Self-assembly of amphiphilic polyoxometalates for the preparation of mesoporous polyoxometalate-titania catalysts†

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Amphiphilic polyoxometalate (POM) surfactants were prepared by covalently grafting double hydrophobic tails with chain lengths C_{12}H_{25}, C_{14}H_{29}, C_{16}H_{33} or C_{18}H_{37} onto the lacunary Wells–Dawson (P_{2}W_{17}O_{61}) headgroup. The critical micelle concentrations (CMCs) of these novel surfactants in aqueous solutions were determined by conductivity, and micelle formation was studied by small angle neutron scattering (SANS). Surprisingly, the amphiphiles with longer hydrophobic tails tend to form less elongated and more globular micelles in water. The self-assembled amphiphilic polyoxometalates were used as templates in the hydrothermal synthesis of mesoporous TiO_{2} containing dispersed, immobilised (P_{2}W_{17}O_{61}) units, which showed enhanced activity for the photodegradation of rhodamine B (RhB). The catalyst was recycled eight times with no loss of efficiency, demonstrating the stability of the hybrid structure. The amphiphilic polyoxometalates, therefore have excellent potential for the synthesis of various types of catalytically active porous materials.

Introduction

Polyoxometalates (POMs) are a class of unique nanoscale transition metal oxide clusters, formed by earth-abundant metals in their highest oxidation states.1,2 Due to their remarkable redox and photochemical properties, they are often used as catalysts for selective reduction3,4 and as inexpensive photocatalysts for the green removal of organic pollutants or transition metals from water.5,6 Similar to semiconductor photocatalysts, which experience electron transfer from the valence band (VB) to the conduction band (CB) under ultraviolet irradiation, POMs undergo electron transfer from the oxygen-based highest occupied molecular orbitals (HOMO) to the lowest unoccupied molecular orbitals (LUMO) on the addenda atoms under UV irradiation,7,8 resulting in a colour change to blue. The charge-transfer excited state POM (POM*) has a highly oxidizing power that is strong enough to oxidise organic species or to generate ·OH radicals.9,10

The incorporation of POMs onto conventional supports, such as SiO_{2}11,12 TiO_{2},13,14 Al_{2}O_{3}11 or metal-organic frameworks,15 through direct dispersion has been investigated to increase the application of POMs for catalysis. However, it has been reported that POMs anchored onto the surface of such supports are not stable since the POMs may be leached out by water or alcohol.16 Studies have therefore been undertaken to modify the inner walls of the support materials to improve POM adhesion: e.g. by grafting organic moieties such as amnosilane or imidazole, to provide strong anchoring of POMs and prevent POM leaching when applied as a catalyst in polar solvent media.16–19 However, this method limits the applications of these materials due to the low thermal stability of the organic anchoring groups at high temperatures.20 Alternatively, researchers have been exploring the encapsulation of POMs into aggregates formed by surfactants or polymers,21–23 with the aim to fabricate polyoxometalate-decorated mesoporous materials via a one-pot synthesis.

Amphiphilic surfactants are of great interest for their applications as templates in the formation of mesoporous materials, which typically form from mixed aqueous solutions of surfactants and inorganic precursors.24–26 Porosity is generated in the inorganic materials after the removal of the organic components from the surfactant template. These mesoporous materials, due to their high specific surface areas and uniform
mesopore size, are particularly interesting as supports for catalysts.\textsuperscript{27,28}

To incorporate POMs into the matrix of inorganic mesostructured materials or synthesise porous hybrid materials where the POMs are accessible, a POM-based amphiphile that can be used as a templating agent is key. Self-assembly is an efficient method to synthesise materials with high surface areas and open networks, and hence the use of POM amphiphiles has the potential to organise accessible polyoxometalates directly and uniformly within the supports. There have been previous reports on the synthesis of surfactants with POMs as headgroups through covalent bonding,\textsuperscript{29–33} but to the best of our knowledge, there have been no detailed studies of the application of POM-based amphiphiles to template mesoporous POM-decorated inorganic materials.

Among various oxide semiconductor photocatalyst materials, titania is recognised as the most suitable material for widespread environmental applications due to its low cost, strong oxidising ability and photostability.\textsuperscript{34,35} Its performance is often reinforced through the incorporation of electron-transporting materials, such as graphene oxide\textsuperscript{36} or graphene,\textsuperscript{37} within the titania matrix. Also, there have been attempts to load polyoxometalates onto TiO\textsubscript{2} through a layer by layer strategy, physical mixing or electrostatic bonding.\textsuperscript{38–40} These studies have demonstrated synergistic effects between TiO\textsubscript{2} and polyoxometalates.

In this paper, we report the characterisation of micellar structures formed by amphiphilic [P\textsubscript{2}W\textsubscript{17}O\textsubscript{61}[(OSi\textsubscript{2}(C\textsubscript{6}H\textsubscript{2}n+1))\textsubscript{2}]]\textsuperscript{−} (Wells–Dawson type POMs with double hydrocarbon tails C\textsubscript{6}H\textsubscript{2n+1}, denoted as POM-2C\textsubscript{n}) with molecular structure illustrated in Fig. 1), the influence of the tail length of the amphiphiles on the micelle shape and degree of counterion ionisation, using conductivity, small angle X-ray scattering (SAXS), zeta-potential and dynamic light scattering (DLS).

The Wells–Dawson anion [α-P\textsubscript{2}W\textsubscript{18}O\textsubscript{62}]\textsuperscript{−} can readily accept multiple electrons without any change in the cluster geometry, and both [α-P\textsubscript{2}W\textsubscript{18}O\textsubscript{62}]\textsuperscript{−} and its lacunary derivative [P\textsubscript{2}W\textsubscript{17}O\textsubscript{61}]\textsuperscript{2−} are often used as co-catalysts for catalytic oxidation and photocatalytic reduction.\textsuperscript{41,42} The siloxane derivatives [P\textsubscript{2}W\textsubscript{17}O\textsubscript{61}[(OSi\textsubscript{2}(C\textsubscript{6}H\textsubscript{2n+1}))\textsubscript{2}]]\textsuperscript{−} are amphiphiles with redox-active metal oxide headgroups and form micelles in water. Therefore, these micelles were used directly as templating agents for the hydrothermal synthesis of POM-TiO\textsubscript{2} mesoporous materials, without the addition of any other co-templating agents. The resulting POM-TiO\textsubscript{2} hybrid materials have relatively high surface areas and better rhodamine B (RhB) photodegradation properties compared to a porous TiO\textsubscript{2} material prepared using a commercial anionic surfactant template.

