

Porous ‘Ouzo-effect’ silica-ceria composite colloid for enhanced corrosion protection

Supporting Information

Martin J. Hollamby, Dimitriya Borisova, Helmuth Möhwald, Dmitry Shchukin*

Max Planck Institute for Colloids and Interfaces, Wissenschaftspark Potsdam-Golm, Am Mühlenberg 1
OT Golm, 14476 Potsdam, Germany

Author current email address: Hollamby.martinjames@nims.go.jp

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*Current corresponding address: National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki, 305-0047, Japan

Experimental

Chemicals

Tetraethyl orthosilicate (TEOS, $\geq 99\%$, puriss), cerium ammonium nitrate (CAN, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, $\geq 98.5\%$, puriss), cetyltrimethylammonium bromide (CTAB, $\geq 98\%$, powder), (3-glycidyloxypropyl)trimethoxysilane (GPTMOS, $\geq 98\%$) were purchased from Sigma-Aldrich and used as received. Ammonium hydroxide (NH_4OH , 30 vol%) and sodium chloride (NaCl , analytical grade) were obtained from Merck. Ethanol (EtOH , absolute, AnalaR NORMAPUR) and propan-2-ol (IPA, AnalaR NORMAPUR) were purchased from VWR. Ethyl acetoacetate (99+%) and zirconium(IV) propoxide solution (TPOZ, 70 wt% in 1-propanol) were purchased from Alfa Aesar. Throughout the work, ultrapure MQ- H_2O was used. Adjustments of pH were typically carried out with aqueous solutions of hydrochloric acid (HCl) or sodium hydroxide (NaOH) (1 mol dm^{-3} , Merck), although in the case of the sol-gel coating synthesis nitric acid (HNO_3 , Aldrich ACS reagent, 70%) was used. The metal substrates used for corrosion testing were sheets of AA2024-T3 that were cut to the desired dimensions (30 x 60 mm).

Characterization techniques

Zeta potential and DLS measurements, (DLS, Malvern Zetasizer 4), transmission electron microscopy (TEM, Zeiss EM912), N_2 adsorption experiments (Macromeritics TriStar 3000 system) and x-ray diffraction (XRD, Bruker D8) were used to characterise the silica, ceria and $\text{CeO}_2@\text{SiO}_2$ particles. To better visualize the inner content of the $\text{CeO}_2@\text{SiO}_2$ particles, ultramicrotomy was used. The particles were placed into a gelatine capsule whereupon the embedding medium (LR white, Plano) was added and cured at $60 \text{ }^\circ\text{C}$ for 4 days. After the polymerization the capsule was cut (Ultratrim). Slices of the sample were made with an ultramicrotome (Leica Ultracut UCT) using a diamond knife. The slices were placed onto a 400 mesh copper grid and carbon-coated, then analyzed by TEM.

UV-vis spectroscopy (8453 UV-visible spectrophotometer, Agilent technologies) was employed to investigate the 8HQ release kinetics (see separate section). Digital photographs of nanoparticle

dispersions and coated substrates after the corrosion test were captured with a Canon PowerShot S5 IS on super macro mode. Corrosion testing was carried out using electrical impedance spectroscopy (EIS). In a typical EIS experiment, the sample substrates (6 x 3 cm) were placed into specially made cells (see supporting information of reference 1) so that 4 cm² of coated metal surface was exposed to the salt solution (1 M NaCl, approx 40 ml), and loosely covered to reduce evaporation whilst still permitting oxygen to enter the system. This allowed the simultaneous measurement of EIS alongside a long-term corrosion test. Into the cell were placed both the reference (saturated calomel) and counter (platinum) electrodes and leads attached to a clean area of the metal substrate (coating was removed using sandpaper). Measurements were carried out inside a Faraday tent using a CompactStat Impedance analyzer (Ivium technologies) at constant potential (1 V), varying the frequency from high (4×10^5 Hz) to low (1×10^{-2} Hz). Five frequencies were typically assessed per decade.

