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Non-covalent polyhedral oligomeric silsesquioxane-polyoxometalates as inorganic–organic–inorganic hybrid materials for visible-light photocatalytic splitting of water†

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A new series of visible light responsive and water-stable inorganic–organic–inorganic hybrid materials such as polyoxometalate (POM) and polyhedral oligomeric silsesquioxanes (POSS) with different metals was prepared, and these materials include $\{[PW_{12}O_{40}][(NH_3CH_2CH_2CH_2)(^tBu)_7Si_8O_{12}]_3\}$ (POM(W)–POSS), $[PMo_{12}O_{40}][(NH_3CH_2CH_2CH_2)(^tBu)_7Si_8O_{12}]_3\}$ (POM(Mo)–POSS) and $[PMo_{10}V_2O_{40}][(NH_3CH_2CH_2CH_2)(^tBu)_7Si_8O_{12}]_5\}$ (POM(MoV)–POSS); these materials containing a cationic electron donor of amino-substituted POSS (POSS–NH₂) on an anionic electron acceptor of POM have been developed for efficient and sustainable photocatalytic H₂ production. It is interesting to note that the synthesized hybrid materials exhibit remarkable photocatalytic H₂ production activities under visible-light irradiation. The maximum H₂ production rate of 485 $\mu\text{mol h}^{-1} \text{g}^{-1}$ is achieved using POM with heterometallic sites, *i.e.*, (MoV)–POSS rather than that having homometallic sites. The enhanced photocatalytic H₂ production is mainly due to improved charge carrier separation by electron-deficient metal sites and a red shift in the absorption, as revealed from photoluminescence and UV-vis spectra. Importantly, POM–POSS hybrid materials demonstrate excellent water stability during photocatalysis due to the hydrophobicity of the hybrid materials, which results from the integration of hydrophobic POSS–NH₂ with POMs in contrast to free POMs. Additionally, the successful integration of POSS–NH₂ into POMs is confirmed using FT-IR, NMR, ESI mass spectroscopy, and elemental and thermogravimetric analyses. The present study may open new possibilities in the design and development of stable POM organic/inorganic hybrid materials for solar energy conversion applications.

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Introduction

Conversion of solar energy into hydrogen energy using sustainable catalysis is one of the major focuses to overcome the future energy demand. Various semiconductor metal oxide photocatalytic systems have been studied for the production of hydrogen from splitting of water.^{1–4} However, polyoxometalate

(POM)-based photocatalysts have gained much attention because their features are similar to those of semiconductor metal oxides.^{5–7} Polyoxometalates (POMs), a class of metal–oxygen anion clusters, exhibit molecular and electronic structure diversities with multiple properties including fast multi-electron transfer, high proton mobility, strong Brønsted acidity and high solubility in various solvents and thus, they have been used in a wide range of applications in diverse areas such as structural chemistry, surface chemistry, electrochemistry, photochemistry and catalysis.^{8–12} Homogeneous POM catalysts are difficult to separate from the reaction mixture at the end of the catalytic reaction, which precludes their reusability and recovery.^{13,14} To overcome these drawbacks, solid supports such as mesoporous silica, zeolites and metal–organic frameworks have been used for dispersing or immobilizing POMs to create tunable porous heterogeneous catalysts with higher surface areas.^{15–20} However, problems such as leaching of metal components and low accessibility of the catalytic active sites by hydrophobic reactants occur because of the hydro-

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philic nature of the inorganic components. The synthesis of inorganic–organic hybrid materials based on POMs has been developed by introducing an organic counterpart through covalent and non-covalent interactions.^{21,22} The covalent modification is facilitated by connecting the organic ligand to a metal center *via* substitution of an oxo group of POM, and these hybrid POM materials are difficult to purify.²³ On the other hand, the synthesis of hybrid POMs by non-covalent modification *via* self-assembly of anionic POMs with appropriate organic counter cations has been shown to provide excellent control of the size, shape, and stability of the hybrid architectures.²⁴ For catalytic applications, the non-covalent hybrid POM–organic ligand is favored as it has the potential to heterogenize POMs without hindering their essential properties.^{25,26}