Experimental

Materials

Na\textsubscript{2}WO\textsubscript{4}·2H\textsubscript{2}O (purity >99%), phosphoric acid (85 wt% in water solution), NH\textsubscript{4}Cl (purity >99.3%), KCl (laboratory reagent grade), dodecyltriethoxysilane (C\textsubscript{12}H\textsubscript{25}SiCl\textsubscript{3}, purity >95%), octadecyltriethoxysilane (C\textsubscript{18}H\textsubscript{33}SiCl\textsubscript{3}, purity >90%), KHCO\textsubscript{3} (purity >99.7%), sodium dodecyl sulfate (SDS, purity >99%) and D\textsubscript{2}O (99.0 atom%) were purchased from Sigma Aldrich. Tetradecyltrioxsilane (C\textsubscript{14}H\textsubscript{29}SiCl\textsubscript{3}, purity >98%) and hexadecyltrioxsilane (C\textsubscript{16}H\textsubscript{31}SiCl\textsubscript{3}, purity >98%) were purchased from Fluorochem. All chemicals were used without further purification. 70 mol% D\textsubscript{2}O in H\textsubscript{2}O was prepared using ultrapure water (18.2 M\textsubscript{Ω} cm, from an ELGA PURELAB flex water purification system).

Preparation of POM-2C\textsubscript{n}

K\textsubscript{10}[α-P\textsubscript{2}W\textsubscript{18}O\textsubscript{62}]·14H\textsubscript{2}O was prepared as previously described by Droge.\textsuperscript{43} Lacunary K\textsubscript{10}[α-P\textsubscript{2}W\textsubscript{17}O\textsubscript{61}]·19H\textsubscript{2}O was synthesised according to the method of Finke et al.,\textsuperscript{44} and then used to prepare POM-2C\textsubscript{n}. A typical reaction is as follows: K\textsubscript{10}[α-P\textsubscript{2}W\textsubscript{17}O\textsubscript{61}]·19H\textsubscript{2}O (1.040 mmol) was dispersed in anhydrous MeCN (180 ml) and stirred under nitrogen for 4 hours. Trichlorosilane, RSiCl\textsubscript{3} (R = C\textsubscript{12}H\textsubscript{25}, C\textsubscript{14}H\textsubscript{29}, C\textsubscript{16}H\textsubscript{33} or C\textsubscript{18}H\textsubscript{37}, 4.94 mmol) was dissolved in anhydrous dichloromethane (60 ml), and an aqueous HCl solution (pH = 2) of TiOSO\textsubscript{4} (0.672 M, 9 ml) was added dropwise to POM suspension with stirring. The obtained mixture was stirred for 12 hours to finish the reaction.

The mixture produced was filtered and then dried using a rotary-evaporator. The powder obtained was washed four times with anhydrous diethyl ether (50 ml) to remove the excess of Trichlorosilane, and was vacuum-dried to give the final product K\textsubscript{n}[P\textsubscript{2}W\textsubscript{17}O\textsubscript{61}[(OSi\textsubscript{2}(C\textsubscript{6}H\textsubscript{2n+1}))\textsubscript{2}]], denoted as POM-2C\textsubscript{n}, with n = 12, 14, 16 or 18.

Synthesis of POM-TiO\textsubscript{2}

The nPOM-TiO\textsubscript{2} hybrid materials were prepared by mixing an aqueous HCl solution (pH = 2) of POM-2C\textsubscript{n} (9.17 mM, 9 ml) and an aqueous HCl solution (pH = 2) of TiOSO\textsubscript{4} (0.672 M, 6 ml) to give final POM-2C\textsubscript{n} and TiOSO\textsubscript{4} concentrations of 5.5 mM and 0.269 M respectively. The reaction was performed at 150 °C in an autoclave with a ramping rate of 5 °C min\textsuperscript{−1}, and then was held at 150 °C for 20 hours. The obtained powder was filtered and washed with water to remove any surfactant excess prior to freeze-drying. The freeze-dried powder
was calcined at 500 °C in air for 5 hours to remove the hydrocarbon tails to generate pores. The effect of temperature on Dawson structured POMs has been extensively studied previously in the literature.\textsuperscript{45-47} According to these studies, the Wells–Dawson conformation of the POM is maintained up to 873 K, which is well above the calcination temperature of our materials. The calcined products were porous TiO\textsubscript{2} materials containing functionalised POM units, and were labelled nPOM-TiO\textsubscript{2} catalyst with \( n = 12, 16 \) or 18 depending on the tail length of the POM-2\( C_\text{} \)\( n \) used in the synthesis. For comparison, a sample of TiO\textsubscript{2} templated by sodium dodecyl sulfate (SDS) was synthesised according to the procedure already described in the literature which used a much higher surfactant concentration (0.26 M SDS) than that used for POM-2\( C_\text{} \)\( n \) templating.\textsuperscript{48}

To study the effect of POM-2\( C_\text{} \)\( n \) surfactant concentration on the material formed, a second 16POM-TiO\textsubscript{2} hybrid material was prepared at a higher concentration of POM-2\( C_\text{} \)\( n \) (22.0 mM) using the same method described above; the resulting material is labelled as 16POM-TiO\textsubscript{2}-2.

The synthesised materials were characterised using transmission electron microscopy (TEM), nitrogen sorption, powder X-ray diffraction (PXRD) and energy dispersive X-ray (EDX) elemental mapping.

**Photocatalytic activity test**

0.015 g nPOM-TiO\textsubscript{2} or SDS templated TiO\textsubscript{2} catalyst was added to 30 ml of an aqueous mixture of RhB (15 mg L\textsuperscript{-1}; 0.031 mM) and H\textsubscript{2}O\textsubscript{2} (1.5 mM). The mixture was exposed to solar light (energy equal to one sun) under stirring for 80 min. During this time 2 mL aliquots of solution were removed from the system every 20 min and centrifuged. UV-vis absorption measurements were conducted on the clear solutions obtained to determine the concentration of rhodamine B (RhB) according to the major absorption intensity at 553 nm, for each degradation stage. The measured solution was added back to the system at every stage to maintain the total volume. A blank experiment was carried out as follows: a 30 ml of an aqueous mixture of RhB (15 mg L\textsuperscript{-1}; 0.031 mM) and H\textsubscript{2}O\textsubscript{2} (1.5 mM) was illuminated by solar light without adding any photocatalyst. The change of RhB concentration with illumination time was recorded using the same method as above.

A control experiment was performed by using 0.20 mg POM-2\( C_{12} \) (4 \( \times \) 10\textsuperscript{-5} mmol, equivalent to the moles of POM in 0.015 grams of 12POM-TiO\textsubscript{2} material estimated by using the EDX elemental mapping result) as the catalyst. A bathochromic shift and obvious drop in the intensity of the main absorption peak was observed in the UV-vis spectrum when POM-2\( C_{12} \) was added to the RhB starting solution in the dark (see discussion below). In this case therefore, the concentration of RhB during solar light illumination was determined using the absorption intensity at 565 nm, the position of the main RhB absorption peak observed after the addition of POM-2\( C_{12} \).

**Ag\textsuperscript{+} reduction**

Polyoxometalates can be reduced by organic electron donors (e.g., alcohols) upon exposure to visible and ultraviolet light.\textsuperscript{49} The nPOM-TiO\textsubscript{2} hybrid material (0.02 g) was dispersed in isopropanol under stirring and illuminated by solar light for about 20 min. The colour of the dispersion changed from white to blue. An aqueous AgNO\textsubscript{3} solution (0.05 M) was added dropwise into the dispersion after removal from light, causing the blue-coloured dispersion to turn to brown abruptly. The brown powder was then filtered, washed with water and air-dried for TEM and EDX elemental mapping analysis.

