Polyoxometalates (POMs) are a well-known class of discrete early transition metal-oxide nanoclusters. This class of molecular metal oxides is unmatched not only in terms of structural diversity but also in reactivity and relevance to analytical chemistry, catalysis, medicine, and nanoscience.\(^1\) The integration of POMs into functional architectures and devices requires the development of methods to position, orient and integrate these nanoclusters into well-defined architectures, thin films or mesophases.\(^4,5\) In this context, we have recently reported the molecular engineering of a highly robust water oxidation electrocatalyst based upon functionalized carbon nanostructures integrating tetraruthenate polyoxometalate Ru\(_4(\mu-O)_4(\mu-OH)_2(H_2O)_4[\gamma-SiW_{10}O_{36}]^{10-}\) (Ru\(_4\)POM).\(^6\)–\(^9\) In particular, the combination of the 2D macromolecular surface of graphene\(^10\) with the structural and electronic features of Ru\(_4\)POM for catalytic water oxidation leads to a minimization of the applied overpotential, endorsing long-term robustness. Thus, exploring the structural properties of graphene- Ru\(_4\)POM hybrids retains a major interest in the field of functional materials for multielectron catalysis with application to artificial photosynthesis. Transmission electron microscopy (TEM) has long been an established approach to study nanostructures in a straightforward way. Recent advances in low voltage, aberration-corrected TEM (AC-TEM) further allow the investigation of electron-beam-sensitive soft materials at an atomic level.\(^11\) Graphene and organic molecules are among these soft materials which benefit from AC-TEM development, since the damage to the delicate nanostructures can be minimized thanks to the low electron beam voltage.\(^12\)–\(^14\) Meanwhile, the stronger electron scattering at low voltage improves the signal to noise ratio of light materials.\(^15\) In addition, by taking time sequence during imaging, the motional dynamics of the studied nanostructures can be monitored, as exemplified by a variety of molecules studied on graphene\(^16\)–\(^18\) and encapsulated into carbon nanotubes, including organometallic species and inorganic clusters.\(^19\)–\(^21\) These studies provide key evidence for the understanding of the interplay between functional molecules and the nanostructured environment. In this paper, we employ AC-TEM to address the interaction between the multielectron catalyst Ru\(_4\)POM and functionalized graphene interfaces using a dynamic approach, where the cross-talk between the material components is interpreted from a novel aspect.

Few-layer graphene (FLG) is utilized as the supporting conductive bed. In order to efficiently attach Ru\(_4\)POM and study the influence of the functional group, the FLG flakes are covalently functionalized with a PANAM dendron by a 1,3-dipolar cycloaddition reaction\(^22,23\) or an N,N,N-trimethyl benzenaminium moiety via a diazonium based reaction. Details of the functionalization are presented in Supporting Information. The graphene platform is designed to host the polyanionic Ru\(_4\)POM via a complementary charge attraction between the negative Ru\(_4\)POM and the positive ammonium groups anchored on the graphene surface.\(^24\)–\(^27\) Figure 1a shows a schematic model of a Ru\(_4\)POM grafting onto a dendron-functionalized graphene surface. The positive end of the organic pendants promotes the electrostatic capture of polyanionic Ru\(_4\)POM. A Ru\(_4\)POM anion contains
two $(\gamma\text{SiW}_{10}\text{O}_{36})^{8-}$ ion clusters embedding a tetraruthenate core, as illustrated in Figure 1b. They form a dumbbell-like shaped structure with the size of approximately 2 nm in length and 1 nm in diameter. The electrostatic capture of polyanion on the positive nano-surface has been confirmed by convergent spectroscopic and microscopy evidence as reported previously.[23] The grafting of Ru₄POM on FLG is revealed by HRTEM imaging as shown in Figure 1c. The inset shows the indexed FT of the graphene layers. The same image as (c) with the FLG contrast subtracted.

Although the HRTEM image contrast of the Ru₄POM anions on the FLG surface is dominated by the strong scattering of the heavy atoms such as W and Ru, the contrast contributed by the functional organic groups needs to be evaluated carefully. Although a recent study on light adatoms/molecules on FLG has pointed out that molecules containing light atoms such as carbon, nitrogen and oxygen, can be observed by low-voltage AC-TEM,[16] our HRTEM image simulations shows that only if the main axis of the carbon chains is oriented parallel to the electron beam, can they show a similar contrast to that of the metal atoms in the Ru₄POM. In these rare cases, extra dark contrast spots in the vicinity of the Ru₄POM can be observed (see Supporting Information). However, in most cases, the organic pendants show low contrast and therefore do not strongly interfere in the study of the inorganic Ru₄POM.