The introduction of polyhedral oligomeric silsesquioxanes (POSS) in POM through electrostatic interaction is expected to create non-covalent POM–POSS hybrid materials with enhanced properties such as thermal stability, chemical stability and mechanical properties due to the rigidity of the inner silicon and oxygen frameworks.^{27,28} POSS are organosilicon compounds with the formula (RSiO_{1.5})₈, and they have a nano-cubic inorganic silicon and oxygen framework decorated by organic groups; they are highly symmetric, easy to functionalize and exceptionally robust with respect to heat and water.²⁹ Unlike organic ligands, POSS are odorless and eco-friendly because no volatile organic compounds are released during the reaction. Recently, amphiphilic mesoporous POM-based non-covalent (ionic) hybrid POSS-BMx(dicationic imidazole ionic liquid)-PW(Keggin-type phosphotungstic acid) materials have been reported as heterogeneous catalysts for epoxidation of cyclooctene, and these materials display high activity and selectivity coupled with excellent recyclability;^{30,31} they can be studied as catalysts for photocatalytic water splitting due to their light harvesting properties. However, the high water solubility of POMs, especially those of POM(W), POM(Mo) and POM(MoV), limits their efficiency and recyclability in photocatalytic water splitting. In this context, Hill *et al.* have reported the immobilization of POMs with TiO₂, Fe₂O₃ and BiVO₄ to improve their activities in the photocatalysis reaction by facilitating electron–hole pair separation and transfer process.^{32–34} In the present study, we have developed highly water-stable POMs by incorporating amino-substituted POSS through a non-covalent approach. The developed hybrid materials such as {[PW₁₂O₄₀][(NH₃CH₂CH₂CH₂)(^tBu)₇Si₈O₁₂]₃ (POM(W)–POSS), [PMo₁₂O₄₀][(NH₃CH₂CH₂CH₂)(^tBu)₇Si₈O₁₂]₃ (POM(Mo)–POSS) and [PMo₁₀V₂O₄₀][(NH₃CH₂CH₂CH₂)(^tBu)₇Si₈O₁₂]₅ (POM(MoV)–POSS)} have been used as heterogeneous catalysts for photocatalytic hydrogen production from water splitting, and they also show high water stabilities and recyclabilities in contrast to bare POMs.

Experimental section

Materials and methods

All chemicals were of analytical grade and used as received. Commercially available starting materials such as phospho-

tungstic acid (Alfa Aesar) and phosphomolybdic acid (Alfa Aesar) were used as supplied. 10-Molybdo-2-vanado-phosphoric acid (H₅PMo₁₀V₂O₄₀) was prepared according to a previously reported method.³⁵ The modified synthetic procedure for aminopropyl heptaisobutyl silsesquioxane [(^tBu)₇(NH₂CH₂CH₂CH₂)Si₈O₁₂] was reported herein using dichloromethane as a solvent instead of THF (ESI†).^{36,37} Elemental analysis was carried out with an elemental Model Vario EL III. IR spectral measurements were performed using a Bruker Alpha-P Fourier transform spectrometer with dried samples pressed into KBr pellets. NMR measurements were obtained with a Bruker Advance DPX-250 spectrometer. Electrospray ionization mass spectral analysis (ESI-MS) was performed on a Shamadzu GC-MS 2020 spectrometer. The diffuse reflectance UV–visible spectrum was recorded on a Specord 210 plus-Analytikjena spectrometer in a wavelength range of 200–800 nm. PL emission spectra of the materials were measured using a spectrofluorometer (Fluoramax4p) at 250 nm excitation wavelength. Electrochemical studies were performed using a CHI 604E bipotentiostat (CH Instruments, Inc., USA).

Synthesis of POM–POSS materials

[PW₁₂O₄₀][(NH₃CH₂CH₂CH₂)(^tBu)₇Si₈O₁₂]₃ (POM(W)–POSS). To a solution of (NH₂CH₂CH₂CH₂)(^tBu)₇Si₈O₁₂ (0.12 g, 0.138 mmol) in ethanol (10 mL), a solution of H₃PW₁₂O₄₀ (0.132 g, 0.046 mmol) in ethanol (10 mL) was added. The reaction mixture was stirred for 24 hours, and the desired product precipitated as a white solid. The precipitate was filtered and thoroughly washed with cold ethanol (10 mL) and water (10 mL). The compound was dried under vacuum. Yield: 0.196 g (78%). Anal. calcd for C₉₃H₂₁₆O₇₆Si₂₄W₁₂N₃P: C 20.30; H 3.96; N 0.76. Found: C 20.90; H 3.16; N 0.82. IR (KBr, cm^{−1}): 3480(br), 2954(s), 1618(m), 1474(m), 1341(w), 1230(m), 1112(s), 987(m), 897(m), 807(s), 738(w), 577(w), 481(m). ¹H NMR (500 MHz, CDCl₃, TMS, ppm): δ = 3.3 (br, 2H, –CH₂CH₂CH₂NH₂), 1.25 (br, 2H, –CH₂CH₂CH₂NH₂), 0.58 (t, 2H, –CH₂CH₂CH₂NH₂), 0.60 (d, 14H, –CH₂ in ^tBu), 1.85 (septet, 7H, –CH), 0.95 (d, 42H, –CH₃). ¹³C NMR (100 MHz, CDCl₃, TMS, ppm): δ = 44.8, 27.2, 25.8, 24.0, 22.6 and 9.7 (aliphatic-carbons). ³¹P NMR (162 MHz, CDCl₃, ppm): δ = −15.8. ²⁹Si NMR (79.30 MHz, CDCl₃, TMS, ppm): δ = −67.2, 67.7, 67.9. TGA: temperature range (weight loss): 50–750 (50.19%). UV-vis DRS (nm): 390.