**Small angle neutron scattering**

**Data collection.** Small Angle Neutron Scattering (SANS) experiments were performed on the LOQ SANS instrument\textsuperscript{50} at the ISIS Neutron and Muon Spallation Source (Oxfordshire, UK) with a typical time-averaged flux of 2 \( \times \) 10\textsuperscript{5} cm\textsuperscript{-2} s\textsuperscript{-1}. The data were collected using a \textsuperscript{3}He-C\textsubscript{F\textsubscript{4}} filled ORDELA “area” detector. The probed \( q \) range was approximately from 0.007 to 0.20 Å\textsuperscript{-1}, where \( q \) is the momentum transfer. The samples were measured in UV-spectrophotometer grade quartz cells with a path length of 1 mm at 25 °C.

The raw spectra were corrected for the background from the solvent, sample cell and other sources using standard workflows in the Mantid software package.\textsuperscript{51} Scattering data were normalised against the scattering from a partially-deuterated polystyrene blend of known molecular weight to put the SANS data on an absolute scale.\textsuperscript{52} so \( I(q) \) equals the differential scattering cross section \( d\Sigma/d2(q) \). The output data was absolute scattered intensity, \( I(q) \) in cm\textsuperscript{-1}, versus the momentum transfer, \( q \) in Å\textsuperscript{-1}.

**Data modelling.** The measured scattering intensity \( I(q) \) as a function of the momentum transfer \( q \), for centrosymmetric particles, is given as:

\[
I(q) = A(\DeltaS)\text{LD}^2 P(q)S(q, \phi)
\]  

(1)

where \( A \) is the scale factor, \( \phi \) is the volume fraction of particles. \( \DeltaS \text{LD} \) corresponds to the scattering length density (SLD) contrast between particles and solvent. \( P(q) \) is the form factor, which corresponds to the orientationally averaged scattering profile of a single particle and can be computed from a structural model. \( S(q, \phi) \) is the structure factor that accounts for the interactions between the particles in the solution.

For a dilute suspension, the interactions between micelles, \( S(q, \phi) \), can be neglected, so \( I(q) \) mainly depends on the shape and size of the particles:

\[
I(q) = A(\DeltaS)\text{LD}^2 P(q)
\]  

(2)

Due to the large SLD difference between the POM-2\( C_{n} \) headgroup (4.42 \( \times \) 10\textsuperscript{-6} Å\textsuperscript{-2}) and tails (\( -0.38 \times 10^{-6} \) Å\textsuperscript{-2}), the SANS patterns were fitted using core–shell models. For some of the scattering data, the core–shell sphere model\textsuperscript{53} gave satisfactory fit results. However, in some circumstances, it gave an unusually large radius, which was not in accordance with the tail length of a surfactant monomer, so a core–shell ellipsoid model\textsuperscript{14,58} was favoured and applied to get better fit results. In the modelling, the core of the micelles was assumed to only contain the hydrocarbon tails, while the shell was formed...
from the headgroups, a partial contribution from the tails and water. Through fitting the form factor $P(q)$, the minimum radius of the core ($R_{\text{min}}$), shell thickness ($t$), core ellipticity ($\epsilon$) and shell neutron scattering length density (SLD) were obtained.

In the semi-dilute regime, where micelles are interacting, the structure factor also has to be taken into account. Since the POM-2Cₙ micelles are charged due to the ionisable headgroups, they experience a Coulomb repulsion modelled using the Hayter Penfold Rescaled Mean Spherical Approximation (RMSA)\(^56\) which gives the volume fraction of charged particles interacting ($\phi$) and the number of charges per micelle $z$ (number of electrons). This model depends on the Debye screening length of interactions. This Debye length can be calculated knowing the temperature ($25$ °C) and the relative permittivity of the medium ($72.08$ for $D_2O$, $72.2$ for $70$ mol% $D_2O$).\(^57\)

Scattering patterns from samples at the same concentration but in two different solvents ($D_2O$ and $70$ mol% $D_2O$) were fitted simultaneously using SasView (version 4.2.1) in order to better constrain the fits using contrast variation. Calculated neutron SLDs of the hydrocarbon tails, the POM headgroup and the solvents used for fitting are listed in ESI Table 1.\(^\dagger\)

Other Techniques

The electrical conductivities of the surfactant aqueous solutions were measured using a METTLER TOLEDO conductivity meter. NMR spectroscopic measurements were carried out using a 500 MHz Bruker Avance II+ spectrometer. Typical samples were made from POM-2Cₙ surfactants dissolved in $D_2O$. The $^{31}P$ NMR was measured with a relaxation time of 20 seconds. IR spectra were measured using a Bruker IR spectrometer at room temperature in a dry box. TGA was applied to measure the change of sample weight as a function of temperature. An alumina crucible with about 100 mg of sample was put into a furnace, which was heated up in air at a constant heating rate of 1 °C min⁻¹, while a sensitive balance recorded sample weight loss. The results are displayed as the loss of mass percentage against temperature in °C. Analysis of carbon, hydrogen and nitrogen (CHN analysis) was carried out with a Carlo Erba 1112 elemental analyser at MEDAC Ltd Brunel Science Centre, Surrey, TW20 0JZ, UK. POM-2Cₙ aqueous solutions at $5.5$ mM were measured at room temperature using dynamic light scattering (DLS) in a Malvern Zetasizer Nano ZSP (Malvern, UK). All samples were filtered through a $0.45$ µm filter (Milllex-HA) to remove any dust before the measurements. Samples were measured at a scattering angle of $173^\circ$ and a wavelength of $632.8$ nm for 120 s, repeated 5 times. The size distribution, weighted in volume, was extracted using the CONTIN method. The zeta-potential of the micelles was also studied, at the same concentration, using the same instrument. Nitrogen sorption measurements were carried out at liquid nitrogen temperature ($77.36$ K) using a Belsorp instrument (BELSorp-mini Inc. Japan). The samples were degassed under vacuum at $523$ K for 1000 min prior to the measurements. Surface areas were calculated using the Brunauer–Emmett–Teller (BET) equation. PXRD measurements were performed on a Stoe STADI P high-resolution system equipped with a Dectris Double MYTHEN 1K strip detector, and employing Cu-Kα₁ radiation ($\lambda = 1.54060 \times 10^{-10}$ m). The samples were measured in the range of $10^\circ < 2\theta < 70^\circ$ at $2^\circ$ per minute. The morphologies of the obtained materials were observed by TEM using a JEOL JEM-2100Plus instrument with an operating voltage at $200$ kV maximum. An Oxford Instruments large area EDX detector, associated with the TEM, and Aztec analysis software were used for high-resolution elemental mapping analysis. Prepared POM-loaded mesoporous TiO₂ materials were characterised using an Anton Paar SAXSess instrument with a PANalytical PW3830 X-ray generator which gave a $q$ range between $0.08$ Å⁻¹ and $2.7$ Å⁻¹. The line X-ray source used was a Cu Kα X-ray tube at 40 kV and 50 mA. X-rays were detected by a reusable Europium excitation based image plate (size: $66 \times 200$ mm) with a 42.3 µm² pixel size. The image plate was subsequently read by a PerkinElmer cyclone reader using OptiQuant software. SAXS profiles were generated by using the SASSquant program.

