Molecule-Based Water-Oxidation Catalysts (WOCs): Cluster-Size-Dependent Dye-Sensitized Polyoxometalates for Visible-Light-Driven O₂ Evolution

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From atomic level to understand the cluster-size-dependant behavior of dye-sensitized photocatalysts is very important and helpful to design new photocatalytic materials. Although the relationship between the photocatalytic behaviors and particles’ size/shape has been widely investigated by theoretical scientists, the experimental evidences are much less. In this manuscript, we successfully synthesized three new ruthenium dye-sensitized polyoxometalates (POM-n, n relate to different size clusters) with different-sized POM clusters. Under visible-light illumination, all three complexes show the stable O₂ evolution with the efficient order POM-3 > POM-2 > POM-1. This cluster-size-dependent catalytic behavior could be explained by the different numbers of Mo₅O₅t (terminal oxygen) bonds in each individual cluster because it is well-known that Mo₅O₅t groups are the catalytically active sites for photooxidation reaction. The proposed mechanism of water oxidation for the dye-sensitized POMs is radical reaction process. This research could open up new perspectives for developing new POM-based WOCs.

Visible-light-driven photocatalysts are very attractive because they could be one of the most promising methods to solve the energy problem and effectively reduce environmental contamination¹⁴⁻¹⁸. The photocatalytic behaviors strongly depend on atomic configuration, band gap positions, size, shape, and surface reactivity. Recent evidence in TiO₂ catalysts has already shown that the facet effect is one of key factors to determine the photocatalytic reactivity because the adsorption/desorption of molecules and photoexcited electrons transfer are extremely sensitive to surface structure states²⁰⁻²¹. However, as another important factor, size-dependent photocatalytic behavior has received much less attention. Although some groups has already shown that certain sizes of nanoparticles might be the key for achieving the high photocatalytic activity from both experimental and theoretical studies, a direct experimental understanding on size-dependent photocatalytic behaviors at atomic scale is unprecedented²²⁻²⁴. This gap in knowledge strongly motivates us to carry out our research on molecule-based water-oxidation-catalysts (WOCs): cluster-size-dependent dye-sensitized polyoxometalates for visible light driven O₂ evolution.

Currently, the widely studied photocatalyst system is metal oxides because of their diverse compositions, high stability, high efficiency, and the possibility of overall water splitting²⁶⁻³⁰. As one branch of metal oxides, polyoxometalates (POMs) -- attractive anionic transition metal nanoclusters, exhibit interesting structural diversity and exceptional physical properties²¹⁻²⁴. Especially, their nanosized geometry, unique optical and electronic properties as well as excellent chemical reactivity make them the promising candidates for photocatalytic H₂ and O₂ evolution²⁵⁻³⁰.

Since the sun emits its maximum flux of photons in visible region, the photocatalytic efficiency will be dramatically enhanced if the photocatalytic reactions could be driven by visible light³¹. Unfortunately, most POMs show no or very little absorption in the visible region²⁻³⁴. It is necessary to extend their absorption by
introducing light harvesting component (or photosensitizer) into POMs. There are two ways to realize this purpose: (1) using inorganic components such as cobalt oxides, ruthenium oxides, copper oxides, or even gold nanoparticles because these materials have diverse colors; and (2) employing metal-organic complexes (e.g. tris(1,10-phenanthroline) ruthenium ([Ru(phen)3]3+) or pure organic dyes (e.g. methyl viologen, methylene blue) because cationic dyes can act as charge-balancing ions. In this research, we are interested in introducing ruthenium complexes into POMs because ruthenium chromophores have been wildly used in photocatalysis, water splitting, and dye-sensitized solar-cell devices. Although in-situ formed organic-inorganic hybrid complexes between POMs and ruthenium chromophore photosensitizers have been demonstrated as visible-light-driven photocatalysts for oxygen evolution, the full understanding of their structure-reactivity relationship and oxidation mechanism seems not to be fully achieved.