Spontaneous emulsification method to produce porous SiO₂ particles

The synthesis involves pre-hydrolysis of TEOS, followed by the spontaneous emulsification step at which point the silica most likely nucleates at the emulsion interface. By changing the degree of pre-hydrolysis, the product can be varied in a controlled manner as described before.² Here, we were interested in the formation of porous particles and so the following method was followed:

In a typical synthesis, TEOS (22.3 ml) and EtOH (absolute, 46.6 ml) were added to a 500 ml flask. To this, a solution of hydrochloric acid (2ml, [HCl] = 0.9 wt%) was added and reacted for 30-60 min. Then a solution of ammonium hydroxide (2ml, [NH₄OH] = 4 vol%) was added and the mixture reacted for a further 30-60 min. Finally, a solution of ammonium hydroxide (280 ml, 3 vol%) was added, which caused the formation of a milky emulsion. This was left overnight to ensure completion, after which the particles were washed three times (by centrifugation, followed by redispersion) in distilled water. It should be noted that due to the lack of a template this washing was really only done to reduce the ionic strength of the solution and thereby stabilize the colloid. Stirring was occasionally applied in the early stages prior to the emulsification step in order to ensure homogeneity but was found to be unnecessary.

The average particle size (hydrodynamic diameter) was estimated by DLS, using the CONTIN algorithm, to be 193 nm, with a polydispersity (fractional standard deviation) of 0.24.

CeO₂ nanoparticle preparation

This method was adapted from one found elsewhere, which used oleic acid instead of CTAB.³ In a typical synthesis, two solutions were prepared, one consisting of (NH₄)₂Ce(NO₃)₆ (3.84 g) in 30 ml water and the other comprising CTAB (2.55 g) in 30 ml water. These solutions were mixed together and stirred for 2 h, giving a viscous yellow solution. Subsequently, ammonium hydroxide (10 ml, 30 vol%) was added, which resulted in a color change to purple. EtOH (200 ml) was then added and the solution centrifuged to collect the particles. These were then washed thoroughly in water to remove the CTAB, which resulted in a further color change to pale yellow, which is the normal color for crystalline CeO₂.

Formation of CeO₂@SiO₂ particles

The starting concentrations of CeO₂ and SiO₂ solutions (pH = 5 to ensure oppositely charged surfaces) were 1.5 and 4.3 wt% respectively, as determined by dried weight vs. solution weight. 46.5 g and 48.0 g of the respective solutions were mixed together, which gave approximately 350 mg CeO₂ per gram of SiO₂. The mixture was placed under reduced pressure for 10 min, with stirring, after which the hybrid particles were washed 3 times by centrifugation (15,000 rpm, 15 min) followed by dispersion in water. The final solution pH was 3.7. The average particle diameter was estimated by DLS to be 235 nm, with a polydispersity of 0.28. These values, in comparison to those for the bare SiO₂ particles, are likely to reflect both the addition of a ceria layer and associated decrease in interparticle repulsions. Unfortunately, we did not possess the necessary facilities to generate a detailed elemental map of CeO₂ content within the SiO₂ particles. It is however apparent from the TEM images and BET analysis (see MS, figure 1 and analysis therein) that ceria nanoparticles are likely to have filled the larger silica pores and in some cases penetrated the centre of the particles. Clearly, optimization (in particular to the ceria particle size) could lead to a greater uptake, which will be the subject of further studies.