[PMo₁₂O₄₀][(NH₃CH₂CH₂CH₂)(^tBu)₇Si₈O₁₂]₃ (POM(Mo)–POSS). POM(Mo)–POSS was prepared using a similar synthetic procedure as that used for POM(W)–POSS, but H₃PMo₁₂O₄₀ was used instead of H₃PW₁₂O₄₀. Yield: 0.158 g (77%). Anal. calcd for C₉₃H₂₁₆O₇₆Si₂₄Mo₁₂N₃P: C 25.11; H 4.89; N 0.94. Found: C 24.67; H 5.23; N 0.88. IR (KBr, cm^{−1}): 3480(br), 2954(s), 1618(m), 1474(m), 1341(w), 1235(m), 1112(s), 968(m), 892(m), 806(s), 738(w), 577(w), 481(m). ¹H NMR (500 MHz, CDCl₃, TMS, ppm): δ = 3.3 (br, 2H, –CH₂CH₂CH₂NH₂), 1.25 (br, 2H, –CH₂CH₂CH₂NH₂), 0.58 (t, 2H, –CH₂CH₂CH₂NH₂), 0.60 (d, 14H, –CH₂ in ^tBu), 1.85 (septet, 7H, –CH), 0.95 (d, 42H, –CH₃). ¹³C NMR (100 MHz, CDCl₃, TMS, ppm): δ = 44.9,

27.3, 25.9, 24.1, 22.7 and 9.8 (aliphatic-carbons). ^{31}P NMR (162 MHz, CDCl_3 , ppm): $\delta = -15.7$. ^{29}Si NMR (79.30 MHz, CDCl_3 , TMS, ppm): $\delta = -67.1$, 67.6, 67.9. Mass spectrum (ESI = 70 eV): positive ion $m/z = 874.20$ [POSS-NH_2]; negative ion $m/z = 1785.13$ [$\text{PMo}_{10}\text{V}_2\text{O}_{40} + \text{H} + \text{K}$] $^-$, 912.32 [$\text{PMo}_{12}\text{O}_{40} + \text{H}$] $^{2-}$ and 607.54 [$\text{PMo}_{12}\text{O}_{40}$] $^{3-}$. UV-vis DRS (nm): 500.

[$\text{PMo}_{10}\text{V}_2\text{O}_{40}$][$(\text{NH}_3\text{CH}_2\text{CH}_2\text{CH}_2)(^i\text{Bu})_7\text{Si}_8\text{O}_{12}$] $_5$ (POM(MoV)-POSS). POM(MoV)-POSS was prepared by using a similar synthetic procedure as that used for POM(W)-POSS, but $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ in water was used instead of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ in ethanol. Yield: 0.107 g (76%). Anal. calcd for $\text{C}_{155}\text{H}_{355}\text{O}_{100}\text{Si}_{40}\text{Mo}_{10}\text{V}_2\text{N}_5\text{P}$: C 30.47; H 5.94; N 1.15. Found: C 31.01; H 5.33; N 1.85. IR (KBr, cm^{-1}): 3480(br), 2954(s), 1618(m), 1474(m), 1341(w), 1235(m), 1112(s), 950(m), 844(w), 739(m), 597(w), 481(m). ^1H NMR (500 MHz, CDCl_3 , TMS, ppm): $\delta = 2.9$ (br, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 1.25 (br, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 0.58 (t, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 0.60 (d, 14H, $-\text{CH}_2$ in ^iBu), 1.85 (septet, 7H, $-\text{CH}$), 0.95 (d, 42H, $-\text{CH}_3$). ^{13}C NMR (100 MHz, CDCl_3 , TMS, ppm): $\delta = 44.8$, 27.2, 25.7, 24.1, 22.6 and 9.7 (aliphatic-carbons). ^{31}P NMR (162 MHz, CDCl_3 , ppm): $\delta = -15.8$. ^{29}Si NMR (79.30 MHz, CDCl_3 , TMS, ppm): $\delta = -67.2$, 67.6, 67.9. Mass spectrum (ESI = 70 eV): positive ion $m/z = 914.23$ [$\text{POSS-NH}_3 + \text{K}$] and 874.20 [POSS-NH_2]; negative ion $m/z = 1741.13$ [$\text{PV}_2\text{Mo}_{10}\text{O}_{40} + \text{Li} + 3\text{H} + \text{H}_2\text{O}$] $^-$, 1723.24 [$\text{PV}_2\text{Mo}_{10}\text{O}_{40} + \text{Li} + 3\text{H}$] $^-$, 1143.50 [$\text{H}_3\text{PV}_2\text{Mo}_6\text{O}_{27}$], 854.60 [$\text{H}_3\text{PV}_2\text{Mo}_4\text{O}_{21}$], 530.00 [$\text{H}_3\text{PMo}_3\text{O}_{13}$], 386.82 [VMo_2O_9] and 324.82 [V_2MoO_8]. TGA: temperature range (weight loss): 160–800 (64.46%). UV-vis DRS (nm): 620.