Kinetics of photocatalytic degradation

UV-vis absorption was used to follow dye degradation performed on a PerkinElmer Lambda 750S UV-vis spectrometer. The rate of photodegradation of rhodamine B (RhB) in the presence of photocatalysts can be calculated from a fit to the experimental data. The Langmuir–Hinshelwood model can be used to describe the kinetics of the photodegradation, and the model is further simplified if possible.\(^58\) Here, the degradation kinetics were approximated as pseudo-first-order kinetics with respect to the concentration of RhB ($C$):

$$-\frac{dC}{dt} = k_{\text{obs}}C$$

where $k_{\text{obs}}$ is the rate constant. Integration of the equation (with $C_t$, $C_0$ are the RhB concentrations at time $t$ and 0 min respectively) gives:

$$\ln(C_t/C_0) = -k_{\text{obs}}t$$

where the values of $k_{\text{obs}}$ (unit: min⁻¹) can be obtained directly from the regression analysis of a linear plot of $\ln(C_t/C_0)$ versus time.

Results and discussion

Characterisation of K₆[α-P₃W₁₈O₆₂]·14H₂O, K₁₀[α₉-P₃W₁₇O₆₄]·19H₂O and POM-2Cₙ

POM-2Cₙ surfactants with structure illustrated in Fig. 1 were prepared from K₆[α-P₃W₁₈O₆₂]·14H₂O, via the lacunary derivative K₁₀[α₉-P₃W₁₇O₆₄]·19H₂O using established methods.\(^44\)

Starting materials and POM-2Cₙ ($n = 12, 14, 16$ and 18) were characterised by $^{31}P$ NMR (Fig. 2A–C and ESI Fig. 1†) and IR spectroscopy (Fig. 2D and ESI Fig. 2†). The $^{31}P$ NMR spectrum of K₆[α-P₃W₁₈O₆₂]·14H₂O (Fig 2A) shows the characteristic peak at $-13.03$ ppm, in addition to two small peaks at around $-11.53$ and $-12.31$ ppm, due to the K₁₀[α₉-P₃W₁₇O₆₄]·19H₂O isomer. After the modifications, two $^{31}P$ NMR peaks were
observed due to the non-equivalent phosphorus atoms both in the K10[α2-P2W17O61]19H2O spectrum (−7.24 and −14.38 ppm, see Fig. 2B) and in the K6[α2-P2W17O61]19H2O (2) K10[α2-P2W17O61]19H2O and (3) POM-2C12 (where the red circle indicates the existence of Dawson structured POM after tail grafting).

In the IR spectra (Fig. 2D), only one type of ν(P–O) vibration was observed at 1087 cm−1 for symmetric K6[α2-P2W17O61]19H2O. For K10[α2-P2W17O61]19H2O, the bands of ν(P–O) vibrations were observed at 1013, 1046 and 1077 cm−1, similar to those reported in the literature. After the attachment of the hydrocarbon tails to form the POM-2C12 surfactant, the three ν(P–O) vibration peaks were retained with the peak at 1046 cm−1 overlapping with the peak at 1083 cm−1. Peaks at 2920 and 2850 cm−1 correspond to the ν(C–H) vibration, indicating the presence of both {P2W17O61} and hydrocarbon chains in the final product. IR spectra of POM-2Cn (n = 14, 16 and 18) were obtained and are found to be similar to that of POM-2C12, suggesting the presence of both polyoxometalate and hydrocarbon chain (see ESI Fig. 2†).

UV-vis absorbance spectra (ESI Fig. 4†), showed a bathochromic shift in the absorption edge upon attachment of the two hydrocarbon chains, so that the POM-2C12 derivatives absorb light over a wider wavelength range compared to the lacunary K10[α2-P2W17O61]19H2O. TGA on the POM-2Cn materials (ESI Fig. 5†), showed a mass loss of 6.73%, 7.00%, 7.13% and 10.05% corresponding to the tail weight percentage in POM-2C12, POM-2C14, POM-2C16 and POM-2C18 (calculated mass loss is 7.0%, 8.1%, 9.2% and 10.2% respectively). Additional CHN analyses suggest a carbon weight percentage of 7.11% and 7.84% and a hydrogen weight percentage of 1.56% and 1.66% in POM-2C14 (C: 6.92%, H: 1.20%) and POM-2C16 (C: 7.82%, H: 1.34%) respectively. The carbon weight percentages from CHN analyses give similar results to the calculated values. The deviation in H weight percentage between the theoretical and the experimental values may be attributed to moisture in the materials. These results confirm the successful synthesis and structural integrity of the POM-2Cn.

Critical micelle concentrations

ESI Fig. 6A–D† show plots of the electrical conductivity vs. the concentration of POM-2Cn in water, and CMC values were determined by the intersections of the two straight lines. The CMCs of the POM-2Cn surfactants versus hydrophobic chain length are plotted in Fig. 4, giving a trend similar to that observed for di-alkyl sulfo succinate surfactants (CMCs given in ESI Table 2†,62,63 alkyl trimethylammonium bromides (abbreviated as CnTAB, CMC values given in ESI Table 3†,64,65 and sodium alkyl sulfates (CMC values in ESI Table 4†,66–70 where a surfactant with longer hydrophobic tail/tails has a lower CMC compared to the one with the same headgroup but shorter hydrophobic part.

Degree of micelle ionisation and free energy of micellisation

The percentage of bound counterions in relation to the number of surfactant ions in the micelles is the fraction of micellar charge neutralized, β, defined as counterion binding.
The degree of micelle ionisation $\alpha$ equals $1 - \beta$, and can be calculated from measurements of conductivity with concentration from the slope measured above the CMC ($m_1$) divided by that below the CMC ($m_2$): $\alpha = m_1/m_2$. The calculated $\alpha$ values are listed in Table 1. It can be seen that micelles formed by POM-$2C_n$ with longer tails have a lower counterion dissociation, therefore higher screening by the counterion. The POM-$2C_n$ surfactants show similar changing trends in $\alpha$ as seen for traditional surfactants, such as di-alkyl sulfosuccinates, $C_n$TAB and sodium alkyl sulfates (ESI Tables 2–4†). The counterion binding $\beta$ and the CMC are related to the free energy of micellisation via equation:

$$\Delta G_{\text{mic}} = (1 + \beta)RT \ln(CMC)$$

(5)

the calculated free energies of micellisation are listed in Table 1 and plotted in Fig. 4. The $\Delta G_{\text{mic}}$ was calculated to be between $-8.5$ and $-15.9$ kJ mol$^{-1}$ at room temperature. The linear relationship in the variation of $\Delta G_{\text{mic}}$ with the tail length is consistent with that observed for $C_n$TAB surfactants. The value of the slope obtained from the line in Fig. 4, $-1.26 \pm 0.05$ kJ mol$^{-1}$, here represents the free energy increment for two CH$_2$ groups (designated as $\Delta G_I$). The $\Delta G_I$ of the POM-$2C_n$ system is much lower than that of $C_n$TAB ($-3.45 \pm 0.2$ kJ mol$^{-1}$) with a single hydrocarbon tail.73

By comparing the $\Delta G_{\text{mic}}$ values of POM-$2C_n$ with those of di-alkyl sulfosuccinate surfactants (ESI Table 2†), it is seen that the POM-$2C_n$ surfactants can form micelles more easily in water because they have longer hydrophobic tails. They also have relatively similar free energies of micellisation with those of single-tailed $C_n$TAB ($n = 12, 14, 16$) surfactants (ESI Table 3†). These results indicate that, despite the fact that POM-$2C_n$ are double-tailed surfactants, they form micelles as easily as conventional single-tailed surfactants and aggregate more efficiently compared to conventional anionic double-tailed surfactants.