Here, we go further to explore cluster-size-dependent dye-sensitized polyoxometalate clusters at atomic level and aim to understand the relationship between cluster sizes and photocatalytic behaviors. Three novel POMs-ruthenium photosensitizer hybrid complexes (denoted as POM-n, n = 1,2,3) have been synthesized and fully characterized through single-crystal X-ray diffraction analysis and other tools. In addition, their visible-light-driven water-oxidation behaviors have also been investigated and the corresponding oxidation mechanism has been studied via both experimental and theoretical methods. Our results provide solid evidence that the cluster sizes in POM-n complexes did affect their photocatalytic behaviors.

Results

All compounds were synthesized either by solution process at room temperature or under solvothermal conditions at 110°C. The starting materials (TBA)2[Mo6O19] and α-(TBA)4[Mo8O26] were prepared according to the literature procedure. POM-1 ([Ru(C12N2H8)3CH3OH][Mo6O19]) was obtained as orange-red crystals in 10 days by slow diffusion of methanol solution of dichlorotriss(1,10-phenanthroline) ruthenium (II) hydrate into DMF solution of (TBA)2[Mo6O19]. POM-2 and POM-3 were synthesized under solvothermal conditions with α-(TBA)4[MoO26] and dichlorotriss(1,10-phenanthroline) ruthenium (II) hydrate as starting materials. For POM-2, additional starting material sulfur is required. The structures were determined from single-crystal X-ray diffraction data collected on APEX II CCD diffractometer.

The crystal structure analysis of POM-n reveals that these materials are made of anionic POM clusters and charge-balancing cations tris(1,10-phenanthroline) ruthenium ([Ru(phen)3]3+). All POM-n crystallized in triclinic space group P-1. The asymmetric unit for POM-1 is constituted of a Linqvist anion, one Ru(phen)3+ chromophore cation, and a methanol molecule (Figure 1a), while POM-2 has one Strandberg-type heteropolyanion [Mo5S2O23]42−, one Ru(phen)3+ cation, two [NH2(CH3)2]2+ species from the decomposition of DMF (Figure 1b), one H2O molecule, and one DMF molecule. As to POM-3, it is made by one α-[Mo6O26]2- anion, two Ru(phen)3+ cations, and one acetonitrile molecule (Figure 1c).

Details of the crystal structure and refinement data are provided in supporting information (Supplementary Table S1). The IR spectra (Supplementary Fig. S1) and experimental powder XRD patterns for

![Figure 1](http://www.nature.com/scientificreports)

**Figure 1** | The structures of hybrid materials POM-1–3.
POM-n (Supplementary Fig. S2–S4) confirmed the phase purity of the bulk materials of POM-1 ~ 3. The diffuse reflectance spectra were recorded on a PerkinElmer Lambda 750 s UV-Vis spectrometer. As shown in Figure 2, the spectra of POM-1, POM-2, and POM-3 show a broad range of absorption in the visible range from ~400 nm to 600 nm. The absorption onsets occur at about 618 nm for POM-1, 587 nm for POM-2 and 601 nm for POM-3, which suggests that the band gaps of the POM-1, POM-2, and POM-3 are 2.01 eV, 2.11 eV and 2.06 eV, respectively. For comparison, UV-Vis absorption of the starting material Ru(phen)$_3$Cl$_2$ were also measured. Since the absorptions of all individual clusters Mo$_5$, Mo$_6$, and Mo$_8$ are less than 400 nm~47, the dramatically-red-shift absorptions hint that POM-n could be good candidates as visible-light-driven photocatalysts.