Photocatalytic hydrogen production

The photocatalytic hydrogen production reaction was carried out under visible-light illumination. Briefly, 5 mg of POM-POSS hybrid was added to 50 ml of 5% aq. TEOA solution in a 100 ml reactor. The reaction solution was stirred for 30 min and evacuated for 30 min. The dissolved oxygen content was removed by purging with N_2 gas. Subsequently, the mixture was irradiated with a 250 W xenon lamp. The reaction progress was monitored by an off-line gas chromatograph with a TCD detector (Shimadzu GC-2014 with Molecular Sieve/5 Å column) using N_2 as the carrier gas.

Results and discussion

Synthesis and characterization of POM-POSS hybrid materials

The POM-POSS hybrid materials (POM(W)-POSS and POM(Mo)-POSS) were prepared by stirring a solution of POSS-NH₂ in ethanol with an ethanolic solution of corresponding POMs in a ratio of 3 : 1 for 24 hours at room temperature (Scheme 1). POM(MoV)-POSS was also synthesized by reacting five equivalents of POSS-NH₂ in ethanol with an aqueous solution of one equivalent of $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ under similar reaction conditions. In a typical reaction, stirring the reaction mixture for a few hours resulted in the precipitation of the desired POSS-POM hybrid material. The successful formation of POM-POSS hybrid materials was confirmed by ^1H , ^{13}C , ^{29}Si NMR, and

FT-IR spectroscopy as well as ESI mass spectroscopy and elemental and thermogravimetric analyses. The solubilities of the POM-POSS hybrid materials are listed in Table S1.† For the compound POM(W)-POSS, the elemental analysis exhibited (weight percentage) C 20.90, H 3.16, and N 0.82, which were in good agreement with the calculated values of C 20.30, H 3.96, and N 0.76 based on the formula of [$\text{PW}_{12}\text{O}_{40}$][$(\text{NH}_3\text{CH}_2\text{CH}_2\text{CH}_2)(^i\text{Bu})_7\text{Si}_8\text{O}_{12}$] $_3$. This result implied that POM(W)-POSS is composed of one $\text{PW}_{12}\text{O}_{40}^{3-}$ anion and three [$(^i\text{Bu})_7\text{Si}_8\text{O}_{12}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3)^+$] cations. POM(Mo)-POSS had an identical elemental composition to POM(W)-POSS between the corresponding POM and POSS; however, POM(MoV)-POSS displayed a composition ratio of one $\text{PMo}_{10}\text{V}_2\text{O}_{40}^{5-}$ anion to five [$(^i\text{Bu})_7\text{Si}_8\text{O}_{12}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3)^+$] cations due to more number of available protons in $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$.

Fig. 1(a) illustrates the FT-IR spectra of the non-covalent hybrids POM(W)-POSS, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and POSS-NH₂. The FT-IR spectrum of POSS-NH₂ indicates a sharp peak at 1112 cm^{-1} due to the asymmetric vibration of Si-O-Si in the silsesquioxane framework. The spectrum of POSS-NH₂ reveals vibrational bands due to the presence of aminopropyl groups at 1474 cm^{-1} ($\delta\text{N-H}$), 3403 cm^{-1} ($\nu\text{N-H}$) and 2954 cm^{-1} ($\nu\text{C-H}$). The Keggin structure of the $\text{PW}_{12}\text{O}_{40}^{3-}$ anion shows four characteristic vibrational bands at around 806, 893, 987 and 1082 cm^{-1} , corresponding to the presence of intra-octahedral oxygen $\nu(\text{W-O-W})$, inter-octahedral oxygen $\nu(\text{W-O-W})$, terminal oxygen $\nu(\text{W=O})$ and central oxygen $\nu(\text{P-O})$. The broad absorption around 3400 cm^{-1} indicates the hydrated nature of $\text{PW}_{12}\text{O}_{40}^{3-}$. For non-covalent hybrids POM(W)-POSS, four Keggin-featured vibrational bands are also detected with only slight shifts, and the bands at 1112, 1474, 3479 and 2954 cm^{-1} are assigned to POSS-NH₂, indicating the presence of both $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and POSS-NH₂ in the non-covalent hybrid POM(W)-POSS.^{30,31} Both POM(Mo)-POSS and POM(MoV)-POSS display similar IR vibrational bands to POM(W)-POSS.

The ^1H NMR spectra of the POM-POSS hybrid materials show peaks for six different protons of both isobutyl and 3-aminopropyl groups of the silsesquioxane framework (Fig. 1b). The presence of a triplet at 0.58 ppm and broad peaks at around 2.9–3.3 ppm and 1.25 ppm corresponds to three different $-\text{CH}_2$ moieties of 3-aminopropyl groups. The broad signal (at around 2.9–3.3 ppm) for the protons of the $-\text{CH}_2$ group attached to the amine groups is shifted to lower field compared to that of the corresponding protons (2.68 ppm) in POSS-NH₂ due to the conversion of more electron donating amine ($-\text{NH}_2$) group into the less electron donating ammonium salt ($-\text{NH}_3^+$) via a protonation reaction; another broad signal (at around 1.25 ppm) for the central $-\text{CH}_2$ protons of the *n*-propyl group shifts to higher field compared to that of the corresponding protons (1.55 ppm) in POSS-NH₂. Although the electron donating nature of the ammonium salt decreases, the two $-\text{CH}_2$ groups adjacent to the central $-\text{CH}_2$ group are electron donating, which shifts the central $-\text{CH}_2$ group signal towards higher field. The ^1H NMR integrations of the peak areas for POSS-NH₂, POM(W)-POSS,

Scheme 1 Synthesis of POM(W)-POSS, POM(Mo)-POSS and POM(MoV)-POSS materials.

