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Introduction

Noble metal nanoparticles (NMNPs) are widely used in the fields of catalytic coupling reactions, degradation of organic dyes, biooptical sensing and medical diagnosis, due to their unique structural morphology, high specific surface area, excellent stability, and good catalytic performance.^{1,2} Since the palladium (Pd)-catalyzed Suzuki–Miyaura reaction was recognized by the award of the Nobel Prize in Chemistry in 2010,^{3–5} Pd-based catalysts have important strategic significance in synthetic chemical catalysis and industrial applications, and have received great attention from researchers. PdNPs have been confirmed as efficient nanocatalysts in various catalysis fields, such as aerobic alcohol oxidation, organic synthesis, low-temperature CO oxidation, catalytic reduction of organic dyes and multiple coupling reactions.^{5–8} One of the main problems in these aspects is that

Quaternized POSS modified rGO-supported Pd nanoparticles as a highly efficient catalyst for reduction and Suzuki coupling reactions[†]

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Functionalized two-dimensional graphene oxide sheets and their inorganic-organic nanohybrids have aroused great interest because of their excellent synergetic effect on metal-based nanocatalyst PdNPs supported on highly hydrophilic quaternized polyhedral oligomeric silsesquioxane (QPOSS) functionalized reduced graphene oxide (rGO) and were successfully constructed as a nanohybrid catalyst for efficient heterogeneous catalytic reactions. Octaammonium POSS (OAPOSS) was first covalently grafted to carboxylated GO nanosheets through an amidation reaction, and then the OAPOSS decorated on rGO nanosheets was quaternized with glycidyltrimethylammonium chloride (GDTMAC) via an epoxide ringopening reaction to obtain a highly functional hydrophilic QPOSS@rGO hybrid. Finally, the PdNPs were loaded onto QPOSS@rGO nanosheets through an in situ reduction route. The guaternary ammonium groups on QPOSS@rGO can strongly coordinate with PdNPs, making it particularly advantageous for stabilizing PdNPs and preventing the leaching of Pd metals. Compared to the PdNPs@rGO catalyst without modification with hydrophilic QPOSS, the low-dose PdNPs@QPOSS@rGO nanocatalysts exhibited outstanding catalytic efficiency in the reduction of methylene blue and nitrophenols. In addition, the as-designed nanocatalysts also showed high catalytic activity for the Suzuki coupling reaction when utilizing pure water as a green solvent. It was proved that QPOSS and rGO can synergistically catalyze and promote the diffusion of reactants. In particular, the PdNPs@QPOSS@rGO nanohybrid catalyst showed no significant loss of catalytic activity after reusing it five times. Our results demonstrated that highly hydrophilic QPOSS endows the resulting PdNPs@QPOSS@rGO nanohybrid with good dispersibility and stability in water, which remarkably further improves the catalytic activity of the nanocatalyst.

> the easy aggregation of metal nanoparticles leads to the inhibition of their catalytic activity, which greatly limits the development prospects of metal nanoparticles.⁹ As is known to all, this is still a scientific challenge that homogeneous metal catalysts are expensive to prepare, low in yield, and difficult to separate resulting in poor reusability. So many studies have shown that fixing metal NPs on various support materials as heterogeneous catalysts to improve the dispersion of metal nanoparticles and catalytic activity is an effective technique to settle the above question.¹⁰ Multiple materials, such as inorganic triiron tetroxide,¹¹ silica,¹² organic polymers,¹³ carbon materials,¹⁴ and metal–organic frameworks (MOFs),¹⁵ have be developed as the efficient supports of metal nanocatalysts.

> Among the many catalyst carriers, it is known that recently developed novel graphene oxide (GO) is one of the most studied carbon nanomaterials. GO is the most promising candidate for catalyst carriers due to its unique structure and surface properties. Two-dimensional (2D) GO nanosheets possess high specific surface area, excellent electron transport ability, and good chemical stability, which can generate the synergy between



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Paper

metal nanoparticles and GO and further enhance the stability and versatility of nanocomposite catalysts.^{16,17} All of these features make GO an interesting option to support Pd nanocatalysts. In addition, the PdNPs are immobilized on the support material of GO as a catalyst, the structures of the catalysts are stable, and it is more convenient for the catalyst separation and recycling in the catalytic systems, but because of the π - π stacking or van der Waals interactions between PdNPs and GO, the as-prepared metal particles heavily aggregate, and the catalytic activity is also very low, which limits their application in organic catalysis.18,19