Adsorption of 8HQ to the CeO₂@SiO₂

A sample of known volume of the CeO₂@SiO₂ colloid was centrifuged (15,000 rpm, 15 min) to recover the particles, which were dispersed in an ethanolic 8HQ solution (10 wt%) of the same volume. This solution was placed under reduced pressure at 70 mbar for 15 min, after which it was removed and left in a cupboard overnight to equilibrate. After this, the particles were recovered (10,000 rpm, 45 min). The solvent and remaining 8HQ was poured off and the tube containing the particles was left upside-down to allow the vast majority of the 8HQ-containing ethanol to flow out. From the tube an approximately 0.1 g sample was taken of the slurry and the remainder used to calculate the weight percent of particles in the slurry (by thoroughly drying overnight in an oven at 90°C). Using this known concentration, a 10 wt% solution in ethanol of the particles was made, which was used in further analysis. For the corrosion testing, this procedure was repeated for the SiO₂ particles (no CeO₂) using both solutions with and without 8HQ (i.e. disperse in pure EtOH not 10 wt% 8HQ/EtOH in the first step). Additionally, the procedure was repeated for CeO₂@SiO₂ particles without 8HQ, to give a complete set of control samples (bare SiO₂, SiO₂+8HQ, bare CeO₂@SiO₂, CeO₂@SiO₂+8HQ) for comparison (all 10 wt% solutions in ethanol).

Release kinetics

Prior to the release measurements, the loaded particles were thoroughly washed 12 times by dispersing in saline solution ($[\text{NaCl}]_{\text{aq}} = 0.5 \text{ M}$) and collecting by centrifugation (15,000 rpm, 30 min) to ensure the elimination of any non-adsorbed 8HQ (saline solution was used in order to reduce the desorption of inhibitor and CeO₂). After the final centrifugation, the particles were dried thoroughly in an oven (80°C). 40 mg of the dried particles were added into 40 ml of stirred aqueous solutions at different pHs (pH = 1, 5, 9, 12). Immediately after mixing the timer was started. The first sample was taken immediately and centrifuged at 15,000 rpm for 2 min (to reduce the influence of any non-adsorbed ceria particles), after which 0.1 ml of the upper liquid phase was removed and diluted by

addition of 1 mol dm⁻³ HCl(aq) (1.9 ml) and the UV-visible absorption spectrum measured. This ensured that the pH at which the absorption was measured was always constant. Samples were taken periodically for up to 6 hours, during which the pH was constantly monitored. Given that the solutions were well mixed by constant stirring, it can be assumed that the removal of samples had little effect on the detected release rate. The solution concentration was calibrated by measuring 8HQ solutions of known concentration and the fraction released calculated by dividing the solution concentration at time = t by the maximum solution concentration measured over all pH values. By factoring in the dilutions and known particle concentration it can be estimated that 4 mg of 8HQ was released per gram of particles, which is quite high considering the rigorous washing steps. Release curves were fitted to a Korsmeyer-Peppas model $\Delta R = kt^n + a$, as described in the text, which was modified to include an additive term (a) to account for burst release. Neutral pH was unable to be tested due to experimental difficulties in holding a stable pH without the use of buffer that could influence the release mechanism.

Forming the coated metal samples

The base SiO₂-ZrO₂ coating was made via a sol-gel process, as reported previously.⁴ The SiO₂-ZrO₂ coating is generally considered to consist of ZrO₂ nanoparticles within a silica/organic matrix. Previous measurements, using electron diffraction (TEM) and XRD suggested that the ZrO₂ particles in the coating are amorphous (e.g. Surface & Coatings Technology 2006, 200, 3084–3094). To make the precursor coating solution, two mixtures, *A* and *B*, were separately prepared. *A* was a solution of GPTMOS (26 ml) in IPA (20 ml), to which a solution of acidified water (prepared using nitric acid, pH = 0.5, 4 ml) was carefully added drop-wise. *B* was a solution of TPOZ (12.5 ml) in ethylacetoacetate (12.5 ml), to which a solution of acidified water (as above, 1.45 ml) was added again drop-wise. Mixture *B* was placed into an ultrasonic bath for 20 min, then mixture *A* was added to it under constant stirring to yield the final coating solution. This was placed into an ultrasonic bath for 60 min and then finally aged overnight. Then, 0.5 g of each of the ethanolic particle suspensions (bare SiO₂, SiO₂+8HQ, bare CeO₂@SiO₂, CeO₂@SiO₂+8HQ, all 10 wt%) was added to 12 ml of the aged precursor coating solution

and shaken to disperse. For the control 'sol-gel coating', 0.5 g EtOH was added to the solution to ensure the solution concentrations remained constant in all cases. The aluminium substrates were chemically cleaned by immersion in solutions of NaOH (1 M, 15 min, 60°C) and nitric acid (20%, 15 min, room temperature). Finally, samples were coated onto cleaned metal substrates using a Bungard RDC 15 dip coater on maximum speed setting (10), with an immersion time of 3 minutes and were cured at 130°C for 60 min.

