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The simple and high yield synthesis of H₆Cu₂[PPD]₆[SiW₉Cu₃O₃₇].12H₂O (PPD= pphenylenediamine) as a new organic-inorganic hybrid polyoxometalate is reported. The new compound consists of trimetal-substitution polyoxometalate of A-β-SiW₉Cu₃O₃₇¹⁰⁻, water PPD molecules coordinated and noncoordinated molecules. and H₆Cu₂[PPD]₆[SiW₉Cu₃O₃₇].12H₂O was firmly grafted on graphene oxide decorated with Fe₃O₄ nanoparticles. These nanocomposites were characterized by elemental analyses, thermogravimetric analysis (TGA), Fourier transform infrared (FT-IR), X-ray photoelectron spectrum (XPS), powder X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), and alternating gradient force magnetometer (AGFM). The results indicate that the size range of the nanoparticles are between 20-60 nm. The catalytic activity of H₆Cu₂[PPD]₆[SiW₉Cu₃O₃₇].12H₂O and the magnetically reusable nanocomposite of GO@Fe₃O₄@H₆Cu₂[PPD]₆[SiW₉Cu₃O₃₇].12H₂O were investigated in the Knoevenagel condensation and synthesis of 2,3-dihydroquinazolin-4(1H)-ones.

Introduction

The design of active, selective and recyclable heterogeneous catalysts based on polyoxometalates (POMs) have attracted great interest because of their controllable shape and size, highly negative charges and their numerous advantageous properties.¹ Keggin-type POMs such as H₃PMo₁₂O₄₀, H₃PW₁₂O₄₀, and H₄SiW₁₂O₄₀ (also known as heteropolyacids, HPAs) are strong Brønsted acid that make them useful as solid-acid catalysts for many acid catalyzed organic transformations.²⁻⁶ Despite the above because of low surface area (< 10 m²/g) and high solubility in water and polar organic solvents.⁷ Dispersion of POMs on a support such as silica,⁸ zeolite,⁹ or design of catalysts based on polyoxometalate nanoparticles¹⁰ can dissolve these problems and improve their catalytic activity.

Functionalization of classical POMs by organic compounds with suitable functional groups not only provides a powerful way to gain multifarious new compounds but also affords a new method to modify catalytic performance of POMs.¹¹The design and synthesis of inorganic–organic hybrid materials based on POMs has received considerable attention due to their application in catalysis, sorption, and electrical conductivity.^{12,13} A wide variety of organic molecules have to be combined with POMs to explore the novel functional property and morphology of the type of inorganic–organic hybrid materials.^{14,15} Magnetic separation renders the recovery of catalysts from liquid-phase reactions much easier than by cross-flow filtration and centrifugation. It is simple, economical and promising for industrial applications.¹⁶ Among the various magnetic nanoparticles under investigation, Fe₃O₄ nanoparticles are arguably the most extensively studied as a core magnetic support because of their simple synthesis, low cost, and relatively large magnetic susceptibility of Fe₃O₄ SPNs-.¹⁷ Thanks to its exceptionally high surface area (2630 m²/g) and abundant oxygenate groups such as epoxy, hydroxyl, and carboxyl groups^{18,19} on their surface, Graphene

oxide (GO) is as an ideal support for improving POMs catalytic activity.²⁰ If the graphene oxide is loaded with Fe₃O₄ nanoparticles, the combined supporting material has key properties such as magnetic separation, the large surface area and ease of functionalizing with various chemical groups to increase their dependence toward target compounds.²¹ Heterogeneous catalysts such as graphene oxide-Fe₃O₄ have attracted a great deal of attention in recent years due to their high catalytic activity and interesting structures.²² The Fe₃O₄-GO magnetic nanoparticles have been most useful control as heterogeneous catalysts because of their numerous applications in biotechnology, nanocatalysis, and medicine.²³ In this paper, we report the synthesis and characterization of the new nanosized polyoxometalate-based inorganic–organic hybrid material, H₆Cu₂[PPD]₆[SiW₉Cu₃O₃7]·12H₂O (HybPOM) and the magnetically reusable nanocomposites of GO@Fe₃O₄@HybPOM as novel and efficient catalysts for synthesis of benzylidenemalononitrile and 2,3-dihydroquinazolin-4(1*H*)-one derivatives. The magnetic properties make the complete recovery of the catalyst possible by means of an external magnetic field.

Experimental

General

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All reagents and solvents were commercially obtained from Merck chemical company and used without further purification. The Na₉H[β -SiW₉O₃₄]·18H₂O was prepared and characterized according to the method mentioned in the literature.²⁴ Graphene oxide (GO) was prepared by modified Hummers' method.²⁵ The C, H, and N microanalyses were carried out with CHNS-O Elemental Analyzer Vario EL III, ELEMENTAR, Hanau-Germany while the amount of Fe, W and Cu were measured by inductively coupled plasma mass spectrometry (ICP-MS). Powder XRD was obtained by an X'PertPro Panalytical, Holland diffractometer in 40kV and 30mA with a CuKa radiation (λ =1.5418Å). The XPS spectra of the supported catalyst was recorded on a

VG Microtech Twin anode XR3E2 X-ray source and aconcentric hemispherical analyzer operated at a base pressure of 5×10^{-10} mbar using AlKa (hu=1486.6 eV). Peak fitting of all spectra were undertaken using the Shirley background correction and Gaussian–Lorentzian peak shapes. Binding energies (BEs) were referenced to C 1s peak at 284.5 eV. Low-resolution survey spectra, as well as higher-resolution spectra for C, Fe, O, W, and Cu were collected. Infrared spectra were recorded on a Bruker Vector 22 FT-IR using KBr plate. The morphology of nanocomposite strate Counter vecaled by a scanning electron microscope (FESEM-TESCAN MIRA3). The elements in the nanocomposite samples were probed with energy-dispersive X-ray (EDX) spectroscopy accessory to the FESEM-TESCAN MIRA3 scanning electron microscopy. The magnetic properties were investigated by a home-made alternative gradient force magnetometer (AGFM) in the magnetic field range of -5000 to 5000 Oe at room temperature. Thermo gravimetric analysis and differential thermal analysis (TGA) were carried out using a STA PT-1000 LINSEIS. PEG with molecular weight of 400 was used in reactions (PEG-400).

Preparation of nano materials

Preparation of H₆Cu₂[PPD]₆[SiW₉Cu₃O₃₇]·12H₂O nanohybrid (HybPOM)

A 2.00 g of Na₉H[β -SiW₉O₃₄]·18H₂O was dissolved in water (100 mL) at room temperature. Cu(C₂H₃O₂)₂·H₂O (3.00 g) was added to the solution while stirring, resulting in a blue solution. Then, 0.7 g of PPD was slowly added to this blue solution while stirring, producing a blue-brown precipitate. After stirring for 4 h, the precipitate color changed from blue-brown to black. Obtained black precipitate was centrifuged and washed several times with water and acetonitrile, then was air-dried at room temperature. Yield 1.6 g, 80%. Anal. Calcd.ForC₃₆H₇₈N₁₂O₄₉SiW₉Cu₅: C, 12.48; H, Published on 14 October 2016. Downloaded by Lund University on 15/10/2016 11:08:29.

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2.25; N, 4.85; W, 47.90; Cu, 9.17. Found: C, 12.11; H, 2.03; N, 4.71; W, 48.95; Cu, 9.95.