Fig. 1 (a) FTIR spectra of POSS-NH₂, H₃PW₁₂O₄₀ and POM(W)-POSS as KBr discs, (b) ¹H NMR spectra of (1) POSS-NH₂, (2) POM(W)-POSS, (3) POM(Mo)-POSS and (4) POM(MoV)-POSS hybrids in CDCl₃.

POM(Mo)-POSS and POM(MoV)-POSS are listed in Table S2.† The peaks at 0.60 (d), 1.85 (septet) and 0.95 (d) ppm correspond to aliphatic -CH₂-, -CH- and -CH₃ protons of the isobutyl moiety.^{36,37} The ¹³C NMR spectra of the POM-POSS materials show well-distinguished peaks for six different carbons of both

isobutyl and 3-aminopropyl groups (Fig. S1†). In the ³¹P NMR spectra of POM-POSS hybrids, a singlet is observed around -15.8 ppm, which corresponds to the phosphorous of the phosphate groups in polyoxometalate precursors (Fig. S2†). In the ²⁹Si NMR spectra of the POM-POSS hybrids, three signals

are observed at -67.2 , -67.7 and -67.9 ppm, which are assigned to the Si atom bounded by propyl groups, the Si atom in the isobutyl group (diagonal to the Si atom in the propyl groups) and the remaining Si atoms, respectively (Fig. S3†).

ESI-MS mass spectrometry of POM(Mo)-POSS in the positive ion mode displayed a peak at m/z 874, which was ascribed to the mass of POSS-NH₂. The negative ion spectrum showed peaks at m/z 1785, 912 and 608, corresponding to mono-charged $[(\text{PMo}_{12}\text{O}_{40})^{3-} + \text{H}^+ + \text{K}^+]^-$, double-charged $[(\text{PMo}_{12}\text{O}_{40})^{3-} + \text{H}^+]^{2-}$ and triple-charged $[(\text{PMo}_{12}\text{O}_{40})^{3-}]^{3-}$ ions (Fig. 2a and b).^{38,39} The fragment intermediate of $[(\text{PMo}_9\text{O}_{27})^{3-} + \text{H}^+ + \text{Na}^+]^-$ was observed at m/z 1347.98, as shown in Fig. 2b. For the POM(MoV)-POSS hybrid, the observed peak at m/z 914 from the positive ion mode was ascribed to the mass of $[\text{POSS-NH}_3^+ + \text{K}^+]$. In addition, the peak at m/z 874 for POSS-NH₂ was also observed for the POM(MoV)-POSS hybrid material. The negative ion mass spectrum displayed the highest mass peaks at m/z = 1741 and 1723, corresponding to $[(\text{PMo}_{10}\text{V}_2\text{O}_{40})^{5-} + \text{Li}^+ + 3\text{H}^+]^- + \text{H}_2\text{O}$ and $[(\text{PMo}_{10}\text{V}_2\text{O}_{40})^{5-} + \text{Li}^+ + 3\text{H}^+]^-$ (Fig. 2c and d).⁴⁰ Nine other fragment peaks for phosphovanadomolybdate clusters were noted (Fig. 2d), and they are listed in Table 1.

TGA profiles of pure $\text{H}_3\text{PW}_{12}\text{O}_{40}$, POSS-NH₂ and POM(W)-POSS were obtained under air atmosphere (Fig. 3a). TGA results for $\text{H}_3\text{PW}_{12}\text{O}_{40}$ revealed a mass loss of about 6% up to a temperature of 150 °C, which was due to the loss of free and adsorbed water. The gradual mass loss of about 2% up to 500 °C was assigned to the release of more hydrated or structural water. The TGA results for POSS-NH₂ showed steady mass losses of about 75% up to 360 °C and 13% up to 600 °C, which were ascribed to the loss of an organic moiety and subsequent decomposition of POSS-NH₂ into SiO_2 .⁴¹ In the case of POM(W)-POSS, the final degradation product with a percentage of 50.19 wt% was observed due to the loss of the organic moiety from POSS-NH₂, decomposition of POSS-NH₂ into SiO_2 and decomposition of the Keggin structure of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ into oxides of tungsten and tungsten-phosphorus. The final residue of 49.81 wt% indicated that POM(W)-POSS is composed of one $\text{PW}_{12}\text{O}_{40}^{3-}$ anion and three $[(^t\text{Bu})_7\text{Si}_8\text{O}_{12}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3)]^+$ cations. A similar observation was found for $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ and its hybrid POM(MoV)-POSS with high weight loss as compared to that of POM(W)-POSS, which showed that one $\text{PM}_{10}\text{V}_2\text{O}_{40}^{5-}$ anion and five $[(^t\text{Bu})_7\text{Si}_8\text{O}_{12}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3)]^+$ cations are present in POM(MoV)-POSS (Fig. 3b).⁴²

Fig. 2 (a) Positive-ion ESI-MS of POM(Mo)-POSS in MeOH/water/acetic acid, (b) negative-ion ESI-MS of POM(Mo)-POSS in MeOH/water/acetic acid, (c) positive-ion ESI-MS of POM(MoV)-POSS in MeOH/water/acetic acid, and (d) negative-ion ESI-MS of POM(MoV)-POSS in MeOH/water/acetic acid.