In order to improve the chemical stability, aqueous dispersion and catalytic activity, surface modification of GO is an essential approach to overcome the above problems. At present, there are a few reports on small molecules or polymer modified GO nanosheet-supported PdNPs as catalysts. For instance, Correia et al. immobilized Pd nanoparticles on organosilane containing amine or thiol group functionalized GO to catalyze Heck and Suzuki reactions.²⁰ The strong interaction between the metal particles and the carrier allows the Pd particle size to be smaller than that of the non-functionalized GO. Although the small molecule functionalized GO inhibited the serious growth of Pd particles, the small molecules easily fall off to cause the leaching of Pd nanoparticles to increase, resulting in catalyst deactivation and catalytic cycles to be significantly reduced. Yu et al. proposed a wet chemical method to prepare GO(apolydopamine(PDA)(aPd nanocomposites toward degradation of MB.²¹ However, it should be noted that the macromolecule modified GO by musselinspired chemistry as nanocatalysts did not exhibit outstanding catalytic activity. Wang et al. used polyethyleneimine (PEI) to couple PdNPs and Fe₃O₄ NPs onto graphene nanosheets for the Tsuji-Trost reaction.²² Yoon et al. demonstrated the preparation of ultrafine Pd supported by ionic block copolymer decorated rGO nanosheets as a catalyst for efficiently degrading methylene blue.23 Although polymer-modified rGO significantly has become a facile strategy as the support of metal nanocatalysts, the composition of the polymers is complex and the Pd nanoparticles are located between the graphene and the polymer or on the surface of the polymer brushes, which hinders the diffusion rate from the hydrophobic reactants to the surface of the metal catalytic center in the Suzuki coupling reaction.²⁴ Therefore, it is necessary to promote the diffusion of the reactants to the catalyst surface, at the same time, fine-tune the size of metal NPs and improve their dispersibility and catalytic activity, but this still remains a challenge.

Polyhedral oligomeric silsesquioxane (POSS) is an inorganicorganic hybrid depicted by the criterion $(RSiO_{1.5})_n$.^{25,26} A hydrophobic cage-shaped inorganic core in POSS is joined by a Si-O-Si bond and eight highly reactive organic groups. Compared with additional inorganic hybrid nanoparticles, nano-sized POSS has many functionalized reaction sites, excellent thermal stability, and chemical stability, and is highly soluble in many organic/ inorganic solvents. These unique properties make POSS become an ideal modification reagent.²⁷⁻³¹ So POSS has been used at present in numerous fields, such as drug delivery, medical devices, low dielectric constant materials, optical devices and

solar cells.³¹⁻³³ Recently, researchers have exploited POSS in various catalytic reactions and achieved good catalytic results. For instance, Lu et al. combined aminopropyl-POSS with terephthalaldehyde (TPA) by a Schiff base chemical reaction.³⁴ A porous covalent network catalyst was formed by coordination of containing-nitrogen groups in POSS-TPAx and Pd(II), which can be utilized in the Suzuki coupling reaction. Arsalani et al. used an octaAmmonium POSS (OA-POSS) nano-crosslinked poly(ethylene glycol) hydrogel as the carrier of Ag nanoparticles to prepare organic-inorganic hybrid catalysts for reducing 4-NP to 4-NA.35 Akbari et al. dispersed PdNPs on a carrier material based on TAP-POSS and poly(acrylamide-co-hydroxyethyl methacrylate) (AAm-co-HEMA) as a heterogeneous catalyst in the Heck coupling reaction in the aqueous phase.³⁶ In particular, in the above catalytic reaction, using POSS-based polymer composites as a metal nanoparticle carrier, it can be found that the introduction of POSS improves the dispersion of nanoparticles. Ervithayasuporn et al. utilized methyl methacrylate functionalized POSS (MMA-POSS-Tn) as a comonomer to prepare new porous polymer-silsesquioxane hybrids, which stabilized Pd nanoparticles for the oxidation of aerobic alcohol in water.³⁷ Chang et al. used the thiolated POSS to encapsulate amorphous palladium nanoclusters as a catalyst for the Heck reaction.³⁸ The large gaps between POSS molecules also provide a transport channel for the input of the reactants. Gruttadauria et al. prepared a novel imidazolium tetrachloropalladate salt catalyst immobilized on a POSS nanocage and demonstrated the effect of the POSS nanocage structure on the yield in the Suzuki reaction as compared with the 1-butyl-3-methylimidazolium tetrachloropalladate catalyst.³⁹ Simone et al. introduced functionalized POSS into polylactic acid composite fibers, and surprisingly found no changes in the structure of the polymers, while the supported palladium nanoclusters achieved good catalytic effects in the Heck coupling reaction.⁴⁰ It can be seen that the unique cubic cage structure and functionalization reaction sites of POSS are favored by many researchers. Therefore, the introduction of the ideal modifier POSS has been proven to be an effective approach in the design of functional composites.