Preparation of GO-Fe₃O₄

GO–Fe₃O₄ composites were synthesized by co-precipitation reaction of Fe²⁺ and Fe³⁺ ions in the presence of GO. To a 200 mL aqueous solution containing FeCl₂·4H₂O (1.7 g) and FeCl₃·6H₂O (2.51 g) (molar ratio 1:2), GO (0.5 g) was added and the mixture sonicated for 30 min. The resulting mixture was deoxygenated by bubbling with nitrogen gas for10 min, followed by heating to 80 °C for 10 min. NH₄OH (10 mL, 8 M) was added rapidly to the heating solution and was left to stir for 1 h. After cooling to ambient temperature, the formed GO–Fe₃O₄ composites were magnetically collected, washed two times with deionized water (100 mL), and dried at 50 °C.

Preparation of GO@Fe₃O₄@HybPOM

To disperse 0.50 g GO-Fe₃O₄ in 30 mL in absolute ethanol, amount of 0.50 g of HybPOM was added and the mixture was sonicated for 10 min to form a homogeneous dispersion. Then, the mixture was stirred under reflux condition for 24 h. The obtained solid was then magnetically collected from the solution and washed three times with water and ethanol and dried at 50 °C. The elemental analysis of GO@Fe₃O₄@HybPOM show that the nanocomposite contains Fe, 25.00; W, 23.00 and Cu, 4.78 %.

General procedure for the Knoevenagel condensation by HybPOM

HybPOM (0.007 g) was added to a mixture of aromatic aldehyde (1 mmol), malononitrile or ethylcyanoacetate (1.2 mmol) in PEG/water = 1:1 (1 mL), and then the mixture was stirred at room temperature for the appropriate time. The progress was monitored by TLC (eluent: n-hexane/EtOAc, 2:1). After completion of the reaction, 5 mL of EtOAc was added and the catalyst was separated by centrifuge, and

then the reaction mixture was extracted with H_2O and EtOAc. The organic layer was dried over MgSO₄ and then evaporated under reduced pressure. After evaporation of EtOAc, the obtained products were recrystallized from hot EtOH and the pure products were obtained in 85-98% yields (Table 2).

General procedure for the Knoevenagel condensation by GO@Fe₃O₄@HybPOM

GO@Fe₃O₄@HybPOM (0.01g) was added to a mixture of aromatic aldehyder ACE control of the control of the control of the mixture was stirred at room temperature for the appropriate time. The progress was monitored by TLC (eluent: n-hexane/EtOAc, 2:1). After completion of the reaction, 5 mL of EtOAc was added and catalyst was separated by an external magnet, and then the mixture was extracted with H₂O and EtOAc. The organic layer was dried over MgSO₄ and then evaporated under reduced pressure. After evaporation of EtOAc, the obtained products were recrystallized from hot EtOH and pure products were obtained in 85-98% yields (Table 2).

General procedure for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones by HybPOM

A mixture of aldehydes (1 mmol), 2-aminobenzamide (1 mmol) and HybPOM (0.005 g) was stirred in ethanol (5 mL) under reflux conditions for the appropriate time, as shown in Table 4. Reaction progress was monitored by TLC. After completion of the reaction (disappearance of starting materials), the reaction mixture was cooled to room temperature, and then the catalyst was separated by centrifuge and reused as such for the next experiment. The decanted was evaporated to remove the solvent; the crude solid product was washed with diethyl ether to obtain pure 2,3-dihydroquinazolin-4(1H)-ones in 90-98% yields (Table 4).

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General procedure for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones by $GO@Fe_3O_4@HybPOM$

A mixture of aldehydes (1 mmol), 2-aminobenzamide (1 mmol) and nanocatalyst (0.007g) was stirred in ethanol (5 mL) under reflux conditions for the appropriate time as shown in Table 4. Reaction progress was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature, and then the catalyst was separated by an external magnet and reused as such for the Vintexite Online experiment. The filtrate was evaporated to remove the solvent; the crude solid product was washed with diethyl ether to obtain pure 2,3-dihydroquinazolin-4(1*H*)-ones in 90–98% yields (Table 4).

The NMR spectra data of organic products

For all NMR measurements the chemical shifts are given with respect to tetramethylsilane (TMS) as an internal standard.

2-Benzylidene-malononitrile (table 2, entry 1):Mp: 82-83 °C;⁵⁵ ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.1 (t, *J* = 8.0 Hz, 2H), 7.6 (t, *J* = 8.0 Hz, 1H), 7.8 (d, *J* = 8.20 Hz, 2H), 8 (s, 1H); ¹³C NMR (100 MHz, CDCl₃); δ = 159.3, 134.2, 133.1, 130.7, 117.2, 117.2, 86.9.

2-(4-methoxybenzylidene)malononitrile (table 2, entry 2):Mp:112-114 °C;^{55 1}H-NMR (400MHz, CDCl₃): δ (ppm):7.91 (d, *J* = 10.5 Hz, 2H), 7.65 (s, 1H), 7.01 (d, *J* = 9.0 Hz, 2H), 3.91 (s, 3H); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 158.9, 154.4, 136.4, 128.9, 121.2, 120.2, 114.3, 112.9, 111.5, 81.5, 55.9.

2-(4-nitrobenzylidene)malononitrile (table 2, entry 4):Mp:158-159 °C;⁵⁵ ¹H-NMR (400MHz, CDCl₃): δ (ppm): 8.41 (d, *J*=8.84, 2H), 8.10 (d,*J*=8.84, 2H), 7.90 (s, 1H); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 156.8, 150.4, 135.8, 131.3, 124.6, 112.6, 111.5, 87.5.

2-(2-chlorobenzylidene)malononitrile (table 2, entry 5):Mp:79-82 °C;⁵⁷ ¹H-NMR (400MHz, CDCl₃): δ (ppm): 7.80 (d, *J*=7.84, 2H), 7.74 (s, 1H), 7.71 (d, *J*=7.84, 2H); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm):158.4, 133.1, 131.8, 129.9, 129.6, 113.4, 112.3, 83.5.

2-(4-chlorobenzylidene)malononitrile (table 2, entry 6):Mp:162-164 °C ;^{58 1}H-NMR (400MHz, CDCl₃): δ (ppm):7.78(m, 3H), 7.69(d, *J*=6.8 Hz, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm):159.6, 134.2, 132.9, 131.1, 130.8, 114.6, 113.5, 84.6.

Ethyl 2-cyano-3-(3-nitrophenyl)acrylate(table 2, entry 8):Mp:130-132 °C_{DOI:101039}/CoRA15339A (400MHz, CDCl₃): δ (ppm):1.44 (t, *J* = 8.00 Hz, 3H), 4.44 (q, *J* = 8.10 Hz, 2H), 7.28 (d,*J* = 8.20 Hz, 1H), 7.76 (t,*J* = 8.25 Hz, 1H), 8.33 (s, 1H), 8.43(d,*J* = 8.78 Hz, 1H), 8.72 (s, 1H); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm):160.9, 151.2, 148.2, 134.8, 132.4, 130.0, 126.4, 126.2, 113.9, 106.3, 62.6, 13.5.

Ethyl 2-cyano-3-phenylacrylate (table 2, entry 9):Mp:50-52 °C;⁵⁵ ¹H-NMR (400MHz, CDCl₃): δ (ppm):1.49(t, *J*= 6.8 Hz, 3H) 4.16(q, *J*= 6.8 Hz, 2H) 6.99-7.01 (m, 3H) 7.65 (d, *J*=8.4Hz, 1H) 7.66-7.90 (m, 2H);¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 162.5, 155.1, 155.0, 133.3, 131.4, 131.1, 129.3, 115.5, 103.0, 62.7, 14.2.

Ethyl 3-(4-chlorophenyl)-2-cyanoacrylate (table 2, entry 12):Mp:87-89 °C;^{60 1}H-NMR (400MHz, CDCl₃): δ (ppm):8.20 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 4.39 (q, *J* = 7.2 Hz,2H), 1.40 (t, *J* = 7.2 Hz, 3H); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 162.2, 153.3, 139.5,132.1, 129.9, 129.6, 115.2, 103.6, 62.8, 14.1.