When imaging Ru₄POM on dendron-functionalized FLG, we observed dynamic motion of the molecular structure. In order to monitor the dynamics of the Ru₄POM when interacting with electrons, a series of images were acquired as function of time under a dose of approximately 1000 e⁻/Å²s. The Ru₄POM changes its orientation with respect to the incoming electron beam continuously. We observed approximately 25 different projections over the period of a 70 s time sequence (see Supporting Information). Some orientations appear to be more stable than others; the Ru₄POM remains stationary longer in these orientations before turning into another. Taking into account the observed orientation changes, the question rises whether the motion of Ru₄POM is constrained, i.e. whether the dendron moiety plays a role in promoting the dynamics of Ru₄POM. In order to further investigate the dynamics of the Ru₄POM in a more quantitative way, 5 projections at different time frames (Figure 2a) were randomly selected to be compared to the calibrated projections of the known Ru₄POM structure as shown in Figure 2b, where HRTEM image simulations were carried out for every 15 degree tilt of Ru₄POM along the Y and Z axis. The rotation of a Ru₄POM around X, Y and Z axes can thus be identified using the simulated rotation map as a calibration. As shown in Figure 2a, each projection is compared to the simulated matrix to find the best fit and thus to quantify its degree of rotation.

Comparing the projections at different time frames with the calibrated Ru₄POM simulations, the Ru₄POM can be first fitted with a Y-tilt of 45 degrees, a 0° Z-tilt and an in-plane rotation (X-tilt) of 260° at 9.6 seconds. In the next projection at 20.0 s, the projection is best fitted with a Y-tilt of 60°, Z tilt of 75° and an in-plane rotation of 220°. Afterwards, all 5 selected projections are calibrated with the best-fit tilt/rotation angle according to the simulation map, and the motion range can be plotted as shown in Figure 2b where the matched projections are highlighted in red. The movement path is suggested by arrows. It can be seen that the motion...
of the Ru$_4$POM molecules on the FLG is constrained. The motion is limited to a Y-tilt $> 45$ degrees, a Z-tilt of $\pm 90$ degrees and in-plane rotation (X tilt) of $\pm 90$ degrees. Considering the symmetry of the Ru$_4$POM, the motion amplitude is mainly limited in tilt around Y axis. In addition to the 3D rotation quantification, the 2D translation of the Ru$_4$POM has also been quantified. Figure 2c plots the relative positions of each projection along the time scale. It is obvious that during imaging, the Ru$_4$POM anion is relatively restrained on the FLG surface without significant shifts. Both the lateral shift and the horizontal shift are limited to $\pm 2$ Å during the 70 s monitoring time, suggesting a strong interaction between the Ru$_4$POM and the dendron-functionalized graphene.

Although the motion is constrained, the Ru$_4$POM shows neither a strong preference for certain orientations nor a dependence on the graphene lattice, suggesting that the interaction between the Ru$_4$POM and the FLG surface is weak as the Ru$_4$POM is not directly bonded to the FLG but indeed via the dendron tether. Large displacements of the Ru$_4$POM on the FLG are not observed throughout the time sequence. Such behaviour indicates that the electrostatic interaction of the Ru$_4$POM with the ammonium groups provides a steady contact thus avoiding its irreversible leaching off the graphene surface. This observation therefore suggests that dendrons are well anchored at the graphene surface. Moreover, the stable anchorage of the Ru$_4$POM is likely to be provided by a cooperative interplay of adjacent dendron arms, favouring a charge balance as observed in homogeneous solution with positive counterions.$^{[29]}$

In order to address the role that the organic linker plays in the structural and dynamic features of Ru$_4$POM-FLG, another graphene derivatization has been considered by the covalent attachment of $N,N,N$-trimethyl benzenaminium moieties (see Supporting Information). Compared with the dendron linker, the smaller size of the benzenamine tether is expected to induce stronger constraints in the motion of the appended Ru$_4$POM. Similarly, the influence of this shorter organic linker is estimated via HRTEM image simulations before investigating the dynamics of benzenamine appended Ru$_4$POM (see Supporting Information). The simulations reveal that the benzenaminium can cause image contrast similar to that of an adatom in the vicinity of Ru$_4$POM, but it is unlikely to modify the contrasts of Ru$_4$POM even if it lies directly below it.
With the role of the benzenaminium organic linker in imaging the Ru₄POM addressed, the dynamics of Ru₄POM on the edge of the moiety-functionalized FLG is investigated. Under the similar imaging condition with a dose of approximately 1000 e⁻/Å² s, a series of HRTEM images are acquired as function of time and analyzed. Along the acquisition time of 38 s, only 5 different projections are identified from the image series as displayed in Figure 3. Compared to the dendron functional group, it is obvious that the Ru₄POM attached to shorter benzenaminium linker displays a lower motion frequency and remains static for a longer time. As shown in Figure 3 a, each projection is compared to the rotated simulation and fitted to its possible tilt orientations as illustrated in the same column. The projections are limited to the rotation range as plotted in Figure 3 b, with a movement path illustrated by arrows. Compared to the Ru₄POM attached to dendron which has a long carbon chain, the Ru₄POM attached to a moiety with a shorter carbon chain shows a smaller tilt range. Although the rotations along the X and Z axis still cover almost a full range, the tilt along Y is limited to ±15 degrees only in the section of Y < 45 degrees. Moreover, these 5 projections include all observed rotations along the time scale, which clearly indicates a lower motion frequency as compared to Ru₄POM attached to a dendron which had over 25 different orientations.