The density of states (DOS) and electronic band structures of POM-1, POM-2 and POM-3 are calculated using the density functional theory (DFT) in CASTEP program. The calculated energy gaps for POM-1, POM-2 and POM-3 are 1.27 eV, 1.83 eV, and 1.71 eV, respectively. Although the theoretical calculation results gave relatively lower band gaps comparing with the experimental data, the band gap values (POM-2 > POM-3 > POM-1) displayed the same trend as experimental values. As depicted in Supplementary Fig. S5–S10, valence bands (VBs) of all three POM complexes near the Fermi level (from −0.5 eV to 0.0 eV) are mainly contributed from the $d$ orbitals of Ru atom in the Ru(phen)$_3^{2+}$ part. The VBs spreading from −2.0 eV to −0.5 eV are mainly constituted of the Mo-oxo clusters. The conduction bands (CBs) above the Fermi energy are mostly made up of the Ru(phen)$_3^{2+}$ sensitizer part. The characteristic of band structures indicated that after removing an electron away from the POM complexes via photo-excitation, a hole will be generated on the orbitals of Ru atom. The small energy gaps between the Ru and Mo-oxo clusters in VBs that close to the Fermi energy make the hole transfer to the Mo-oxo clusters possible by capturing electron from the photo-excited Mo-oxo clusters to the reduced Ru$^{3+}$ atom. The holes located in Mo-oxo clusters could be used to oxidize water molecules, making the POM complexes as potential WOCs, which will be further studied via photocatalytic experiments.

The catalytic activity for water oxidation of all compounds was investigated by using typical photocatalytic setup with Na$_2$S$_2$O$_8$ as sacrificial electron acceptor. All three photosensitizer-POM complexes act as heterogeneous water oxidation catalysts since they are not soluble in water. Note that there is no O$_2$ evolution happening when the blank solution (only containing the Ru(phen)$_3$Cl$_2$ and Na$_2$S$_2$O$_8$) are illuminated under visible light ($\lambda > 420$ nm). Also, when only the starting materials (TBA)$_2$[Mo$_5$O$_{19}$] and $\alpha$-(TBA)$_4$[Mo$_8$O$_{26}$] and sacrificial reagent Na$_2$S$_2$O$_8$ are present in the solution, no any O$_2$ evolution is observed under visible light illumination. This result clearly indicates that the POMs starting materials and the ruthenium photosensitizer have no visible-light photocatalytic activity for water oxidation. When the solutions of POM-1, POM-2 and POM-3 were studied under the same conditions, O$_2$ evolution was investigated from all of them, as shown in Figure 3. The O$_2$ evolution for all three photocatalysts almost linearly increased with irradiation time, indicating that three dye-sensitized POM complexes can be used as stable and efficient water oxidation catalysts (WOCs). The total amount of O$_2$ generated for POM-1 is about 8.1 $\mu$mol after three hours’ illumination. The amount of O$_2$ generated for POM-2 is 4.4% higher than POM-1 (11.7 $\mu$mol), indicating that [Mo$_5$S$_2$O$_{23}$]$^{4-}$ anion has higher catalytic efficiency for water oxidation than [Mo$_6$O$_{19}$]$^{6-}$ cluster. POM-3 that containing $\alpha$-[Mo$_8$O$_{26}$]$^{4-}$ anion displayed the best water oxidation activity oxygen evolution since POM-3 is 2.2 times larger than that for POM-1 after 3 h illumination. When a longer photo-reaction time was performed, the amount of O$_2$ generated for POM-1, POM-2 and POM-3 after 12 h are 23.7 $\mu$mol, 31.6 $\mu$mol, and 45.0 $\mu$mol, respectively. The O$_2$ evolution results of three complexes showed that the catalytic efficiency of POMs is cluster-size dependent with water oxidation efficiency order: $\alpha$-[Mo$_5$O$_{19}$]$^{4-}$ > [Mo$_6$S$_2$O$_{23}$]$^{6-}$ > [Mo$_8$O$_{19}$]$^{6-}$. This result is in agreement with the number of Mo = O$_t$ (terminal oxygen) bonds in POM-3 (14), POM-2 (10), and POM-1 (6) because it is well known that the $M = O_t$ bonds are the active sites for photooxidation in POMs-based photocatalysts.

To investigate the catalytic stability of the ruthenium dye-sensitized POM clusters, a three-run test of photocatalytic water oxidation was carried out for POM-3, as shown in Figure 4. No additional co-catalyst and sacrificial electron acceptor were added between each run test. There was almost no decrease in the oxygen evolution after three-run test, indicating the quite good stability of POM-3 as molecular WOCs. The results illustrated that the ruthenium chromophore and POMs hybrid complexes can be used as stable and efficient molecular WOCs. The detailed structures of these complexes could benefit the understanding of water oxidation mechanism for POMs based WOCs and the development of new type POMs-WOCs.