2-Phenyl-2,3-dihydroquinazolin-4(1*H***)-one(table 4, entry 1):**Mp:223-224 °C;⁶² ¹H-NMR (400 MHz, DMSO-d6): δ (ppm):8.29 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 7.1 Hz, 2H), 7.41-7.35 (m, 3H), 7.26 (t, *J* = 7.8 Hz, 1H), 7.11 (s, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 6.69 (t, *J* = 7.8 Hz, 1H), 5.76 (s, 1H); ¹³C-NMR (100 MHz, DMSO-d6) δ (ppm):163.6, 147.8, 141.6, 133.3, 128.4, 128.3, 127.3, 126.8, 117.1, 114.9, 114.4, 66.5.

2-(4-Bromophenyl)-2,3-dihydoquinazolin-4(1H)-one (table 4, entry 2):Mp:197-200 °C;⁵² ¹H-NMR (400 MHz, DMSO-d6): δ (ppm):8.17-8.13 (m, 1H), 7.80-7.78 (m, 1H), 7.63-7.60 Published on 14 October 2016. Downloaded by Lund University on 15/10/2016 11:08:29

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(m, 3H), 7.47-7.45 (m, 2H), 7.28-7.24 (m, 1H), 6.74 (d, *J*= 8.4, 1H), 6.71-6.68 (m, 1H), 5.76 (s, 1H); ¹³C-NMR (100 MHz, DMSO-d6) δ (ppm):164.3, 154.4, 148.1, 133.9, 132.3, 130.2, 130.0, 127.8, 126.5, 118.1, 117.8, 114.9, 110.3, 61.3.

2-(4-Chlorophenyl)-2,3-dihydroquinazolin-4(1*H*)-one(table 4, entry 4):Mp:202-203 °C;⁶² ¹H-NMR (400 MHz, DMSO-d6): δ (ppm):8.33 (s, 1H), 7.62 (dd, *J* = 8.0 Hz, *J* = 1.1 Hz, 1H), 7.52 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.27-7.23 (m, 1H), 7.14 (s, 1H), 6.76 (dd, *J* = 8.0 Hz, *J* = 1.1 Hz,1H), 6.70-6.66 (m, 1H), 5.77 (s, 1H); ¹³C-NMR (100 MHzce Online DMSO-d6) δ (ppm):163.4, 147.6, 140.6, 133.3, 132.9, 128.7, 128.2, 127.3, 117.2, 114.9, 114.4, 65.7.

2-(2-Chlorophenyl)-2,3-dihydroquinazolin-4(1*H*)-one (table 4, entry 5): Mp: 228-230 °C ;⁶³ ¹H-NMR (400 MHz, DMSO-d6): δ (ppm):8.40 (s, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.53 (s, 1H), 7.44-7.41 (m, 3H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.21 (s, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 6.70 (t, *J* = 7.6 Hz, 1H), 5.78 (s, 1H); ¹³C-NMR (100 MHz, DMSO-d6) δ (ppm):164.1, 148.3, 141.9, 137.9, 133.6, 129.5, 128.7, 127.8, 127.6, 124.3, 117.6, 115.2, 114.8, 66.9.

2-(2-Hydroxy-4-methoxyphenyl)-2,3-dihydroquinazolin-4(1H)-one(table 4, entry 6): Mp:262-263 °C;^{64 1}H-NMR (400 MHz, DMSO-d6): δ (ppm):9.35 (s, 1H), 7.68 (d, J = 6.8 Hz, 1H), 7.57 (s, 1H), 7.22 (d, J = 8.4 Hz, 1H), 7.15-7.13 (m, 1H), 6.98 (s, 1H), 6.68-6.66 (m, 2H), 6.38 (s, 1H), 6.29-6.27 (m, 1H), 5.96 (s, 1H), 3.65 (s, 3H); ¹³C-NMR (100 MHz, DMSO-d6) δ (ppm):163.5, 159.2, 147.7, 143.3, 133.3, 129.4, 127.3, 118.9, 117.0, 114.9, 114.3, 113.6, 112.5, 66.2, 55.0.

2-(3-Nitrophenyl)-2,3-dihydoquinazolin-4(1H)-one(table 4, entry 7): Mp:180-182 °C;⁶³ ¹H-NMR (400 MHz, DMSO-d6): δ (ppm):8.25 (s, 1H), 8.09 (d, *J*= 7.2, 1H), 7.89 (d, *J*= 6.4, 1H), 7.83-7.80 (m, 1H), 7.70-7.63 (m, 2H), 7.30 (t, *J*= 7.2, 1H), 7.04 (s, 1H), 6.80-6.72 (m, 2H), 6.36 (s, 1H); ¹³C-NMR (100 MHz, DMSO-d6) δ (ppm):163.2, 149.3, 147.4, 147.2, 133.5, 128.0, 127.3, 123.5, 117.4, 114.8, 114.5, 65.2. **2-(4-Methoxyphenyl)-2,3-dihydoquinazolin-4(1***H***)-one(table 4, entry 9): Mp:182-183 °C;⁶⁴ ¹H-NMR (400 MHz, DMSO-d6): δ (ppm):8.20 (s, 1H), 7.64-7.62 (d,** *J***= 6, 1H), 7.28-7.24 (t,** *J***= 6, 1H), 7.15 (d,** *J***= 1.6, 1H), 7.04-6.97 (m, 2H), 6.95 (s, 1H), 6.78-6.76 (d,** *J***= 8, 2H), 5.71 (s, 1H), 3.77 (s, 3H); ¹³C-NMR (100 MHz, DMSO-d6) δ (ppm):163.6, 159.4, 147.9, 133.4, 133.2, 128.1, 127.3, 117.0, 114.9, 114.3, 113.6, 66.2, 55.1.**

2-(4-Methylphenyl)-2,3-dihydroquinazolin-4(1*H*)-one (table 4, entry 10): Mp: 225-226 °C ;⁴⁹ ¹H-NMR (400 MHz, DMSO-d6): δ (ppm):8.22 (s, 1H), 7.62 (dd, *J* = 8.0 Hz, *J*^{View} Article Online Hz, 1H) 7.38 (d, *J* = 7.8 Hz, 2H), 7.25-7.21 (m, 1H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.04 (s, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.68-6.64 (m, 1H), 5.71 (s, 1H), 2.29 (s, 3H); ¹³C-NMR (100 MHz, DMSO-d6) δ (ppm):164.1, 148.4, 139.1, 138.2, 133.7, 129.3, 127.8, 127.2, 117.5, 115.4, 114.9, 66.8, 21.2.

Results and discussions

In this paper, we report a simple and mild synthesis route through self-assembly polyoxometalate and *p*-phenylenediamine (PPD) as organic ligand π -electron donor to produce a polyoxometalate-based inorganic-organic hybrid. First, by addition of Cu²⁺ ion to the lacunary 9-tungstosilicate, β -SiW₉O₃₄¹⁰⁻ solution, trimetallo derivatives of [SiW₉Cu₃O₃₇]¹⁰⁻ are formed. The solution color is turned from colorless to blue. With addition of PPD molecule to the blue aqueous solution, a blue-brown precipitate formed. PPD molecule via one of its NH₂ groups replaced terminal water molecules from substituted Cu²⁺ ions. The precipitate color finally changed from blue-brown to black because of charge transfer interaction between POM cluster anion and PPD organic molecule.²⁶ The proposed structure for anionic section of nanohybid material is shown in Fig. 1.