The weight loss during curing of the bare sol-gel coating was experimentally determined (by weighing coated substrates before and after curing) to be of order 65%. The density of the precursor coating solution was found by weighing a known volume to be approximately 0.92 g cm^{-3} , so 12 ml = 11 g, which would give 3.9 g of dried coating. On this basis, the concentration of particles in the final coating samples is of order 1.3 wt%. Initially only this concentration was tested (for simplicity). The optimization of particle concentration was not carried out, given the poor performance of the sol-gel coating as a passive barrier.

Supporting figures

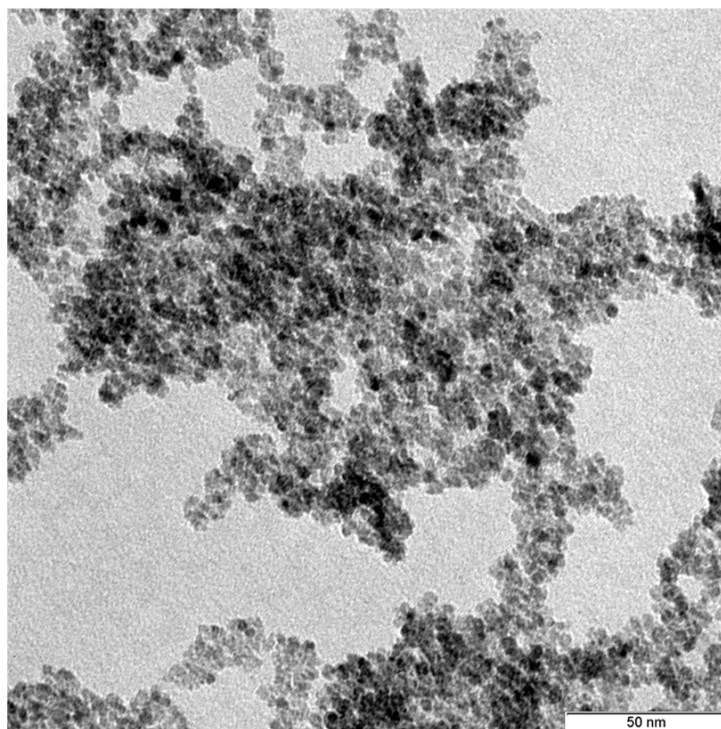


Figure S1. TEM image of CeO_2 nanoparticles showing approximately spherical, aggregated particles with diameters of order 5 nm.

