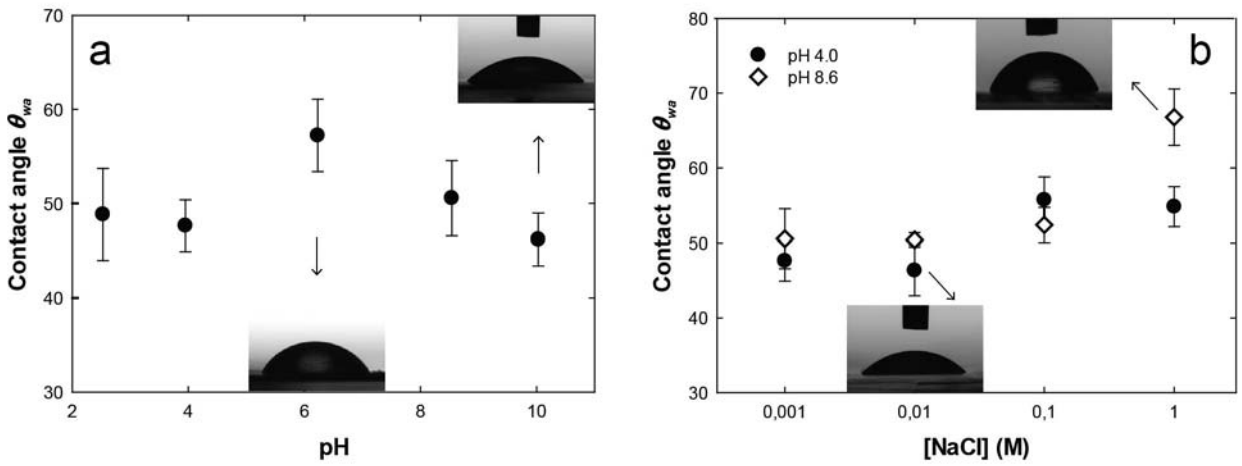
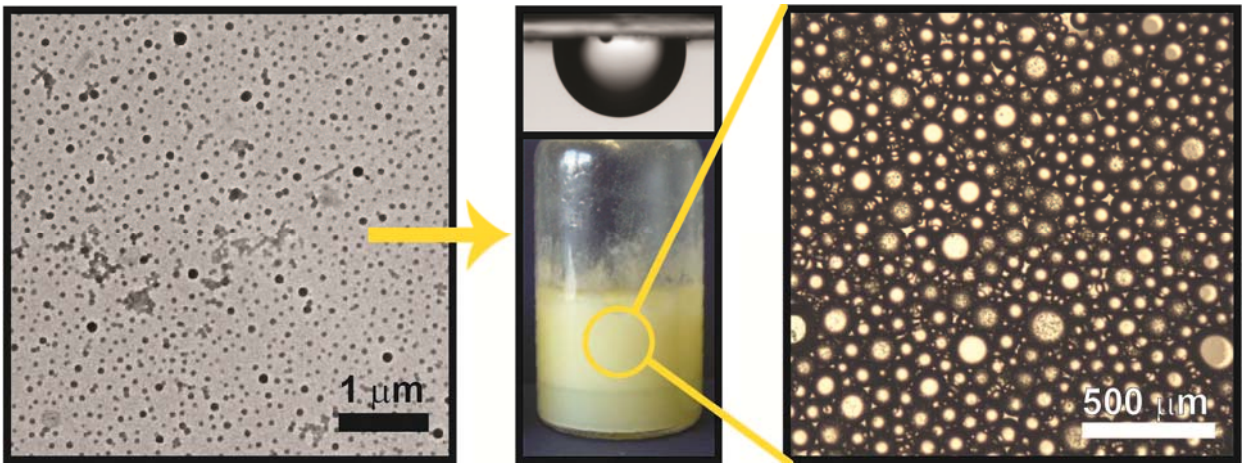
Electronic Supplementary Information

Water-in-air three-phase contact angle measurements. A 1 wt% zein solution in an aqueous ethanol mixture (90 (v/v)% EtOH) was prepared by magnetic stirring at room temperature. Homogeneous zein films were deposited onto pre-cleaned glass substrates by heating zein solutions at 70°C for 15 minutes. Before further use, these zein films were stored in a desiccator. The static contact angle was measured using a DataPhysics OCA15 setup. Water-in-air contact angles θ_{wa} were measured by depositing water droplets (1-2 μL) with a certain [NaCl] and pH onto zein films under ambient atmosphere. Contact angles were determined automatically, approximating the contour of the imaged droplets with a Laplace-Young fit. Measurements were averaged over at least five droplets. SI Fig.1a shows how θ_{wa} depends on the pH of the aqueous phase. Both at pH values below and above the isoelectric point pI (at pH~6.5) θ_{wa} varies between 46° and 50°, whereas it attains a value of 57±4° at pH 6.2. This is in accordance with the expectation of positively (at pH<pI) and negatively (at pH>pI) charged zein being more hydrophilic than zein in a surrounding phase with a pH close to pI, where many of the chargeable groups remain uncharged rendering the material more hydrophobic. The influence of ionic strength on θ_{wa} was studied at pH values of 4.0 and 8.6 (SI Fig. 1b). In the corresponding emulsions, shown in Fig. 7 and 9 respectively, the aqueous phase in samples with 0.1M and 1M NaCl was free of zein particles and hence transparent. At pH 4.0 θ_{wa} has values between 46° and 48° at low ionic strength, but zein becomes more hydrophobic at higher ionic strength with θ_{wa} increasing to 55-56°. A similar trend is observed at pH 8.6: although the value for θ_{wa} at 0.1M NaCl (52±2°) is not much higher than at lower ionic strengths (50±2°), θ_{wa} increases substantially to 67±4° at 1M NaCl reflecting an increase in hydrophobicity. These observations agree with the measurements of the oil-in-water contact angle θ_{ow} on zein films displayed in Fig. 2, a situation more closely resembling the actual microscopic zein-decorated oil-in-water emulsion interface. Here, at both low and high pH the wettability of the zein film by the oil phase increases (i.e. the wettability by the aqueous phase decreases) upon increasing the ionic strength from 1mM (θ_{ow} 98±5° at pH 4.0 and 95±5° at pH 8.6) to 1M NaCl (θ_{ow} 87±3° at pH 4.0 and 85±3° at pH 8.6). From all contact angle data, we may conclude that, for both positively and negatively charged zein colloidal particles, zein becomes more hydrophobic at ionic strengths above 0.1M NaCl. Under these conditions, zein prefers the oil-water interface over the aqueous continuous phase and may even partly migrate to the oil continuous phase, which explains the absence of zein in the aqueous phase.



SI Fig.1 Contact angle θ_{wa} between a water droplet and a zein film in air varying with (a) pH at 1mM NaCl and (b) [NaCl] at pH values of 4.0 and 8.5.



The fabrication of fully natural, surfactant-free and biodegradable Pickering oil-in-water emulsions is demonstrated for zein colloidal particles, introducing water-insoluble proteins as a novel class of particle-stabilizers.