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Fig. 1 The proposed structure to anionic section of nanohybrid materials of HybPOM.

For easier recovery and separation instead of centrifuge, functionalized nanosized polyoxometalate of HybPOM was placed on the GO-Fe₃O₄ magnetic nanoparticles. GO-Fe₃O₄ nanoparticles were prepared by Hummers' method procedure.²⁵

A quantitative analysis of O 1s XPS spectra of GO sample by Gaussian curves fitting show that the relative atomic concentrations (atom %) of carboxyl or carbonyl groups, epoxy, hydroxyl, or carboxyl groups, and oxygen atoms in water and/or chemisorbed oxygen species are 24.08, 47.56 and 28.35%, respectively.

Due to abundant functional groups (such as epoxy, hydroxyl, and carboxyl groups) on the surface, graphene oxide (GO) is ready to the attack the nucleophiles.

Organic compounds with functional amine groups may be loaded onto GO surface through the nucleophilic substitution followed by formation of C-N bond. It may also be loaded onto the surface of graphene oxide by the chemical reaction between amino groups and carboxylic acid groups on the edge of GO sheets (scheme 1). Such methods are strong enough to firmly deposit organic substrates with amine groups on the graphene oxide sheets.²⁷

Common methods such as titration with Hammett indicators and temperature programmed desorption of adsorbed molecules such as ammonia or pyridine, adsorption microcalorimetry

and NMR spectroscopy have been employed to describe the acidity of POMs in the solid state both qualitatively and quantitatively. Potentiometric titration with n-butylamine allows us to estimate the number of acid sites and their distribution.²⁸ The titration curves show that HybPOM and Go/Fe₃O₄/HybPOM with the initial electrode potential -165.9 and -73.8 mV are classified as very weak and weak acids, respectively. Difference in the acid strength of HybPOM and Go/Fe₃O₄/HybPOM is attributed to the total number of free NH₂ groups on them. For Go/Fe₃O₄/ HybPOM, some of the NH₂ groups are involved in the bonding extint contract of Go/Fe₃O₄/HybPOM is attributed to HybPOM and Go/Fe₃O₄/HybPOM is presented in the supporting information (Fig. S3).





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Fig. 2 FT-IR spectra of (a) PPD, (b) $[SiW_9O_{37}Cu_3(H_2O)_3]^{10-}$ and (c) HybPOM.

FT-IR spectra of HybPOM hybrid material show the characteristic band of PPD and the trimetallo derivatives of $[SiW_9O_{37}Cu_3(H_2O)_3]^{10}$ heteropolyanions moieties with some variations in the band vibrational frequencies or intensities (Fig. 2). The alkaline salts of complex anions which often crystallize with many water molecules and involve hydrogen bonds lead to a decrease in the frequencies of the metal-oxygen stretching. With large organic PPD molecules,²⁹ as is expected, the effects arising from cation size, cation polarizing power and crystallization solvent molecules are diminished so that the POM characteristic bands are observed clearly in the range $1000-700 \text{ cm}^{-1}$.

The N–H stretch band (3300–3400cm⁻¹) from PPD molecule overlap with OH stretching vibration band (~3500 cm⁻¹) from water molecule but other bands can be observed in the IR spectra of HybPOM hybrid materials.

In Fig. 3 FT-IR spectra of GO, GO/Fe₃O₄, HybPOM were given for comparison with that of GO@Fe₃O₄@HybPOM.



Fig. 3 FT-IR spectra of (a) GO, (b) GO/Fe₃O₄, (c) HybPOM and (d) GO@Fe₃O₄@HybPOM.

Peaks at 573-630 cm⁻¹ in the IR spectra of GO/Fe₃O₄ and GO@Fe₃O₄@HybPOM are attributed to Fe–O stretching vibration. The complete IR pattern of corresponding trimetallo POM of $[SiW_9Cu_3O_{37}]^{10-}$ with some variations in band frequencies and intensities were observed in those of GO@Fe₃O₄@HybPOMin range of 1000-700 cm⁻¹. A small blue shift is observed in the frequencies of the band stretching due to disappearance of anion-anion interactions. The vibration modes of the quinoidal benzene rings appear at 1510 and 1620 cm⁻¹ for GO@Fe₃O₄@HybPOM which overlapped with the bending vibrations of amide bond of N–H.³⁰ The C-N stretching vibrations appear at 1200-1400 cm⁻¹. The O-H and N-H stretching vibrations appear as broad and strong bands at range of 3200-3650 cm⁻¹.

The GO-Fe₃O₄ powder exhibit a total mass loss of 12.35 % at 100-800 °C, which are attributed to the removal of adsorbed water and the decomposition and vaporization of various oxygen-containing functional groups at different positions on the surface of the GO-Fe₃O₄ (Fig. 4a).

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Fig. 4 TG analysis of (a) GO@Fe₃O₄, (b) HybPOM and (c) GO@Fe₃O₄@HybPOM.

The thermogravimetric analysis (TGA) curve of the hybrid materials HybPOM show two mass loss regions below 600°C (Fig. 4b). First, 30–200°C with 6.12 weight loss which are assigned to lattice water loss equal to 12 (6.24 %) molecules for HybPOM. Second, 200–550°C with approximately 18.19 weight loss for HybPOM is attributed to loss of 6 (18.73 %) PPD molecules.

Results of TGA are confirmed well by CHN analysis of HybPOM. TGA of $GO@Fe_3O_4@HybPOM$ (Fig. 4c) nanocomposite exhibit two steps of mass loss at 25-225 °C and 225-800 °C with 8.60 and 17.50% weight loss, respectively, which are attributed to the release of water and PPD molecules along oxygen-containing functional groups on GO-Fe_3O_4 surface..

This large weight loss indicates the loading of the polyoxometalate-based inorganicorganic hybrid material on the GO-Fe₃O₄. From the TGA curves, it can be concluded that GO@Fe₃O₄@HybPOM nanocomposites exhibit a higher thermal stability than

HybPOM nanohybrides. This enhancement in the thermal stability is due to some ionic interaction between graphene-Fe₃O₄ and the amine group of the aniline ring. These may form a coordinate bond between Fe and N, as Fe can facilitate back bonding between the d-orbital and NH_2 group of the aniline ring.³⁰



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Fig. 5 XRD spectra of (a) Na₉H[β -XW₉O₃₄]·nH₂O, (b) HybPOM, (c) GO@Fe₃O₄ (d) GO@Fe₃O₄@HybPOM and (inset) GO.

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The compounds of β -SiW₉O₃₄¹⁰⁻ (Fig. 5a) and PDA are crystalline in the solid state, while X-ray powder diffractions show that HybPOM is typical amorphous state, implying that the hybrid materials have less-ordered structures (Fig. 5b). However, it can be observed that the XRD of HybPOM contain XRD pattern of both β -SiW₉O₃₄¹⁰⁻ and PPD. X-ray diffraction (XRD) measurements were also performed to obtain crystalline structural information for the GO, GO-Fe₃O₄, GO@Fe₃O₄@HybPOM. The broad diffraction peak around 18.72° corresponds to C (002) reflection of GO (Fig. 5 inset).³⁰

At the GO-Fe₃O₄, the intense diffraction peaks indexed to (220), (311), (400), (422), (511), (440), and (533) planes appearing at $2\theta = 30.52^{\circ}$, 35.85° , 43.58° , 53.96° ,

57.43°, 63.16° and 74.65°, respectively, and the peak positions and relative intensities match well with the standard XRD data for the cubic phase Fe₃O₄ with a face-centered cubic (fcc) structure (JCPDS No. 19–629) (Fig. 5c).³¹ Disappearance of the reflection plane at (002) and merging of the planes of Fe₃O₄ show the good interfacial interaction between the planes. The XRD of GO@Fe₃O₄@HybPOM show corresponding peaks of the GO-Fe₃O₄ and the amorphous XRD pattern of HybPOM as background (Fig. 5d).