**SANS study of POM-$2C_n$**

Above their CMCs, the POM-$2C_n$ surfactants assemble in water. The shape of these aggregates is expected to have important influences in the field of micellar catalysis, photochemistry and materials templating, and is therefore interesting to investigate. We used SANS to probe the micelles formed by these surfactants in aqueous solutions.

The best fit for the micelles formed by POM-$2C_{12}$ in water was obtained from a core–shell ellipsoidal model. The SANS patterns and their corresponding fits are plotted in Fig. 5 for the D$_2$O contrast, while the fitted parameters along with the definition of the abbreviations are listed in Table 2. The elongation of the micelles was found to be dependent on the concentration: the ellipticity, $\epsilon$, indicating the degree of elongation, varies from $4.0 \pm 0.4$ to $5.1 \pm 0.4$. Similarly, $R_{\text{min}}$ ranges from $11 \pm 1 \text{ Å}$ to $15 \pm 1 \text{ Å}$, slightly below the length of fully extended C$_{12}$H$_{25}$ chains according to the Tanford equation ($16.7 \text{ Å}$). Measurements of solutions prepared using 70 mol% D$_2$O as solvent (a value that was calculated to contrast match the POM-$2C_n$ headgroup) were also made (ESI Fig. 7A†). Fitting the data at 70 mol% D$_2$O still required a shell in the model, but with a lower SLD than that calculated for both dry POM and solvent (ESI Table 5†), suggesting that a portion of the hydrocarbon tail is present in the shell. The shell thickness was found to decrease with increasing concentration (from $22 \pm 1 \text{ Å}$ at 16.6 mM to $13 \pm 1 \text{ Å}$ at 99.1 mM). Except for the lowest concentration, these values (see Table 2) are in the same range as the dry $\{P_{10}W_{10}O_{38}\}$ headgroup size (between 12 and 17 Å due to the ellipsoidal shape of the headgroup).78

With increasing concentration, a broad peak emerged at around $q = 0.06 \text{ Å}^{-1}$. The peak indicates the intermicellar inter-
actions and was fitted using the RMSA model. The fits show a moderate increase in the charge per micelle with increasing concentration. The value for the charge on the micelle (around $3.6 \pm 0.3$) is surprisingly low given the potential $-6$ charge available to the headgroup, suggesting that although the conductivity results indicate that counterion dissociation is relatively high to the headgroup, suggesting that although the conductivity results indicate that counterion dissociation is relatively high.

POM-2C$_{14}$ also forms ellipsoidal micelles in water according to the modelling of the SANS patterns given in Fig. 5B (D$_2$O contrast) and ESI Fig. 7† (70 mol% D$_2$O contrast). Fit parameters associated with the form factor of POM-2C$_{14}$ micelles were found to have little dependence on the surfactant concentration (see Table 2). These micelles were less elongated compared to their POM-2C$_{12}$ counterparts, with an ellipticity of $2.0$. $R_{\text{min}}$ was found around 17–18 Å, again slightly smaller than the size of the fully extended C$_{14}$H$_{29}$ chain (19.2 Å) estimated by the Tanford equation. The hydrated shell thicknesses were found to be 15 ± 1 Å at 5.5 mM and 18 ± 1 Å for higher concentrations, which lies in the size range (12–17 Å) of [P$_2$W$_{17}$O$_{61}$]$^-$.

![Table 2](image)

**Table 2** Fitted core–shell ellipsoidal model parameters* for POM-2C$_{12}$ and POM-2C$_{14}$ micelles in D$_2$O

| Conc. (mM) | $R$ (Å) | $\varepsilon$ | $t$ (Å) | $z$ (e) | SLD ($\times 10^{-6}$ Å$^{-2}$) | $\phi$ |
|-----------|---------|--------------|---------|---------|-------------------------------|--------|
| (±0.1)    | (±1)    | (±0.3)       | (±1)    | (±0.5)  | (±0.2)                        | (±0.005) |
| POM-2C$_{12}$ |    |              |         |         |                               |        |
| 16.6      | 11      | 4.5 ± 0.3    | 22      | 1.0     | 5.3                           | 0.096  |
| 49.7      | 12      | 4.6 ± 0.3    | 16      | 1.0     | 5.0                           | 0.140  |
| 66.4      | 12      | 5.1 ± 0.4    | 15      | 1.3     | 4.6                           | 0.153  |
| 99.1      | 15      | 4.0 ± 0.4    | 13      | 1.5     | 4.8                           | 0.160  |
| POM-2C$_{14}$ |    |              |         |         |                               |        |
| 5.5       | 17      | 1.9 ± 0.3    | 15      | 4.4     | 5.1                           | 0.111  |
| 10.6      | 17      | 2.1 ± 0.3    | 18      | 3.7     | 5.3                           | 0.034  |
| 33.0      | 18      | 2.0 ± 0.3    | 18      | 3.6     | 5.3                           | 0.094  |
| 55.2      | 17      | 2.1 ± 0.2    | 18      | 4.3     | 5.0                           | 0.137  |

* $R_{\text{min}}$, the minimum radius of the core; $R_{\text{max}}$, the maximum radius of the core; $\varepsilon$, $R_{\text{max}}/R_{\text{min}}$ (ellipticity); $\phi$, volume fraction; SLD, neutron scattering length density; $t$, shell thickness; $z$, micellar surface charge.

![Fig. 6](image)

**Fig. 6** SANS patterns of (A) POM-2C$_{16}$ and (B) POM-2C$_{18}$ micelles in D$_2$O at different concentrations. The fits are given as black lines.

