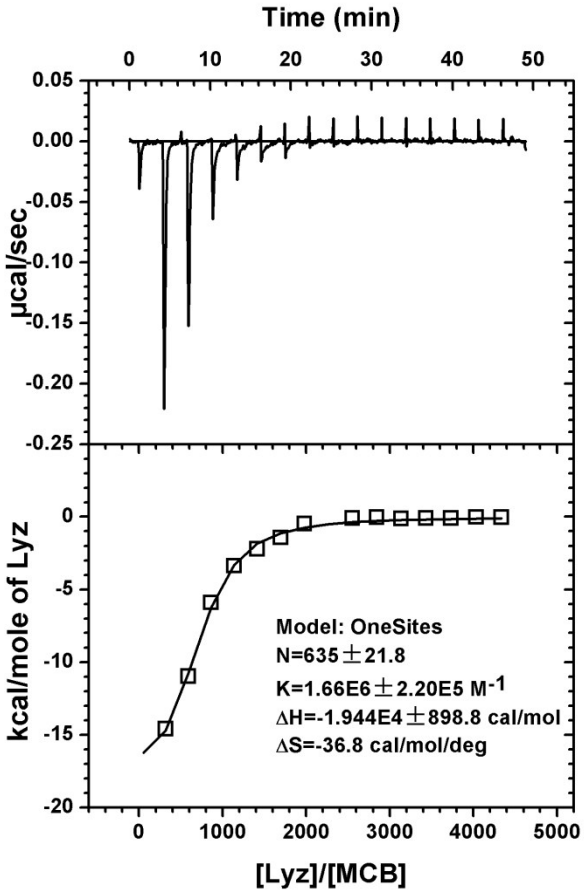

Fig. S3 ITC date for MCB-100 and Lyz at pH 9.0 (a) raw data; (b) integrated data, and fitting line by one-site binding model.

References

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(3) S. Wang, K. Chen, Y. Xu, X. Yu, W. Wang, L. Li and X. Guo, *Soft Matter,* 2013, **9**, 11276−11287.