Fig. 6 SEM images of (a) HybPOM, (b) GO, (c) GO@Fe₃O₄(d) GO@Fe₃O₄@HybPOM

The SEM images of HybPOM reveal the relatively uniform spherical nanometer particles with a diameter of less than 80 nm (Fig. 6a). The SEM images of GO sheets, GO-Fe₃O₄, and GO@Fe₃O₄@HybPOM composites are presented in Fig. 6b-c. The images illustrate that the GO sheets shows a stacked and crumpled morphology (Fig. 6b).³² From the SEM image, it could be observed that the surface of GO sheets were decorated tightly with Fe₃O₄ nanoparticles (Fig. 6c).

Interestingly, Fe₃O₄ nanoparticles were only observed on the basal surface and the edges of GO at very high coverage and without significant aggregation. This indicates that Fe₃O₄ nanoparticles were mainly nucleated and grown on GO substrate and that their free nucleation was effectively suppressed. The stacking of GO-Fe₃O₄ observed in SEM images is probably due to strong magnetic interaction among Fe₃O₄ nanoparticles in neighboring layers. The SEM images of GO@Fe₃O₄@HybPOM show that these magnetic nanocomposites are uniform with a mean size of $\frac{50^{\circ}}{10.1039/C0RA15339A}$ particles, but with some self-aggregation (Fig. 6d).

In order to shed more light on the elemental composition and preparation progress, the chemical compositions of HybPOM and GO@Fe₃O₄@HybPOM were analyzed by EDX. The EDX analysis of HybPOM hybrid material shows peaks of W, O, Si, C, N, Cu (Fig. 7a).



Fig. 7 EDX spectra of (a) HybPOM, (b) GO@Fe₃O₄@HybPOM.

The magnetization of GO–Fe₃O₄ and GO@Fe₃O₄@HybPOM was measured at room temperature, as shown in Fig. 8. The magnetic hysteresis loops are S-like curves. For GO–Fe₃O₄ hybrid, the magnetic remanence was nearly zero (Fig. 8a). This indicated that there was almost no remaining magnetization when the external magnetic field was removed, suggesting that GO–Fe₃O₄ exhibit a superpara magnetic behavior.





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Fig. 8 Magnetization curves of (a) GO@Fe₃O₄, (b) GO@Fe₃O₄@HybPOM.

The specific saturation magnetization of GO–Fe₃O₄, is 49.31emu/g, which is smaller than the reported value of bulk Fe₃O₄ of 92 emu/g.³³ The specific saturation magnetization of GO@Fe₃O₄@HybPOM is 17.94 emu/g (Fig. 8b). Decrease in saturation magnetization observed for GO@Fe₃O₄@HybPOM could be attributed to the increased mass and the loading polyoxometalate-based inorganic–organic hybrids. Even with this reduction in the saturation magnetization, complete magnetic separation of GO@Fe₃O₄@HybPOM was achieved in <10 s by placing a magnet near the vessels containing the aqueous dispersion of the nanoparticles.

XPS analysis was used to gain further insights into chemical compositions of samples. Fig. 9a depicts the XPS survey spectrum of GO@Fe₃O₄@HybPOM. As expected, W 4f, C 1s, N 1s, O 1s, Fe 2p and Cu 2p peaks were observed in the XPS survey spectrum. The W 4f spectrum can be deconvoluted into doublets, as indicated in Fig. 9b. This doublet consists of W 4f_{7/2} line at 35.2 eV and W 4f_{5/2} line at 37.2 eV, which are assigned to the W in the W–O bond configuration and typically observed for the W^{6+} .³⁴



Fig. 9 XPS survey spectra of (a) GO@Fe₃O₄@HybPOM and high-resolution XPS spectra of N 1s (inset), and Cu 2p (inset) (b)W 4f, (c) C 1s, (d) O 1s, (e) Fe 2p.

The peaks observed at 284.5 and 530.4 eV (Fig. 9c and d) can be assigned to the binding energy of C 1s and O 1s, respectively. From the C1s XPS spectrum, different peaks corresponding to C-C, C-N, C-O and C=O are observed at 284.5, 285.3, 286.0 and 286.8, respectively. The peak of the COOH at 287.8 eV almost disappeared upon the amide formation with the amine groups of HybPOM. The binding energy appears at 399-402 eV which could be attributed to the N1s protonated and nonprotonated N atoms (Fig. 9a inset). The binding energy peaks at 711.8 and 725.1 eV (Fig. 9e) are corresponding to Fe 2p_{3/2} and Fe 2p_{1/2}, respectively, which are very close to the literature values.³⁵ The disappearance of charge transfer satellite of Fe 2p_{3/2} around 720 eV reveals the formation of mixed oxides of Fe²⁺ and Fe³⁺ such as Fe₃O₄. The XPS spectra from 953 to 935 eV demonstrate the photoelectron spectrum of the Cu 2p. As shown in Fig. 9a (inset), there are two main Cu 2p XPS peaks at 933.2 and 953.1 eV, which could be due to the Cu²⁺ double peaks for Cu 2p_{3/2} and Cu 2p_{1/2}, respectively.³⁶⁻³⁸ The satellite peak at 941.6 eV located at higher binding energy than

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that of the main Cu $2p_{3/2}$ peak, is typically associated with copper in the bivalent binding energy state.³⁶⁻³⁹

Catalytic studies

Catalytic application of nanohybrids of HybPOM and nanocomposites of GO@Fe₃O₄@HybPOM for the Knoevenagel condensation

The Knoevenagel reaction is one of the most important reactions to form C-C bonds to the important olefin syntheses. The Knoevenagel adducts are_{DOL} availabilities online intermediates for further transformations such as Diels–Alder and Michael additions.⁴⁰ Knoevenagel condensations of aldehydes and active methylene compounds have been carried out in the presence of a base⁴¹ or Lewis acid.⁴² In this study, the catalytic activity of HybPOM organic–inorganic polyoxometalates hybrids were investigated in the Knoevenagel condensation reaction as novel, efficient and heterogeneous catalysts under mild conditions. First, in order to optimize the Knoevenagel condensation reaction conditions, the reaction was achieved with benzaldehyde and malononitrile as model reaction (Table 1).

Table 1. Optimization of different parameters for the synthesis of benzylidenemalononitrile^a.

	С ^о Ц	H + (
Entra	HybPOM (GO@Fe3O4@HybPOM) (g)	solvent	T(°C)	HybPOM			GO@Fe3O4@HybPOM		
				Time	Conversion	Yield b(%)	Time	Conversion	Yield b(%)
1	0 (0)	H ₂ O	r.t	10 h	trace	trace	10h	trace	trace
2	0.02 (0.02)	H ₂ O	r.t	10h	30	20	10h	40	35
3	0.04 (0.04)	H ₂ O	70	10h	50	45	10h	40	37
4	0.005 (0.007)	PEG/H2O	r.t	70 min	100	80	60min	100	98
5°	0.007 (0.010)	PE G/H ₂ O	r.t	10 m in	100	96	20min	100	98
6	0.010 (0.01)	PEG/H2O	r.t	10 min	100	95	20min	100	96
7	0.030 (0.03)	PEG/H2O	r.t	10 min	100	94	20min	100	95
8	0.007 (0.010)	PEG/H2O	70	5 min	100	95	10	100	97

Reaction conditions: benzaldehyde (1 mmol), malononitrile (1.2 mmol), solvent (1 mL),), rt, air.^bIsolated yield. The bold letters represent the most effective reaction conditions.