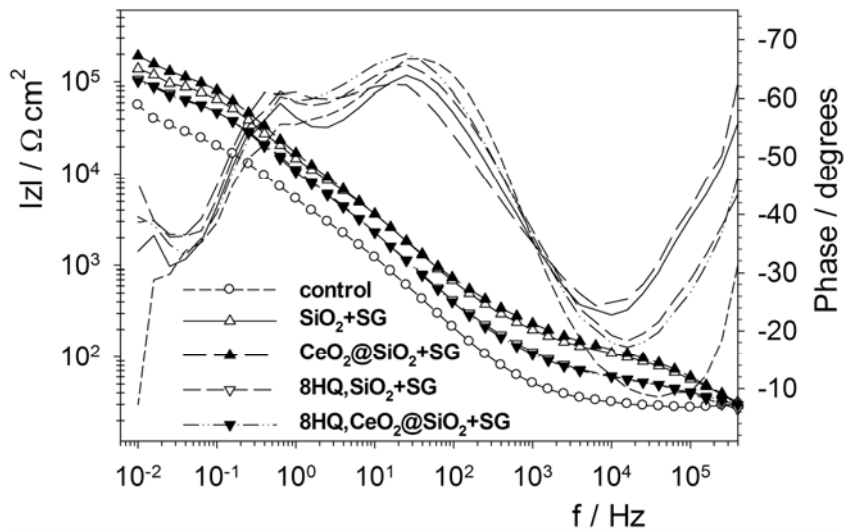


Figure S2. Bode plots showing the change in absolute impedance and signal phase shift with frequency for the coated substrates after 5 days immersion.

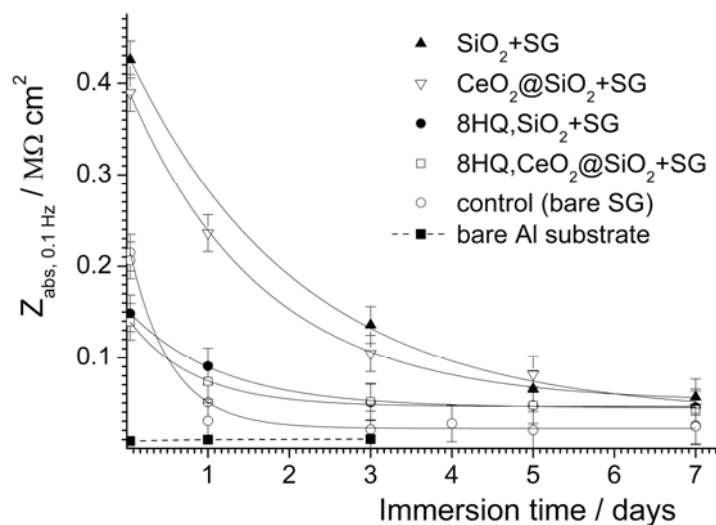


Figure S3. Plot showing the decrease in the measured value of absolute impedance at 0.1 Hz ($Z_{abs, 0.1Hz}$) over the course of the corrosion test for the different samples. The values for the bare Al substrate are also shown and do not change greatly in three days, implying a constant corrosion rate. Repeats were carried out and repeat data is shown (0, 1, 4 days) for the control, exhibiting good reproducibility.

pH	a	k	n
1	0.56	0.062	0.35
5	0.28	0.058	0.25
9	0.21	0.037	0.35
12	0.66	0.121	0.17

Table S1. Fitted parameters to the Korsmeyer-Peppas model from the releases of 8HQ at different pH values (see manuscript text).

Calculating Capacitance, Resistance from EIS data

The absolute impedance, Z_{abs} is defined as follows, where R is the resistance and X_c the capacitive reactance:

$$Z_{abs} = \sqrt{R^2 + X_c^2}$$

Here, $R = Z_{abs}\cos\theta$ and $X_c = Z_{abs}\sin\theta$, where θ is the phase difference between the applied voltage and measured current ('phase' on figure S2). Using these equations, values for R and X_c were calculated from the measured values of Z_{abs} and θ . Then, using X_c , the values for capacitance, C at different frequencies, f was calculated using the following equation:

$$C = \frac{-1}{2\pi f X_c}$$

These values were used to make the plots shown in figure 3g, h.

Supporting references:

1. M. J. Hollamby, D. Fix, I. Dönch, D. Borisova, H. Möhwald, and D. Shchukin, *Adv. Mater.*, 2011, **23**, 1361-1365.
2. W. T. Minehan and G. L. Messing, *Colloid. Surf.*, 1992, **63**, 181-187.
3. T. Taniguchi, T. Watanabe, N. Sakamoto, N. Matsushita, and M. Yoshimura, *Crystal Growth & Design*, 2008, **8**, 3725-3730.
4. D. G. Shchukin and H. Möhwald, *Small*, 2007, **3**, 926-943.