Although POSS has been used to good effect in the field of catalysis, the application of PdNPs supported by POSS modified graphene oxide nanohybrid materials in catalysis is less reported. In this work, the 2D GO surface was functionalized with highly hydrophilic QPOSS which was utilized as a carrier for the in situ growth of PdNPs to successfully construct an efficient multiphase nanohybrid catalyst in Scheme 1. The catalytic activity of the as-designed nanocatalyst Pd@QPOSS@rGO was systematically investigated using the reduction of methylene blue (MB) and nitrophenol (NP) as model reactions. The performance of PdNPs@QPOSS@rGO as a catalyst for the green catalysis of the Suzuki-Miyaura coupling reaction in the aqueous phase was also evaluated. Due to the synergistic catalysis of QPOSS@rGO and PdNPs, the PdNPs@QPOSS@rGO nanohybrid as a catalyst with good dispersion stability in water was demonstrated to possess outstanding catalytic performance in various heterogeneous catalysis reactions.



Scheme 1 Schematic depiction of the preparation and catalytic application of the PdNPs@QPOSS@rGO catalyst.

Experimental

Materials

Graphene oxide sheets were prepared by following previously published work (see the ESI†).⁴¹ Glycidyltrimethylammonium chloride (GDTMAC) and octaAmmonium POSS (OAPOSS) were provided from Aladdin. Sodium chloroacetate, methanol, triethylamine, sodium hydroxide, isopropanol, methylene blue (MB), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimidehydrochloride (EDC), *o*-, *m*- and *p*-nitrophenols, *N*-hydroxysuccinimide (NHS), aryl bromide, arylboronic acid, potassium carbonate and palladium(n) chloride (PdCl₂, 55–60%) were supplied by Shanghai Macklin Reagent Co. Ltd.

Characterization

Transmission electron microscopy (TEM) observation was conducted utilizing a JEM-2100F electron microscope, and the as-prepared samples were dispersed in deionized water, and put on an ultrathin carbon supported film. The infrared absorption spectra of the samples were obtained using a Magna 560 FTIR Fourier transform infrared (FTIR) spectrometer. The UV-vis absorption spectra were obtained from 200 to 800 nm utilizing a SHIMADZU UV-2550 UV-vis spectrophotometer. Thermogravimetric analysis (TGA) of materials was performed using a PerkinElmer TGA-2 thermogravimetric analyzer (heating rate: 10 °C min⁻¹, nitrogen atmosphere). The X-ray photoelectron spectroscopy (XPS) spectra were obtained from the surface with a diameter of 500 mm in area by means of a Quantum 2000 spectrometer on an X-ray photoelectron spectrometer (X-TOOL, ULVAC-PHI) using non-monochromatized Al Ka excitation radiation. X-ray diffraction (XRD) patterns were obtained using a Rigaku D/max-TTR-III diffractometer with Cu Ka radiation. The Pd metal content in the composites was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, USA, Thermo Jarrel Ash, Franklin).

Preparation of carboxylated graphene oxide

0.1 g of graphene oxide (GO), 100 mL of deionized water, 5.0 g of sodium chlorohexanoate and 5.0 g of NaOH were mixed in a 250 mL Erlenmeyer flask, and the solution was sonicated for 2 h under ice bath conditions. The above mixture was collected

by centrifugation, then washed three times with deionized water, and finally vacuum-dried to obtain carboxylation graphene oxide.

Preparation of OAPOSS@rGO

20 mg of GO, 32 mg of EDC, and 12 mg of NHS were evenly dispersed in 10 mL of distilled water and sonicated for 30 min; 40 mg POSS and 41.4 mg triethylamine were dissolved in 10 mL N,N-dimethylformamide. Then, the above two dispersions were mixed before being stirred for 24 h at 25 °C. The product was separated by centrifugation and washed twice with methanol and water, respectively. The obtained crude product was collected by centrifugation, washed three times with ethanol and water to remove unreacted OAPOSS and vacuum-dried at room temperature to obtain the final sample.