As shown in Table 1, the amount of 0.007 g of HybPOM was found to be ideal for the Knoevenagel condensations and the best results were obtained using PEG/water = 1:1 (PEG, polyethylene glycol) as solvent. A series of aromatic aldehydes carrying either electron-donating or electron-withdrawing substitutions were subjected to the optimized reaction conditions and the expected products were obtained in short time periods and at high yields (Table 2).

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Table 2. Synthesis of benzylidenemalononitrilederivatives catalyzed by HybPOM and

GO@Fe3O4@HybPOM catalysts^a.

$ \begin{array}{c} $									
		a tat and and	Hyb (0.0	POM 07 g)	GO@Fe3O	4@HybPOM 01 g)			
Entry	R1	R ²	Time (min)	Yield (%) ^{b, c}	Time (min)	Yield (%)b.c	Conversion (%)	Mp (°C) [Ref.]	
1	C ₆ H ₄	CN	10	96	20	98	100	80-82(82-83)55	
2	4-CH3OC6H4	CN	45	95	50	95	100	111-113(112-114)55	
3	3-NO2C6H4	CN	15	90	15	97	100	99-101(101-103)56	
4	4-NO2C6H4	CN	15	96	20	97	100	156-158(158-159)55	
5	2-C1C6H4	CN	35	95	70	93	100	80-82(79-82)57	
6	4-C1C6H4	CN	20	89	30	94	100	162-163(162-164)58	
7	4-CH3OC6H4	CO ₂ Et	125	85	130	85	100	78-80(79-81)55	
8	3-NO2C6H4	CO ₂ Et	25	85	35	95	100	130-131(130-132)59	
9	C ₆ H ₄	CO ₂ Et	60	90	70	95	100	49-51(50-52)55	
10	4-NO ₂ C ₆ H ₄	CO ₂ Et	20	95	30	97	100	169-170(169-170)60	
11	2-C1C6H4	CO ₂ Et	130	95	140	92	100	48-50(48-50)61	
12	4-C1C6H4	CO ₂ Et	140	93	150	88	100	86-88(87-89)60	

^aReaction conditions: aromatic aldehyde (1 mmol), malononitrile or ethylcyanoacetate (1.2 mmol), PEG/H₂O (1 ml), rt, air. ^aIsolated yield ^aAll the products were identified and characterized by comparison of their physical and spectral data with those reported in the literature (see Supporting Information).

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There are several advantages for supporting HybPOM on the GO-Fe₃O₄, such as, easier recovery, improvement of efficiency and magnetic separation. Knoevenagel condensation was carried out to investigative the catalytic activity of $GO@Fe_3O_4@HybPOM$ nanocomposites. As shown in Table 1, amount of 0.010 g of $GO@Fe_3O_4@HybPOM$ was found to be ideal for the Knoevenagel condensations and the best results were obtained using PEG/water = 1:1 (PEG, polyethylene glycol) as solvent.

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Like the above conditions, Knoevenagel condensation was probed by $GO@Fe_3O_4@HybPOM$ catalysts under the optimized reaction conditions (Table 2). As shown in Table 1, the expected products were obtained in short time periods and at high yields.

Catalytic application of nanohybrid of HybPOM and nanocomposite of GO@Fe₃O₄@HybPOM for the synthesis of 2,3-dihydroquinazolin-4(1H)-one derivatives

2,3-Dihydroquinazolin-4(1*H*)-ones is an important class of heterocyclic compounds influencing numerous cellular processes.⁴³ These exhibit a wide range of biological activities such as antitumor, antibiotic, antidefibrillatory, antipyretic, analgesic, antihypertonic, diuretic, antihistamine, antidepressant, and vasodilating behavior.⁴⁴ Several strategies for their synthesis were already developed: condensation of anthranilamide with an aldehyde or ketone using p-toluenesulfonic acid as a catalyst,⁴⁵ desulfurization of 2-thioxo-4(3*H*)-quinazolinones,⁴⁶ reaction of isatoic anhydride with Schiff-bases,⁴⁷ one-step conversion of 2-nitrobenzamides to 2,3-dihydro-4(1*H*)quinazolinones,⁴⁸ and a one-pot three-component condensation of isatoic anhydride, aldehydes and amines.⁴⁹

The catalysts reported for the above stated one-pot procedure include inorganic catalysts like aluminiumtris (dihydrogen phosphate),⁵⁰ silica sulfuric acid,⁵¹ magnetic Fe₃O₄ particles,⁵² reaction media like ionic liquid⁵³ and Asymmetric Brønsted acid.⁵⁴Some of these methodologies involve strongly acidic conditions, toxic catalysts, hazardous organic solvents and long reaction times. Thus, there is a need for a non-acidic and novel catalyst that could overcome the above drawbacks.

After successfully synthesizing a series of benzylidenemalononitrile derivatives in excellent yields, we also explored the use of this catalyst system for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones from aldehyde derivatives and 2-aminobenzamide.

The preliminary investigation was to screen the solvent and different amounts of catalyst on the reaction of benzaldehyde with 2-aminobenzamide (Table 3). The model reaction was carried out in the presence of different solvents, temperatures and amounts of catalyst. The best results were obtained with 2-aminobenzamide (1 mmol) and benzaldehyde (1 mmol) in the presence of catalyst HybPOM (0.005 g) and EtOH (5 mL) as solvent under reflux condition (Table 3, entry 3).

 Table 3. Optimization of different parameters for the synthesis of 2,3-dihydroquinazolin-4(1H) View Article Online

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Entry	HybPOM		HybPOM			GO@F ₃ O ₄ @HybPOM		
	(GO@F ₃ O ₄ @HybPOM) (g)	Solvent (1:1)	Time (min)	Conversion (%)	Yield (%) ^a	Time (min)	Conversion (%)	Yield (%) ^a
1	0(0)	EtOH	200	trace	trace	200	trace	trace
2	0.003(0.003)	EtOH	60	85	80	70	80	70
3 ^b	0.005(0.007)	EtOH	25	100	96	45	100	85
4	0.007(0.10)	EtOH	25	100	97	30	100	97
5°	0.005(0.007)	EtOH	150	65	60	30	73	95
6 ^d	0.005(0.007)	PEG /H ₂ O	35	75	70	150	75	70
7 ^e	0.005(0.007)	PEG	30	77	75	25	82	80
8	0.005(0.007)	EtOAc	60	75	70	70	77	75
9	0.005(0.007)	CH ₂ Cl ₂	110	75	75	90	87	85

^aIsolatedyield. ^bThe bold letters represent the most effective reaction conditions, ^bsolution atrt. ^{d,e}solution at 100°C.

After optimizing the reaction conditions, the reaction of various aldehydes with 2aminobenzamide were tested. Results are summarized in Table 4. Synthesis of 2,3dihydroquinazolin-4(1H)-one derivatives was carried out to investigative catalytic activity of GO@Fe₃O₄@HybPOMnanocomposite.

The model reaction was carried out in the presence of different solvents, various temperatures and different amounts of catalyst. The best results were obtained with 2-aminobenzamide (1mmol) and benzaldehyde (1 mmol) in the presence of catalyst GO@Fe₃O₄@HybPOM(0.007 g) and EtOH (5 mL) as solvent under reflux conditions (Table 3, entry 3). After optimizing the reaction conditions, the reaction of various aldehydes with 2-aminobenzamide were tested. Results are summarized in Table 4.

Table 4. Synthesis of 2,3-dihydroquinazolin-4(1H)-one derivatives catalyzedby HybPOM and GO@Fe3O4@HybPOM catalysts.