In fitting each projection to a simulated orientation, some adatoms can be found in the vicinity of the Ru₄POM as in Figure 2 a and 3 a. They can be attributed to the interference of the organic spacer. Nevertheless, in certain projections the fit is still not perfect. In the case of the dendron-functionalised FLG, it is hard to determine whether the difference is due to a structural change in the Ru₄POM, or it is due to the imaging influence from dendrons. In the case where the benzenaminium is used as a functional group, the imaging influence on altering the Ru₄POM is strongly reduced. As illustrated in Figure S8, when the Ru₄POM overlaps with the benzenaminium along the projection direction, the contrast is mostly enhanced rather than altered. Therefore, in the case of benzenaminium moiety acting as functional group, it is possible to study whether the difference between simulation and real-time imaging is due to a structural distortion of the Ru₄POM itself (providing only few moieties are below Ru₄POM along projection direction).

An example is taken from the first column of Figure 3 a. It is noticed that although the left subcluster of γ-SiW₁₀O₃₆ fits perfectly into the simulated pattern, the Ru core and the right subcluster do not match the simulation. Moreover, the simulated pattern has a smaller length compared to the HRTEM image. A distortion of the structure is therefore taken into consideration, as illustrated in Figure 4. Figure 4 a presents the simulated pattern of a perfect Ru₄POM structure, whereas Figure 4 b presents the acquired HRTEM image. The positions of Ru and W atoms are indicated by red dots in Figure 4 b. When the outline of the structure is projected to fit the simulated pattern, it can be seen only one half subcluster matches well, as indicated by solid red dots. The mismatched dots are indicated by circles. It is noticed that the central core of Ru is distorted by comparing two images; moreover, by simply shifting the other half subcluster, the acquired structure can match the simulated pattern. Therefore, the tetraruthenate core is distorted and the upper half of γ-SiW₁₀O₃₆ subcluster shifted to create a dilated structure as shown in Figure 4 f and g. Figure 4 f is viewed along Y axis and it can be compared to the perfect structure shown in Figure 4 d, where the distorting of the Ru core is obvious. Figure 4 g is viewed along Z axis and can be compared with the perfect structure shown in Figure 4 e, where dilation is revealed. The HRTEM image simulation of this dilated structure is presented in Figure 4 c, which matches the acquired HRTEM image to a large degree. The other four projections shown in Figure 3 a have similar Ru core distortion and structure dilation, as illustrated in Supporting Information. Thus a distortion of the

Figure 3. (a) Projections from a time sequence of a Ru₄POM attached to N,N,N-trimethyl benzenaminium moiety and their corresponding orientations. (b) A plot showing the orientation changes as highlighted by the red. The movement path is indicated by arrows.
ligands is crucial.[7,8] Our results have demonstrated the robustness of the Ru POM structure during intensive electron interaction with a considerable dose of electrons during live imaging. Moreover, our results pinpoint one key requirement of high performance catalytic surfaces, i.e. the ability of reactive sites to evolve and accommodate structural changes along the development of the reaction progress and upon turn-over regimes. In this respect, the configurational freedom of Ru POM hosted on FLG and within the poly-charged environment of organic dendrons, recalls homogeneous conditions and rules out any detrimental surface confinement. The retention of Ru POM dynamic properties, dictated by weak surface interactions, favours exposition to solvent, ligand exchange within the ruthenium coordination sphere, low reorganization energy and high surface area. These are all winning points to shape functional interfaces for electrocatalytic applications and low over-potential requirements as experimentally observed.[23,24]

Summarizing, we have demonstrated the possibility of imaging Ru POM on a FLG surface by AC-TEM at 80 kV. The dynamical rotation of a single Ru POM molecule can be monitored in the microscope and analysed in a time sequence. The rotation of the Ru POM shows no preference with respect to the graphene surface, but shows a constrained motion in both rotation and lateral translation. Compared to the functional group of moiety with a short carbon chain, Ru POM anions attached to dendrons with a long carbon chain have a higher degree of motion freedom and frequency. This indicates that a functional anchor of a larger size allows Ru POM to interact with the environment in a more active manner but still provides the Ru POM with solid connection to the conducting bed of graphene. The results indicate that both morphology and reactivity of the resulting material can be tailored through the selection of appropriate functionalization strategies. This study confirms the key role played by a tailored modification of the nano-graphene platform to assist dynamic phenomena at the catalyst site during turnover regime.

Experimental Section

Aberration (Cs) corrected high resolution TEM (HRTEM) were performed on a FEI Titan 80–300 cubed microscope fitted with an aberration-corrector for the imaging lens and the probe-forming lens as well as a monochromator. The microscope was operated at 80 kV to minimize the beam damage during acquisition. The monochromator was excited to provide an energy resolution of approximately 0.3 eV. The C value was tuned to +10 μm. All imaging was performed under focus, close to the Scherzer imaging conditions (~8 nm for a C value of +10 μm). JEMS (http://cimewww.epfl.ch/
communications

people/stadelmann/jemsWebSite/jems.html) simulation was performed using multislice method to simulate the HRTEM images under the similar imaging conditions during acquisition. The C₃ value was set to be 10 µm for simulation. All simulations were performed at Scherzer defocus (~8 nm).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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