Table 1 Negative-ion ESI-MS data of POM(Mo)-POSS and POM(MoV)-POSS

Compounds	Species	<i>m/z</i>
PMo ₁₂ O ₄₀ ³⁻ in POM(Mo)-POSS	[Mo ₄ O ₁₃] ²⁻	295.77
	[Mo ₇ O ₂₂] ²⁻	510.00
	[PMo ₁₂ O ₄₀] ³⁻	607.54
	[PMo ₁₂ O ₄₀] ³⁻ + H ⁺	912.32
	[PMo ₁₂ O ₄₀] ³⁻ + H ⁺ + Na ⁺	1347.98
	[PMo ₁₂ O ₄₀] ³⁻ + H ⁺ + K ⁺	1785.13
PV ₂ Mo ₁₀ O ₄₀ ⁵⁻ in POM(MoV)-POSS	[PVMo ₂ O ₁₄] ²⁻	248.89
	[PMo ₃ O ₁₃] ²⁻	263.39
	[Mo ₄ O ₁₃] ²⁻	295.87
	[PVMo ₃ O ₁₆] ²⁻	312.86
	[V ₂ Mo ₈] ²⁻	325.82
	[H ₂ PVMo ₁₀] ²⁻	399.87
	[VMo ₂ O ₉] ²⁻	386.82
	[H ₃ PMo ₃ O ₁₃] ²⁻	530.00
	[V ₂ Mo ₈ O ₃₁] ²⁻	682.69
	[H ₂ PV ₂ Mo ₄ O ₂₁] ²⁻	854.60
	[H ₃ PV ₂ Mo ₆ O ₂₇] ²⁻	1143.50
	[PV ₂ Mo ₁₀ O ₄₀] ⁵⁻ + Li ⁺ + 3H ⁺	1723.24
	[PV ₂ Mo ₁₀ O ₄₀] ⁵⁻ + H ₂ O + Li ⁺ + 3H ⁺	1741.24

Morphological and optical studies

The morphologies of POM(W)-POSS, POM(Mo)-POSS and POM(MoV)-POSS hybrids were studied by scanning electron microscopy (SEM). As presented in Fig. 4, all the hybrids exhibited agglomerated nanosheet morphologies with uniform distributions. However, the sizes of the agglomerated nanosheets varied with respect to the metals sites of POMs. The average lengths of POM(W)-POSS, POM(Mo)-POSS and POM(MoV)-POSS nanosheets were found to be 240.3, 492.3 and 622.0 nm, respectively (Fig. S4†). Furthermore, less agglomerated nanosheets were observed with single metal site POMs such as POM(W)-POSS and POM(Mo)-POSS, whereas

POM(MoV)-POSS exhibited agglomerated nanosheets of high length (622.0 nm), which might be due to the presence of two different metal sites causing high agglomeration and increase in size.

The optical absorption and band gap of the hybrid catalysts were studied using UV-vis DRS spectra. As shown in Fig. 5, the absorption edge of POSS-NH₂ was observed at 250 nm. However, in the case of non-covalent POM-POSS hybrid materials such as POM(W)-POSS, POM(Mo)-POSS and POM(MoV)-POSS, red shifts were observed in the absorption edges at 390, 500 and 620 nm, respectively. The red shifts in the absorptions of POM-POSS hybrid materials were observed mainly due to the successful integration of POSS-NH₂ and POMs. In addition, the band gaps of the POM-POSS hybrid materials were calculated by the Kubelka-Munk function. The calculated band gap energies of POSS-NH₂, POM(W)-POSS, POM(Mo)-POSS and POM(MoV)-POSS were 5.0, 3.2, 2.5 and 2.0 eV, respectively. It was clearly seen from the band gap energy that the optical band gap for the POM-POSS hybrids shifted towards the visible region after the conjugation between POSS-NH₂ and POMs, and the metal sites of the POM-POSS hybrid materials facilitated more absorption in the visible region. However, the maximum band gap reduction was observed with POM(MoV)-POSS, and it can be explained by the presence of two different metal sites (Mo and V), which further increased the strong ionic interaction with POSS-NH₂ and reduced the band gap energy.⁴³ Thus, a reduction in the band gap energy extended the incident photon absorption towards the visible region, thereby improving the photocatalytic hydrogen production performance. In addition, the UV-vis DRS spectra of all free POMs displayed reliable visible-light absorptions with colors (Fig. S5†). After integration of POMs with POSS-NH₂, the optical absorptions of POM-POSS hybrids shifted towards the blue region in comparison with those of pristine POMs, which also indicated the formation of POM-POSS hybrid materials.