$R^{CHO} + CONH_2 - Cat.$ $R^{Cat.} + CONH_2 - Cat.$ $R^{Cat.} + $									
		НуъРОМ (0.005 g)		GO@FejQ.@	НуьРОМ (0.007)				
Entry	Aldehyde	Time (min)	Yield (%) ^{a,b}	Time (min)	Yield (%)**	Mp (°C) [Ref.]			
1	С—сно	30	97	30	97	223-224(224,224,226,226 Online DOI: 10.1039/C6RA15339A			
2	в — Сно	30	90	40	98	197-200(198-200) ³²			
3	CHO Br	45	88	50	93	184185(184)54			
4	с1-СНО	40	95	45	95	202–203(198-201) ⁶²			
5	С	55	92	55	90	228-230(230-231) ⁴³			
6	н,со-Сно	30	95	30	96	262-263(262-263)54			
7	NO ₂ CHO	50	90	60	90	180-182(180-182) ⁶³			
8	C BO	35	92	45	95	165-167(165-166) ⁴⁵			
9	н,со — — сно	25	90	30	95	182-183(182-183)64			
10	н,с-Сно	40	93)	50	95	225-226(223-225)**			

*All the products were identified and characterized by comparis on of their physical and spectral data with those reported in the literature (see Supporting Information). *Isolated Yield.





Catalysts recovery and reuse

Finally, the reusability of the nanohybrid and nanocomposite were investigated. Fig. 10 shows the yield of five consecutive cycles for the preparation of 2-benzylidenemalononitrile (a) and 2-Phenyl-2,3-dihydroquinazolin-4(1*H*)-one (b) by nanohybrid of HybPOM andGO@Fe₃O₄@HybPOM, respectively.

After the reaction reached completion, the catalyst was recovered, washed with EtOAc and then reused in the next run. The heterogeneous catalyst showed good recyclability and can be reused for at least five times without significant loss of its catalytic activity. The FT-IR spectrum showed no significant structural changes for catalysts after five consecutive runs (Fig. 11). In order to determine whether the metal leaches out from the solid catalyst during reaction, the hot filtration test was undertaken for the synthesis of 2-(3-bromophenyl)-2,3-dihydoquinazolin-4(1H)-one from the reaction of 2-aminobenzamide with 3-bromobenzaldehyde. The catalyst was separated by applying an external magnet when the reaction had proceeded to nearly 50% completion, and the filtrate was allowed to react further.



Fig. 11 FT-IR spectra of (A) (a) recycled HybPOM for 5 times (b) HybPOM and (B) (a) recycled GO@Fe₃O₄@HybPOM for 5 times (b) GO@Fe₃O₄@HybPOM.

The reaction monitoring showed that no further progress of the reaction is observed, confirming that the metal does not leach from the nanocatalyst under hot conditions. The metal Fe, W and Cu leaching from $GO@Fe_3O_4@HybPOM$ were tested by ICP-MS. The results showed that Fe, W and Cu contents of the $GO@Fe_3O_4@HybPOM$ after consecutive runs compared with those of the initial $GO@Fe_3O_4@HybPOM$ were only decreased by less than 1 %.

Conclusion

In summary, in this paper we have described 1) a simple and high yield synthesis of new functionalized organic–inorganic polyoxometalates hybrids of $H_6Cu_2[PPD]_6[SiW_9Cu_3O_{37}].12H_2O$ (HybPOM) and 2) preparation of new $GO@Fe_3O_4@HybPOM$ nanocomposite by successfully supporting of HybPOM onto graphene oxide decorated with Fe_3O_4 nanoparticles. HybPOM -functionalized

graphene hybrid materials were synthesized by covalently bonding HybPOM onto grapheme oxide via the amide formation and the chemical reaction between aminefunctionalized POM and oxygen-containing groups (e.g., epoxy and carboxyl groups) in graphene oxide. The new organic-inorganic polyoxometalates hybrid and nanocomposite were characterized by the elemental analyses, TGA, FT-IR, XPS, XRD, SEM, EDX and AGFM. The results indicate that the size ranges of the nanocomposites are between 20-60 nm. The catalytic activity of new NPsview Agisle Online DOI:10.1039/CGRA15339A synthesis investigated the Knoevenagel condensation 2,3in and of dihydroquinazolin-4(1H)-ones. The nano organic-inorganic hybrids and their magnetically reusable nanocomposites were found as effective and easily recoverable heterogeneous catalyst for a wide range of arylaldehydes. Therefore, the newly developed hybrid materials are promising for a wide range of multifunctional applications.

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References

(a) M. T. Pope, *Heteropoly and Isopoly Oxometalates*; Springer: Berlin, 1983, (b)
 F. Hussain, U. Kortz, B. Keita, L. Nadjo and M. T. Pope, *Inorg. Chem.*, 2006, 45, 761.
 Y. Ono. In *Perspectives in Catalysis*; J. M. Thomas, K. I. Zamaraev, Eds.;
 Blackwell: London, 1992; p 341.

3 (a) I. V. Kozhevnikov, Russ. *Chem. Rev.*, 1987, **56**, 811; (b) F. Lefebvre, F. X. Liu-Cai and A. Auroux, *J. Mater. Chem.*, 1994, **4**, 125.

4 Y. Izumi, K. Urabe, M. Onaka, Zeolite, Clay and Heteropoly Acids in Organic Chemistry, VCH, Weinheim, Kodansha, Tokyo, 1992.

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RSC Advances

- 5 I. V. Kozhevnikov, Chem. Rev., 1998, 98, 171.
- 6 N. Mizuno and M. Misono, Chem. Rev., 1998, 98, 199.
- 7 M. Kooti and M. Afshari, Mater. Res. Bull., 2012, 47, 3473.
- 8 X. M. Yan, J. H. Lei, D. Liu, Y. C. Wu and W. Liu, *Mater. Res. Bull.*, 2007, **42**, 1905.
- 9 N. Dubey, S. S. Rayalu, N. K. Labhsetwar and S. Devotta, Int. J. Hydrogen Energy,

2008, 33, 5958.

View Article Online DOI: 10.1039/C6RA15339A

- 10 K. Zhu, D. Wang and J. Liu, Nano Res., 2009, 2, 1.
- 11 A. Dolbecq, E. Dumas, C. R. Mayer, and P. Mialane, Chem. Rev., 2010, 110, 6009.
- 12 C. Sanchez and F. Ribot, New. J. Chem., 1994, 18, 1007.
- 13 P. Judeinstein and C. Sanchez, J. Mater. Chem., 1996, 6, 511.
- 14 S. Liu and Z. Tang, Nano Today, 2010, 5, 267.
- 15 D. Gatteschi, L. Pardi, A. L. Barra and A. Müller, Nature, 1991, 354, 463.
- 16 S. Laurent, D. Forge, M. Port, A. Roch, C. Robic, L. V. Elst and R. N. Muller, *Chem. Rev.*, 2008, **108**, 2064.
- 17 A. Hu, G. T. Yee and W. Lin, J. Am. Chem. Soc., 2005, 127, 12486.
- 18 K. Nakada, M. Fujita and G. Dresselhaus, Phys. Rev. B, 1996, 54, 17954.
- 19 H. He, J. Klinowski and M. Forster, Chem. Phys. Lett., 1998, 287, 53.
- 20 J. P. Tessonnier, S. Goubert-Renaudin, Sh. Alia, Y. Yan and M. A. Barteau, *Langmuir*, 2013, **29**, 393.
- 21 A. H. Lu, E. L. Salabas and F. Schüth, Angew. Chem., Int. Ed., 2007, 46, 1222.
- 22(a) G. M. Scheuermann, L. Rumi, P. Steurer, W. Bannwarth and R. Mulhaupt, *J. Am. Chem. Soc.*, 2009, **131**, 8262; (b) N. R. Shiju and V. V. Guliants, *Appl. Catal. A: Gen.*, 2009, **356**, 1; (c) L. D. Pachon and G.Rothenberg, *Appl. Organomet. Chem.*, 2008, **22**, 288.