![Table 3](image)

**Table 3** Fitted core–shell model parameters* for POM-2C$_{16}$ and POM-2C$_{18}$ micelles in D$_2$O

| Conc. (mM) | $R$ (Å) | $t$ (Å) | $z$ (e) | SLD ($\times 10^{-6}$ Å$^{-2}$) | $\phi$ |
|-----------|---------|---------|---------|-------------------------------|--------|
| (±0.1)    | (±1)    | (±1)    | (±0.2)  | (±0.5)                        | (±0.005) |
| POM-2C$_{16}$ |    |         |         |                               |        |
| 5.5       | 20      | 19      | 4.2     | 5.6                           | 0.019  |
| 16.3      | 22      | 19      | 4.3     | 5.7                           | 0.053  |
| POM-2C$_{18}$ |    |         |         |                               |        |
| 5.8       | 22      | 17      | 4.9     | 5.6                           | 0.015  |
| 17.2      | 22      | 17      | 5.5     | 5.5                           | 0.049  |
| 29.1      | 22      | 17      | 5.2     | 5.3                           | 0.077  |

* $R$, the radius of the core; $\phi$, volume fraction; SLD, neutron scattering length density; $t$, shell thickness; $z$, micellar surface charge.

From the SANS fitting, an increase in the radius of the micelles (comparing $R_{\text{min}}$ for ellipsoids and $R$ for spheres) was observed with increasing hydrophobicity of the surfactant, in agreement with observations made for commercial C$_n$TAB surfactants and sodium alkyl sulfates. Moreover, the tail length strongly influences the shape of the micelles, with an obvious change from an ellipsoid to a sphere as the hydrocarbon tail of the surfactants becomes longer. As illustrated in Fig. 7, POM-2C$_{12}$ and POM-2C$_{14}$ both form ellipsoid micelles in aqueous solutions, however, the ellipticity of POM-2C$_{14}$ (around 2) is less than half of that of POM-2C$_{12}$ (around 4.5),
while both POM-2C_{16} and POM-2C_{18} form spherical micelles. In contrast, commercial single-tailed surfactants, such as C_{n}TAB and sodium alkyl sulfates, undergo an increase of the micelle ellipticity with increased tail length (see the calculated ellipticity listed in ESI Tables 3 and 4† using the information provided by references).^{64,67}

For the POM- C_{n} surfactants, the theoretical packing parameters, calculated for different tail lengths but assuming the same equilibrium area per molecule (the cross-sectional area of the headgroup estimated according to the size of the headgroup,^{78} 124.3 Å^2), lies close to the 1/3 limit between spherical and rod-like micelles, without any clear trend explaining the experimental data. This suggests that the equilibrium area per molecule may be different between them due to the difference in the repulsion between the surfactant headgroups. Considering the repulsive interactions, as listed in Tables 2 and 3, the surface charge increases with the tail length which may induce a larger equilibrium area per molecule. Therefore the packing parameter (v/l, where, v is the equilibrium area per molecule, l is the hydrophobic tail length, the volume-to-length ratio v/l of the tail is independent of the tail length for common surfactants) decreases with increased tail length, giving a value under 1/3, which predicts the formation of spherical micelles.^{79} This is consistent with the SANS results where longer tailed surfactants form more globular micelles.

Dynamic light scattering (DLS) was used to detect the hydrodynamic radius distributions of the micelles, shown in Fig. 8A. The singular peak in the DLS volume-weighted size distribution results suggests that there is only one population of micelles in each solution. An increase in size obtained from DLS is observed with tail length, C_{14}H_{29}, C_{16}H_{33} and C_{18}H_{37} give a hydrodynamic radius of 31 ± 5, 41 ± 5, and 48 ± 5 Å respectively, in agreement with the increase of micellar size observed from SANS fitting results. It is noted that the size of the POM-2C_{12} micelles (48 ± 5 Å) probed by DLS is relatively larger compared to those of POM-2C_{14} and POM-2C_{16}, micelles, likely due to their ellipsoidal shape, which is not taken into account in DLS analysis. The POM-2C_{n} micelles exhibit strongly negative surface charges as evidenced by their zeta-potentials (see Fig. 8B), giving similar results to the conductivity measurements (longer-tailed surfactant forms micelles with less charged surfaces), but opposite trend to the micelle charge information obtained from SANS fitting. The reason for the opposite trend between SANS results and zeta-potentials remains unclear at this stage.

**POM-TiO_{2} materials synthesised using POM-2C_{n} micelles as templates**

Catalysts were prepared by mixing POM-2C_{n} (n = 12, 16 and 18) with titania precursor in acidic solution, followed by a hydrothermal treatment, filtration and calcination at 500 °C to remove the organic 2C_{n}H_{2n+1} chains from the material (see TGA analysis of the POM-2C_{12} in ESI Fig. 5A,† showing the organic part is burnt away). Several studies have demonstrated that the Wells–Dawson structure remains stable up to 600 °C,^{45–47} so it is expected to remain intact during calcination. Transmission electron microscopy (TEM) images of the 12POM-TiO_{2} material (Fig. 9A) show aggregates of small spherical particles. A higher resolution image focusing on a selected area of the 12POM-TiO_{2} material, made via HRTEM (Fig. 9B), clearly shows lattice fringes which indicate an ordered crystalline structure of the TiO_{2}. Although the \{P_{2}W_{17}O_{61}\} units have a very small size and a low concentration in the material (Table 4), they can be seen as black dots in the HRTEM micrograph because of their high electron density. Several of these dots are highlighted using green dashed circles in Fig. 9B.

EDX elemental mapping analysis also evidences the presence of the POM units within the hybrid material. The
element distributions of the 12POM-TiO2 associated with the TEM image in Fig. 9A, are given in ESI Fig. 9.† It was clear that both W and Ti elements are uniformly distributed within the material, suggesting the existence of POMs within the hybrid material.

To verify the structural integrity of the Dawson structure of the POMs within the material, IR spectroscopy of the 12POM-TiO2 material was attempted (see ESI Fig. 10†). Due to the small amount of POMs in the material (Ti:W = 122:1, see Table 4), the characteristic peaks of Dawson structured POM were observed as a single broad peak at ca. 1080 nm⁻¹ in the IR spectrum.

Reduced POMs are known to reduce metal ions in situ to metal nanoparticles. Therefore, to corroborate the preservation of POM within the porous TiO₂,⁸⁰ the photocatalytic reduction of Ag⁺ was carried out. Experimental details can be found in the Experimental section. EDX elemental mapping analysis was applied to the collected brown product, and the Ag element distribution is shown in ESI Fig. 11B,† suggesting Ag nanoparticles are present in the product. This indicates that POM units are present and are chemically active.

The PXRD patterns of SDS templated TiO₂, 12POM-TiO₂, 16POM-TiO₂ and 18POM-TiO₂ materials (Fig. 10) demonstrate the characteristic diffraction peaks of anatase TiO₂ (space group: 141/amd, JCPDS no. 21–1272). We found no diffraction evidence for the POM phase (see ESI Fig. 12†), since the POM within the TiO₂ are dispersed but not crystallised. This is also seen in the PXRD pattern of dried POM-2C₁₂ surfactant which also shows no diffraction peak (see ESI Fig. 13†). Small angle X-ray scattering showed no long-range ordering of the pores within the SDS templated TiO₂ or the nPOM-TiO₂ materials (see ESI Fig. 14†).