**Discussion**

It has been reported that all photocatalytic reactions based on POMs will involve OH$^-$ radicals if water is present in reaction systems. This finding makes us believe that the possible mechanism of water oxidation in our dye-sensitized POMs is radical cation process.

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**Figure 2** | UV-Vis absorption spectra of Ru(phen)$_3$Cl$_2$, POM-1, POM-2, and POM-3.

**Figure 3** | Kinetics of light induced O$_2$ formation from water oxidation with sodium persulfate as a sacrificial electron acceptor for POM-1–3.
When the ruthenium dye is excited under the visible light, the originally-formed triplet state [Ru(phen)3]2+,1,* is quenched by the S2O82− to form [Ru(phen)3]3+ cation. Then, one electron is transferred from the Mo(VI) = O3 to [Ru(phen)3]3+, resulting in the formation of radical cation Mo(VI) = O3·* + [Ru(phen)3]2+. The radical cation Mo(VI) = O3·* can further oxidize water to produce O2 molecules. The proposed radical cation process is partially confirmed by experimental results. When radical scavenging reagent hydroquinone was added to the solution of POM-1, no O2 evolution is observed. HPLC analysis of as-obtained solution showed that p-benzoquinone was formed as the oxidation products because hydroquinone can trap OH· radicals (Supplementary Fig. S11)45.

In conclusion, three new ruthenium dye-sensitized POM hybrid complexes have been successfully synthesized and their structures were determined by single crystal X-ray diffractometry. Although all materials employ the same cation Ru(phen)3+ as charge-balancing species, the anion parts have different size of clusters: [Mo6O19]2− for POM-1, [Mo5S2O23]− for POM-2, and [Mo8O26]4− for POM-3. Under visible-light illumination, all three complexes show stable O2 evolution with the efficient order POM-3 > POM-2 > POM-1, which is in agreement with the number order of Mo = O3 (terminal oxygen) groups in clusters because it is well-known that Mo = O3 groups are the catalytically active sites for photooxidation reactions. The possible water-oxidation mechanism is proposed to be radical cation process, which is verified via experimental and theoretical studies. These photocatalysts have been demonstrated to show quite good stability as molecular WOCs. This research could provide a new strategy to develop new POM based WOCs.

Methods

Materials. All chemicals were purchased from Alfa Aesar, TCI chemical and Aldrich and used without further purification. (TBA)2[MnO4] and a (TBA)4[MoO4]2 were synthesized according to literatures64,65.

Synthesis of compound [Ru(C2H4N2H3)2(CH3CN)][MoO4] (POM-1). (TBA)2[MnO4] (0.1 mmol, 136 mg) was dissolved into 4 mL of DMF. To the solution, 10 mL of methanol solution containing Dichloroiridin(1,10-phenanthroline) ruthenium(II) hydride (0.1 mmol, 77 mg) was layered on the top in a test tube. Then, the tube was sealed and kept for 10 days. Orange-red crystals were obtained in 85% yield with respect to Ru.

Synthesis of compound [Ru(C2H4N2H3)2][C2H4N2][C3H7NO] [MoS2O23] (POM-2). Dichloroiridin(1,10-phenanthroline) ruthenium(II) hydride (0.1 mmol, 72 mg), α-(TBA)2[MoO4]2 (0.05 mmol, 108 mg) and sulfur (0.5 mmol, 32 mg) were added to a mixture solution of DMF (4 mL) and acetonitrile (2 mL). The mixture solution was sealed in a Teflon-lined steel autoclave and heating at 110 °C for 5 days. The orange-red crystals were isolated after filtration in 52% yield with respect to Ru.

Synthesis of compound [Ru(C2H4N2H3)2][C2H4N2][C3H7NO] [MoS2O23] (POM-3). The DMF (4 mL) and acetonitrile (2 mL) solution of Dichloroiridin(1,10-phenanthroline) ruthenium(II) hydride (0.2 mmol, 144 mg) and α-(TBA)2[MoO4]2 (0.1 mmol, 216 mg) was sealed in a Teflon-lined steel autoclave and heating at 110 °C for 5 days. The orange-red crystals were isolated after filtration in 82% yield with respect to Ru.