View Article Online DOI: 10.1039/C6RA15339A

23(a) V. Polshettiwar and R. S. Varma, Tetrahedron, 2010, 66, 1091; (b) K. Wang, L.

X. 5 Yu, S. Yin, H. Li and H. Li, Pure Appl. Chem., 2009,81, 2327; (c) W. Liu, B. J.

Li, C. L. Gao and Z. Xu, Chem. Lett., 2009,38, 1110.

24 G. Herve and A. Teze, Inorg. Chem., 1977, 16, 2115.

25 M. Hirata, T. Gotou, S. Horiuchi, M. Fujiwara and M. Ohba, *Carbon*, 2004, **42**, 2929.

26 J. L. Xu, M. Li and E. Wang, *Materials Letters*, 2002, **54**, 303.

27 J. Li, X. Zeng, T. Renand and E. V. D. Heide, Lubricants, 2014, 2, 137.

28 E. Rafiee, M. Joshaghani, S. Eavani and S. Rashidzadeh, Green Chem., 2008, 10, 982.

29 C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck and R. Thouvenot, *Inorg. Chem.*, 1983, **22**,207.

30 K. Singh, A. Ohlan, V. Hung Pham, R. Balasubramaniyan, S. Varshney, J. Jang, S. H. Hur, W. M. Choi, M. Kumar, S. K. Dhawan, B. S. Kongd and J. S. Chung, *Nanoscale*, 2013, **5**, 2411.

31 B. Shen, W. Zhai, M. Tao, J. Ling, and W. Zheng, *ACS Appl. Mater. Interfaces*, 2013, **5**, 11383.

32 J. C. Meyer, A. K. Geim, M. I. Katsnelson, K. S. Nosvoselov, T. J. Booth and S. Roth, *Nature*, 2007, **446**, 60.

33X. Yang, X. Zhang, Y. Ma, Y. Huang, Y. Wang and Y. Chen, J. Mater. Chem., 2009, **19**, 2710.

Published on 14 October 2016. Downloaded by Lund University on 15/10/2016 11:08:29

34 L. Salvati, L. E. Makovsky, J. M. Stencel, F. R. Brown and D. M. Hercules, J. Phys. Chem. 1981, 85, 3700.

35 S. H. Xuan, W. Q. Jiang, X. L. Gong, Y. Hu and Z. Y. Chen, *J. Phys. Chem. C*, 2009, **113**, 553.

36 Z. H. Ai, L. Z. Zhang, S. C. Lee and W. K. Ho, J. Phys. Chem. C, 2009, 113, 20896.

Published on 14 October 2016. Downloaded by Lund University on 15/10/2016 11:08:29

RSC Advances

- 37 Q. Hua, D. L. Shang, W. H. Zhang, K. Chen, S. J. Chang, Y. S. Ma, Z. Q. Jiang, J.
- L. Yang and W. X. Huang, Langmuir, 2011, 27, 665.
- 38 J. H. Zhong, G. R. Li, Z. L. Wang, Y. N. Ou and Y. X. Tong, Inorg. Chem., 2011, **50**, 757.
- 39 H. Zhu, M. Du, D. Yu, Y. Wang, L. Wang, M. Zou, M. Zhang and Y. Q. Fu, J.
- Mater. Chem. A, 2013, 1, 919.
- 40 L. F. Tietze, Chem. Rev., 1996, 96, 11.
- 41 T. Sugino and K. Tanaka, Chem. Lett., 2001, 30, 110.
- 42 D. S. Bose and A. V. Narsaiah, J. Chem. Res. S., 2001, 3, 36.
- 43 D. J. Connolly, D. Cusack, T. P. O'Sullivan and P. J. Guiry, Tetrahedron, 2005, 61 10153; N. Isambert, M. M. S. Duque, J. C. Plaquevent, Y. Ge'nisson, J. Rodriguez and T. Constantieux, Chem. Soc. Rev., 2011,40, 1347; M. A. P. Martins, C. P. Frizzo, A. Z. Tier, D. N. Moreira, N. Zanatta, and H. G. Bonacorso, Chem. Rev., 2014, 114 (20), PR1-PR70; P. Murthy, D. Rambabu, G. R. Krishna, C. M. Reddy, K. R. S. Prasad, M. V. Basaveswara Rao and M. Pal, Tetrahedron Lett., 2012, 53, 863.
- 44 B. V. Subba Reddy, A. Venkateswarlu, C. Madan and A. Vinu, Tetrahedron Lett., 2011, 52, 1891.
- 45 M. Bakavoli, O. Sabzevari and M. Rahimizadeh, Chin. Chem. Lett., 2007, 18, 1466.
- 46 J. M. Khurana and G. Kukreja, J. Heterocycl. Chem., 2003, 40, 677.
- 47 V. B. Rao and C. V. Ratnam, Indian J. Chem. Sect. B., 1979, 18,409.
- 48 C. L. Yoo, J. C. Fettinger and M. J. Kurth, J. Org. Chem., 2005, 70, 6941.
- 49 M. Wang, T. Zhang, Y. Liang and J. Gao, Chin. Chem. Lett., 2011, 22, 1423.
- 50 R. S. Hamid, R. O. Ali and H. Moones, Synth. Commun., 2010, 40, 1231.
- 51 S. Peyman, D. Minoo, A. Z. Mohammad and B. Mostafa, Syn. letters, 2005, 7, 1155.

- View Article Online DOI: 10.1039/C6RA15339A

52 A. Rostami, B. Tahmasbi, H. Gholami and H. Taymorian, *Chin. Chem. Lett.*, 2013,24, 211.

53 J. X. Chen, W. K. Su, H. Y. Wu, M. C. Liu and C. Jin, Green Chem., 2007, 9, 972.

54 M. Rueping, A. P. Antonchick, E. Sugiono and K. Grenader, *Angew. Chem. Int. Ed.*, 2009, **48**, 908.

55 J. A. Cabello, J. M. Campelo, A. Garica, D. Luna, J. M. Marinas, *J. Org. Chem.*,
 1984, 49, 5195.

56 Y. Q. Cao, Z. Dai, R. Zhang and B. H. Chen, Synth. Commun., 2004, 34, 2965.

57 C. Yue, A. Mao, Y. Wei and M. Lu, Catal. Commun., 2008, 9, 1571.

58 In: Aldrich Chemical Co. (Ed.), The Aldrich Library of Infrared Spectra 3rd ed., 1981.

59 A. K. Mitra, A. De and N. Karchaudhuri, Synth. Commun., 1999, 28, 2731.

60 B. M. Choudrary, M. Lakshmi-Kantam, B. Kavita, C. V. Reddy and F. Figueras, *Tetrahedron*, 2000, **56**, 9357.

61 A. Kumar, M. Dewan, A. Saxena, A. De and S. Mozumdar, *Catal. Commun.*, 2010, 11, 679.

62 B. L. Vilas, P. V. Shinde and M. S. Shingare, Tetrahedron Lett., 2013, 54, 5778.

63 S. Rostamizadeh, A. M. Amani, R. Aryan, H. R. Ghaieni and N. Shadjou, *Synth. Commun.*, 2008, **3**, 3567.

64 A. Ghorbani-Choghamarani and M. Norouzi, J. Mol. Cata. A: Chem., 2014, **395**, 172.

65 S. S. Parmar, R. Kumar and R. C. Arora, Indian J. Med. Res., 1969, 57, 245.

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