Both SDS templated TiO₂ and nPOM-TiO₂ materials show a type IV nitrogen sorption isotherm (see ESI Fig. 15A†). The resulting nPOM-TiO₂ materials have relatively high surface areas, listed in Table 4 along with their mean pore diameters (pore size distributions are illustrated in ESI Fig. 15B†). nPOM-TiO₂ materials have smaller mean pore sizes compared to SDS templated TiO₂ due to the occupation of POMs within the pores. The mean pore diameter of 12POM-TiO₂ material lies between the minimum size (2Rmin = 2.2 nm) and the maximum size (2Rmax = 9.9 nm) of the POM-2C₁₂ micelles. The 16POM-TiO₂ and 18POM-TiO₂ materials have slightly larger mean pore sizes compared to their corresponding micellar diameter (4.0 and 4.4 nm). Larger pores (around ca. 60–100 nm) were also observed in 12POM-TiO₂, which contribute to this sample having the largest surface area among nPOM-TiO₂ materials. The mean pore size of the 18POM-TiO₂ material is about 17.5% larger in comparison to 16POM-TiO₂ which demonstrates the tunability of the pore size through using larger spherical micelles as soft templates.

To evaluate the effect of the POM surfactant concentration on the structural properties of the material, a second TiO₂ material was prepared using POM-2C₁₆ at a higher concentration (22.0 mM) and labelled 16POM-TiO₂-2. EDX elemental mapping shows the presence of POM in the 16POM-TiO₂-2 (see ESI Fig. 16†). The POM content in 16POM-TiO₂-2, indicated by the Ti:W ratio listed in Table 4, is much higher than for 16POM-TiO₂. This suggests that the amount of POM in the hybrid materials can be tuned by the concentration of the POM-2C₁₆ used in the preparation solution. No diffraction peaks are observed in the SAXS pattern (ESI Fig. 17†), again suggesting no long-range organisation of the pores. The 16POM-TiO₂-2 material has a slightly higher surface area compared to 16POM-TiO₂ (179 m² g⁻¹ versus 169 m² g⁻¹) and a relatively smaller mean pore size (5.0 nm versus 5.3 nm), parameters given in Table 4. The sorption isotherm of 16POM-TiO₂-2 (ESI Fig. 18†) shows a more obvious hysteresis loop than for 16POM-TiO₂, indicating the presence of more well defined mesopores.

**Photocatalytic properties**

Dawson structured {P₂W₁₁O₄₁} was chosen as the focus of this work for its photocatalytic properties. The photoabsorption of 12POM-TiO₂ in the range of 250–800 nm shows an absorbance shoulder for wavelengths between ca. 400 and 700 nm (ESI Fig. 19A†). The 12POM-TiO₂ possesses a bandgap at around 3.3 eV (obtained by plotting (Ah)² as a function of the energy), similar to that of TiO₂ (ESI Fig. 19B†).⁸¹ The band gap does not change after the decoration of TiO₂ with POM, however, the resulting material now shows absorbance in a wavelength range where TiO₂ normally would not absorb.⁸²,⁸³

**Table 4** Ti:W atomic ratios obtained from EDX analysis, surface areas obtained from BET analysis and mean pore sizes

| Material          | Ti:W | Surface area (m² g⁻¹) | Mean pore size (nm) |
|-------------------|------|----------------------|---------------------|
| 12POM-TiO₂        | 122:1| 191 ± 8              | 6.4 ± 0.5           |
| 16POM-TiO₂        | 154:1| 165 ± 6              | 5.3 ± 0.6           |
| 18POM-TiO₂        | 169:1| 148 ± 5              | 6.2 ± 0.4           |
| 16POM-TiO₂-2      | 12:1 | 179 ± 5              | 5.0 ± 0.6           |
| TiO₂              | —    | 99 ± 5               | 8.3 ± 0.4           |

Fig. 10 PXRD patterns of nPOM-TiO₂ materials (n = 12, 16 or 18).
The photocatalytic properties of the nPOM-TiO₂ materials were tested via the degradation of RhB during irradiation of these materials with solar light (see for example ESI Fig. 20†). Their photocatalytic behaviours were compared to SDS templated TiO₂ which has a surface area of ca. 99 m² g⁻¹. The nPOM-TiO₂ (n = 12, 16 and 18) materials showed higher activities than that of the SDS templated TiO₂ (Fig. 11A). The photodegradation properties of the POM amphiphiles alone, compared to the POMs supported within the 12POM-TiO₂ material were evaluated under the same conditions, by using the same number of moles of POM-2C₁₂ as that of the POM species in 0.015 grams of 12POM-TiO₂. A bathochromic shift and an obvious drop in the intensity of the main absorption peak were observed in the UV-vis spectrum of RhB (see ESI Fig. 20B†) after POM-2C₁₂ was added to the starting solution (RhB, 0.031 mM; H₂O₂, 1.5 mM). This shift in the spectrum has been previously reported and can be explained by strong electrostatic interactions between RhB molecules with the negatively charged polyoxometalate species.⁸⁴,⁸⁵ Due to the shift in the spectrum, the concentration of RhB in this solution was determined using the absorption intensity at 565 nm rather than at 553 nm as for the nPOM-TiO₂ materials. As seen in Fig. 11A, around 11% of RhB was decomposed by POM-2C₁₂ in 80 min, which is ca. one-tenth of the amount that the equivalent amount of POM within 12POM-TiO₂ decomposed over the same time. These results suggest a synergistic effect between POMs and TiO₂ in the nPOM-TiO₂ materials that we prepared.

Among the nPOM-TiO₂ materials, the 12POM-TiO₂ exhibited the best degradation performance, with almost 80% of the RhB degraded after 20 min. 16POM-TiO₂ and 18POM-TiO₂ were less effective in the first 20 min, decomposing ca. 65% and 45% of RhB respectively. The degradation rates fit a first-order model well. The slope of a linear plot of ln (Cₜ/C₀) versus irradiation time gives the apparent degradation rate constant (Fig. 11B). The obtained fitting parameters related to the kinetics, apparent degradation rate constant kₐ₀, and correlation coefficient r, are listed in Table 5. There is an obvious rate enhancement of nPOM-TiO₂ compared to porous TiO₂, increasing from 0.0096 to 0.0513 min⁻¹. Correlation coefficients, r, are found to be between 0.9683 and 0.9910, indicating the excellent linear response in the studied range of concentrations.

The Ti to W atomic ratio in each material obtained from EDX elemental mapping analysis is listed in Table 4. The 12POM-TiO₂ hybrid material has a relatively higher W content compared to 16POM-TiO₂ and 18POM-TiO₂, and also had the highest POM content in the materials synthesised at this POM amphiphile concentration. The value of kₐ₀ decreases as the amount of POM present in the nPOM-TiO₂ materials decreases. Therefore, besides the high surface area induced by the surfactant templating, the higher POM content of the prepared 12POM-TiO₂ also contributes to its outstanding properties in RhB photodegradation compared to the other materials studied here.

When the ratio of POM to TiO₂ was increased, in the 16POM-TiO₂-2 compared to 16POM-TiO₂, the degradation of RhB was completed more rapidly than when 16POM-TiO₂ was used (60 min versus 80 min as shown in ESI Fig. 21†). This suggests the possibility of tuning the photocatalytic properties of the hybrid materials through altering the POM content.