Materials characterization. The optical diffuse reflectance spectra were measured on a Perkin-Elmer Lambda 750 s UV-Vis spectrophotometer equipped with an integrating sphere. Powder X-ray diffraction data were recorded on a Bruker D8 Advance diffractometer with a graphite-monochromatized Cu Kα radiation. FTIR spectra were recorded from KBr pellets by using a Perkin Elmer FTIR Spectrum GX spectrometer. The quantitative analysis of the product was directly carried out by an Agilent 1100 HPLC using an ultraviolet detector and was determined by inner standard method. A Hypersil ODS (C18) column (4.6 mm 5 l 9 250 mm) was used and the mobile phase was 0.1 M water solution of H2SO4 DI water at a flow rate of 0.3 mL/min. The column temperature was 40 °C and the detection wavelength was 210 nm. The biodiesel samples were diluted with DI water.

Crystallographic measurements. Data collection of crystals was carried out on Bruker APEX II CCD diffractometer equipped with a graphite-monochromatized Mo Kα radiation source (λ = 0.71073 Å). Empirical absorption was performed, and the structure was solved by direct methods and refined with the aid of a SHELXTL program package. All hydrogen atoms were calculated and refined using a riding model. The CCDC number for POM-1, POM-2, and POM-3 are 900119, 900120, and 900121, respectively.

Computational methods. The band structures and DOS of three POM crystals were studied by density functional theory based quantum chemical calculations using Cambridge Series Total Energy Package (CASTEP) program, implemented in the Materials Studio 5.0. Single crystal structural data determined by single-crystal XRD analysis was used to generate the geometries of POM-1-3. All the calculations were done using the GGA-PBE functional and ultrasoft pseudo-potentials with a kinetic energy cut off of 300 eV.

Photocatalytic oxidation of water for O2 generation. Typically, 10 μmol of the prepared catalysts were suspended in 10 mL aqueous solution of 10 mM Na2S2O8. The suspension was purged with argon for 3 h to drive away the residual oxygen before the photocatalytic water oxidation was carried out by irradiating the suspension with a 300-W xenon lamp (MAX-302, Asahi Spectra, USA) coupled with a UV cut-off filter (λ = 420 nm). The gas product composition was analyzed every 30 min by an Agilent 7890A gas chromatograph (GC) with TCD detector.

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Acknowledgments
The work is supported by the Singapore National Research Foundation through the Competitive Research Programme under Project No. NRF-CRP5-2009-04 (J.G., Y.Z. and C.J.L.), Q.Z. acknowledges the financial support from start-up grant (Nanyang Technological University), AcRF Tier 1 (RG 18/09) and Tier 2 (ARC 20/12) from MOE, CREATE program (Nanomaterials for Energy and Water Management) from NRF, and New Initiative Fund from NTU, Singapore. S.C., S.C.J.L. and C.X. thank the support from NTU seed funding for Solar Fuels Laboratory.

Author contributions
Q.Z. was the overall project leader who initiated the topic and advised on the research. Q.Z. and J.G. wrote the manuscript text. J.G., Y.L., P.C.S.M., L.Y., S.C.J.L. and Y.Z. were responsible for the synthesis and characterization of POM-based photocatalysts. S.C., Q.T., Z.C. and C.X. contributed to the part of water oxidation. K.Y., L.Y. and R.G. were responsible to the part of crystal structure. All authors reviewed the paper.

Additional information
Supplementary information accompanies this paper at http://www.nature.com/scientificreports

Competing financial interests: The authors declare no competing financial interests.

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How to cite this article: Gao, J. et al. Molecular-Based Water-Oxidation Catalysts (WOCs): Cluster-Size-Dependent Dye-Sensitized Polyoxometalates for Visible-Light-Driven O2 Evolution. Sci. Rep. 3, 1853; DOI:10.1038/srep01853 (2013).