Fig. 3 TGA spectra for (a) POSS-NH₂, H₃PW₁₂O₄₀ and POM(W)-POSS, and (b) POSS-NH₂, H₅PMo₁₀V₂O₄₀ and POM(MoV)-POSS.

Fig. 4 Scanning electron microscopy (SEM) images of (a, b) POM(W)POSS, (c, d) POM(Mo)-POSS and (e, f) POM(MoV)-POSS hybrids.

Photoluminescence and transient photocurrent studies

To study the electron-hole pair separation efficiencies of POSS-NH₂, POM(W)-POSS, POM(Mo)-POSS and POM(MoV)-POSS, photoluminescence spectroscopy (PL) was carried out with an excitation wavelength (λ_{ex}) of 250 nm, and the results are shown in Fig. 6a. All of the POM-POSS hybrid materials showed decreased PL intensities compared to pristine POSS-NH₂, which indicated that the incorporation of POSS-NH₂ with POMs considerably reduced the recombination of electron-hole pairs due to the presence of transition metal sites. Subsequently, the luminescence intensity of POM(MoV)-POSS was lower than those of other materials, thus revealing the presence of two different metal sites; this further improved

the electron-hole pair separation by inducing electron deficient behavior, which enhanced the photocatalytic hydrogen production activity.⁴⁴ To further authenticate photo-electron generation and electron-hole pair separation of POM-POSS hybrid materials, a photocurrent experiment was performed. As clearly seen from Fig. 6b, POSS-NH₂ did not show any photocurrent response, whereas POM-POSS hybrid materials showed significant photocurrent responses under identical conditions. Interestingly, POM(MoV)-POSS showed an enhanced photocurrent response compared to POM(W)-POSS and POM(Mo)-POSS, which was consistent with PL quenching and photocatalytic hydrogen production activity. Therefore, these results further confirmed that the two different metal sites facilitate superior photocatalytic activity.

Fig. 5 (a, b) UV-Vis absorption spectrum (DRS mode) and Tauc plot of POSS-NH₂, (c & d) UV-Vis absorption spectra (DRS mode) and Tauc plots of POM(W)-POSS, POM(Mo)-POSS and POM(MoV)-POSS hybrids.

Fig. 6 (a) PL spectra and (b) transient photocurrent measurements of POSS-NH₂, POM(W)-POSS, POM(Mo)-POSS and POM(MoV)-POSS hybrids.

Photocatalytic hydrogen production

The catalytic efficiencies of all the synthesized POM-POSS hybrid materials were investigated towards photocatalytic hydrogen production under visible-light illumination, and triethanolamine (TEOA) was used as the sacrificial agent. It is reported that free POMs are highly soluble in water and cannot be used as heterogeneous catalysts.⁴⁵ However, it is very inter-

esting to note that after the incorporation of POSS-NH₂ with POMs, the solubility of POMs decreased due to an increase in the hydrophobicity, due to which the POM(W)-POSS, POM(Mo)-POSS and POM(MoV)-POSS hybrid materials could be used as heterogeneous catalysts for photocatalytic hydrogen evolution. Thus, initially, we carried out the photocatalytic hydrogen production reaction using POSS-NH₂ alone, but no hydrogen evolution was observed under visible-light illumina-

tion owing to its wide band gap, as revealed from the UV-vis DRS spectra (Fig. 5). However, POSS-NH₂-incorporated POMs exhibited substantial photocatalytic hydrogen production activity under identical conditions (Fig. 7a). As seen from Fig. 7b, the relative order of photocatalytic hydrogen production activity was POM(MoV)-POSS (485 $\mu\text{mol h}^{-1} \text{g}^{-1}$) > POM(Mo)-POSS (371 $\mu\text{mol h}^{-1} \text{g}^{-1}$) > POM(W)-POSS (302 $\mu\text{mol h}^{-1} \text{g}^{-1}$) > POSS-NH₂ (0 $\mu\text{mol h}^{-1} \text{g}^{-1}$). These results clearly demonstrated that the photocatalytic hydrogen production activity was mainly facilitated by POMs and not by POSS-NH₂. Besides, the integration of POSS-NH₂ with POMs reduced the solubility of POMs in water and enhanced the stability of the hybrid materials. A high rate of hydrogen evolution was observed using POM(MoV)-POSS as a photocatalyst due to increase in the two different metal sites, which significantly enhanced the Lewis acidity. As a result, the photogenerated electrons were rapidly accepted by the Lewis acid sites, which reduced the electron hole-pair recombination, as evident from the photoluminescence spectra, thereby increasing the photocatalytic hydrogen production activity. Similar results were reported by Fukuzumi *et al.* for photoredox cata-

lysts.^{46,47} In addition, the presence of two different metal sites in POM(MoV)-POSS led to enhanced optical band gap towards the visible region; this resulted in more photon absorption in the visible region, as was previously identified with UV-vis DRS spectra. The H₂ production efficiency of the POM(MoV)-POSS photocatalyst was also compared with those of previously reported hybrid material-based photocatalytic systems (Table S3[†]). As seen in Table S3,[†] POM(MoV)-POSS showed higher activity than non-metal-based hybrid materials as a photocatalyst.