Furthermore, the RhB photodegradation activity of 12POM-TiO₂ is still remarkably high after eight continuous photo-catalytic cycles (see Fig. 12). The complete photodegradation of RhB is still obtained after 80 min at the 8th cycle, while there is a slight decrease of the amount of RhB degraded after 20 min (ca. 70% versus 80% for the 1st cycle). The PXRD pattern of 12POM-TiO₂ after 8 cycles indicates an anatase phase (ESI Fig. 12†), equivalent to that in the fresh

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Table 5 Kinetic parameters obtained from the fitting of the experimental results in Fig. 11B

| Material     | kₐ₀ (min⁻¹) | r   |
|--------------|-------------|-----|
| 12POM-TiO₂   | 0.0513 ± 0.0016 | 0.9683 |
| 16POM-TiO₂   | 0.0414 ± 0.0008 | 0.9799 |
| 18POM-TiO₂   | 0.0367 ± 0.0003 | 0.9910 |
| TiO₂         | 0.0096 ± 0.0003 | 0.9708 |

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Fig. 11. (A) Plot of normalised degraded concentration of RhB, 1 – Cₜ/C₀, in the presence of different catalysts versus irradiation time. A blank measurement was recorded for comparison. (B) Plot of ln(Cₜ/C₀) against irradiation time, C₀ and Cₜ are the RhB concentrations at time t and 0 min respectively.

Fig. 12. Performance of 12POM-TiO₂ in RhB degradation over several cycles.
material, showing the stability of the TiO$_2$ structure over several cycles.

The photocatalytic pathway can be summarised as follows: (1) the electrons are excited from the valence band (VB) to the conduction band (CB) of TiO$_2$ under UV irradiation. (2) The electrons at the CB of TiO$_2$ transfer to the POMs. Furthermore, POMs are photo-exited simultaneously and the electrons from both the CB of TiO$_2$ and the photoexcitation of POMs accumulate together on the POMs to form charge-transfer excited POMs (designated as POMs*). (3) POMs* transfer electrons to oxygen in the solution to form reactive oxygen species, while photoexcited holes react with water to form ‘OH radicals, and (4) these radicals are involved in the process of photodegradation. POMs have been proven to enhance the photocatalytic properties of TiO$_2$ in several studies, since they efficiently reduce the recombination rate of photoexcited holes and electrons in TiO$_2$. Therefore, step (1) is enhanced. Step (2) is accelerated here due to the intimate contact between POMs and TiO$_2$ given by the synthesis method. Moreover, POMs not only behave as charge separators in the hybrid materials but also photocatalysts that contribute to the photodegradation. Furthermore, the electrostatic interaction between oppositely charged POMs and RhB molecules also reinforces step (4). Overall, the decorating POMs speed up the degradation efficiency due to their rapid transportation of electrons, their ability to decrease the recombination rate of electron–hole pairs and their intrinsic photocatalytic properties, rather than by narrowing the band gap.

Chen, et al. have studied the photocatalytic degradation of 2,4-dichlorophenol by PW$_{12}$O$_{40}^–$/TiO$_2$ prepared by physical mixing, and the performance was improved by nearly 20% within the first 50 min when 0.8 mM PW$_{12}$O$_{40}^–$ was present. This method, however, limits the recyclability of the PW$_{12}$O$_{40}^–$ due to its solubility in water. Photodegradation of 1,2-dichlorobenzene using systems of TiO$_2$ and polyoxometalates (PW$_{12}$O$_{40}^–$, SiW$_{12}$O$_{40}^4–$ or W$_{16}$O$_{42}^4–$) were studied by Ozer and co-workers. The addition of POM anions into the TiO$_2$ suspension resulted in a significant rate enhancement, with PW$_{12}$O$_{40}^–$ the most effective anion. The reaction rate reached a limit of 0.03 min$^{-1}$, 600% greater than pure TiO$_2$ system, when the addition of PW$_{12}$O$_{40}^–$ was at ca. 0.15 mM. In comparison to our work, the degradation rate constant of 12POM-TiO$_2$ is 0.051 min$^{-1}$, which is around 500% greater than that of the SDS templated TiO$_2$ material (0.0096 min$^{-1}$), while, importantly our materials also provide recyclability. Pearson et al. conducted a series of studies on materials obtained by loading H$_2$P$_2$W$_{12}$O$_{40}$ onto TiO$_2$ nanoparticles or TiO$_2$ nanotubes as a co-catalyst. The degradation of Congo red dye was improved by around 14% compared to the original TiO$_2$ within the first 30 min. However, the recyclability of the materials was not studied.

Thus, our system enables an improvement in photodegradation properties as well as providing improved recyclability, with photocatalytic performance maintained for at least eight continuous photo-catalysis cycles, compared to the addition of polyoxometalates into a TiO$_2$ suspension or the previous studies discussed above. The POM content in the POM-TiO$_2$ materials can be tuned through varying the concentration of POM amphiphiles. This synthesis method provides a stronger anchoring of polyoxometalates within the hybrid material and intimate contact between the polyoxometalates and TiO$_2$, ensuring their stability during use, easy recovery and reuse of the materials.

Conclusion

Novel surfactants with inorganic POMs as head groups and double-hydrocarbon chains (C$_{12}$, C$_{14}$, C$_{16}$ or C$_{18}$) were successfully synthesised. The micelle morphologies were studied using SANS to reveal core–shell structures. The shape of the micelles can be tuned by changing the length of the hydrophobic tails, such that surfactants with longer hydrophobic tails tend to form less elongated and more globular micelles. Moreover, SANS evidenced strong interactions due to Coulomb repulsion between negatively charged micelles. These data were supported by DLS and zeta-potential measurements. The micelles were used to template TiO$_2$ through a hydrothermal method to form, after calcination, nPOM-TiO$_2$ hybrid catalysts ($n$ = 12, 16 or 18). Through this method, the POM-TiO$_2$ hybrid materials were tested by the photodegradation of aqueous RhB solution as a model reaction. The results reveal that the nPOM-TiO$_2$ photocatalysts possess enhanced photodegradation properties in comparison with SDS templated TiO$_2$, confirming their superior photocatalytic activity. The rate constants of the photodegradation extracted here were found to be almost 5 times higher for the 12POM-TiO$_2$ materials compared to porous TiO$_2$ templated by SDS. This study demonstrates the highly promising use of POM–2C$_n$ amphiphiles as templating agents in the synthesis of porous POM-TiO$_2$ hybrid catalyst, having well-dispersed polyoxometalates within a porous anatase TiO$_2$ matrix. Using the same method, it is possible to increase the polyoxometalate content in the material by using a higher concentration of the initial surfactant solution. Furthermore, other metal oxide materials loaded with polyoxometalates could be synthesised using similar methods, offering a flexible and straightforward approach to harness the functionality of polyoxometalates in porous materials for catalysis.

Conflicts of interest

There are no conflicts to declare.

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