Apart from activity, the photostability of the photocatalyst is a foremost parameter for commercial applications. To study the photostability of the POM-POSS catalyst during hydrogen production, recyclability experiments were performed with the best catalyst POM(MoV)-POSS. For this experiment, generated gas was evacuated at fixed time intervals before the next cycle. As seen in Fig. 7c, no prominent change was observed in the hydrogen production activity, and this demonstrated high photostability of the photocatalyst. Moreover, the stability of the hybrid photocatalyst materials was further ascertained by FTIR spectroscopy (Fig. 7d). In the FT-IR spectra, no signifi-

Fig. 7 (a) Photocatalytic H₂ production activity using POSS-NH₂, POM(W)-POSS, POM(Mo)-POSS and POM(MoV)-POSS hybrids, (b) average rate of H₂ evolution activity ($\mu\text{mol h}^{-1} \text{g}^{-1}$), (c) recyclability test, (d) FT-IR spectra of POM(MoV)-POSS before and after photocatalytic hydrogen production reaction.

Fig. 8 Mott-Schottky plots for (a) POM(W)-POSS, (b) POM(Mo)-POSS and (c) POM(MoV)-POSS.

Fig. 9 (a) Energy level diagram of POM(W)-POSS, POM(Mo)-POSS and POM(MoV)-POSS. (b) Possible mechanism for the photocatalytic hydrogen production reaction.

cant change was noted for pure and 5 cycle-used POM(MoV)-POSS. Furthermore, a broad peak appeared at 3300 cm^{-1} in the FT-IR spectrum after 5 cycles, which might be due to the adsorption of water molecules by the metal sites during the photocatalysis reaction.⁴⁸ In addition, the stability of the POM(MoV)-POSS hybrid was also assessed with SEM analysis; no significant change was noted after 5 cycles, as depicted in Fig. S6.†

To study the changes in flat band potentials of synthesized POM-POSS hybrids with respect to their metal sites, we performed Mott-Schottky analysis. As seen in Fig. 8, all the hybrids showed an n-type characteristic curve. From the Mott-Schottky analysis, the flat band potentials of POM(W)-POSS, POM(Mo)-POSS and POM(MoV)-POSS were calculated as -1.13 , -1.20 and -1.26 V vs. Ag/AgCl, respectively. Based on the flat band potentials and the band gaps of the POM-POSS hybrids, an overall energy diagram was constructed, and it is presented in Fig. 9a. It is interesting to note that the flat band potentials of the conduction bands gradually increased toward more negative values than the H^+/H potential with respect to the metal sites. However, the maximum negative flat band potential was observed with the POM(MoV)-POSS hybrid (-1.26 V). The more negative flat band potential of the POM(MoV)-POSS hybrid reduced H^+ into H_2 , which was consistent with photocatalytic H_2 production activity.^{49,50}

On the basis of the above-mentioned results and discussions, we proposed a tentative mechanism for visible light-induced photocatalytic hydrogen production of POSS-NH₂-incorporated POM hybrid materials (Fig. 9b). In this process, POSS-NH₂ enhanced the electron-hole pair separation but did not absorb visible light since it has a wide band gap (5.0 eV); this result was supported by the photoluminescence results as the emission intensity of POSS-NH₂-incorporated POM hybrid materials was lower compared to that of POSS-NH₂. When visible light was incident on the hybrid materials, the electrons were excited to the conduction band, resulting in the generation of holes in the valence band. This electron-hole pair generation was previously identified by transient photocurrent measurements. Subsequently, the photogenerated holes reacted with triethanolamine (TEOA) and produced H^+ . Meanwhile, photo-excited electrons reduced H^+ to H_2 .^{51,52}

Conclusion

In this contribution, a new series of highly water-stable POM-POSS hybrid materials have been successfully synthesized and characterized by FT-IR, NMR spectroscopy, ESI mass spectroscopy, and elemental and thermogravimetric analyses. Incorporation of POSS-NH₂ with polyoxometalates enhances the stability of the POM-POSS hybrid by converting POM from hydrophilic to hydrophobic. Effective heterogenization of POMs is mainly due to the presence of the aminopropyl group on POSS and the protons of POM, and they influence the formation of ion pair compounds. Notably, the synthesized POM-POSS hybrid materials exhibit visible light-driven superior

photocatalytic H_2 production activity due to rapid electron-hole separation and a red shift in the optical absorption. Compared with previous reports, the present study demonstrates comparable H_2 production activity, high stability and ease of recovery of the catalyst after the catalytic reaction. Therefore, this research can provide a powerful strategy to design and construct water-stable POM-based hybrid materials for sustainable catalysis.

Conflicts of interest

There are no conflicts to declare.

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