Synthesis of quaternized OAPOSS@rGO (QPOSS@rGO)

20 mg of OAPOSS@rGO, 41.4 mg of GDTMAC and 20 mL of distilled water were mixed in a three-necked flask under nitrogen gas. The black mixture was stirred for 1 h at room temperature and next for 4 h at 80 °C. After the temperature of the reaction system was cooled to room temperature, diethyl ether was added to precipitate the product. The final product was centrifuged before washing them with isopropyl alcohol many times to remove unreacted GDTMAC and dried in a vacuum oven at 25 °C.

Preparation of QPOSS@rGO supported PdNPs (PdNPs@QPOSS@rGO)

30 mg of QPOSS@rGO in 150 mL of distilled water was sonicated for 0.5 h to uniformly disperse QPOSS@rGO. PdCl₂ (0.885 mg mL⁻¹, 6.0 mL) was poured into the QPOSS@rGO dispersion for ultrasonication for 2.0 h. 6.0 mL of the freshly prepared solution of NaBH₄ (0.2 M) was poured to the above system before continuously stirring at room temperature for 24 h. The sample was collected by centrifugation and washed several times with ethanol and water to remove unsupported palladium nanoparticles and PdCl₂, followed by drying in a vacuum oven at room temperature. The amount of Pd in the PdNPs@QPOSS@rGO catalyst was determined by ICPAES to be about 3.48 wt%.

Catalytic reduction of methylene blue (MB)

The catalytic activity of the as-prepared nanohybrid catalyst was evaluated using the reduction reaction of blue methylene (MB) to colorless leuco methylene blue (LMB). In detail, 2.0 mL MB aqueous solution (5.0 mg L⁻¹) and 1.0 mL of fresh NaBH₄ aqueous solution (0.5 M) were mixed in a quartz cuvette and agitated for 5 s, and the last 20 μ L of the PdNPs@QPOSS@rGO (0.1 mg mL⁻¹) catalyst was added to the above solution before stirring for a couple of seconds. The catalytic process was tracked using an ultraviolet-visible spectrophotometer.

Catalytic reduction of nitrophenols

The catalytic activity of the as-prepared nanohybrid catalyst was also investigated using the catalytic reduction of *o*-, *m*-, and *p*-nitrophenols. 1.0 mL of a fresh NaBH₄ aqueous solution (0.2 M), 6.5 μ L of the *m*-, *o*-, *p*-nitrophenol aqueous solution (0.05 M) and distilled water (2.0 mL) were mixed in the UV

Paper

Evaluation of the catalytic performance for Suzuki coupling reactions

Phenylboronic acid (0.6 mmol), aryl halide (0.5 mmol), distilled water (5.0 mL), K_2CO_3 (1.5 mmol) and the PdNPs@QPOSS@ rGO nanocatalyst (0.3 mol% Pd) were added to a round bottom flask before stirring at 80 °C for 2 h. The obtained organic product was collected *via* centrifugation and was extracted three times with 10 mL of ethyl acetate. The finally acquired product was analyzed by gas chromatography (GC). The PdNPs@QPOSS@rGO nanocatalyst was also recycled by centrifugation and washing with a large amount of water and ethyl acetate to wash off residual salts and organics for reuse in the catalytic procedure.

Results and discussion

TEM was utilized to observe the morphological characteristics of different samples GO, OAPOSS@rGO and PdNPs@OPOSS@ rGO. Fig. 1a shows the GO morphology with a representative corrugated thin stratified structure, which shows no difference with the feature reported in the literature,⁴¹ indicating the successful preparation of GO. Compared to the smooth surface structure of GO, OAPOSS@rGO has a distinctly different morphology as depicted in Fig. 1b. After grafting POSS, the primary smooth monolayer of GO becomes rough and it can be clearly seen that there are many dots on the surface of GO.⁴² This result proves that the lattice-free POSS molecules have been successfully anchored on the GO. Fig. 1c displays the TEM image of PdNPs decorated on the QPOSS@rGO nanosheets. We can clearly observe that PdNPs are evenly dispersed on the QPOSS@rGO surface, effectively avoiding the aggregation of PdNPs in the presence of QPOSS. The as-obtained PdNPs have a uniform size, and the average diameter of the particles is about NJC

7.5 nm (Fig. 1d). In order to evaluate the effect of QPOSS, we also prepared a composite of PdNPs supported on pure GO sheets to compare the dispersibility of the catalyst (PdNPs@rGO). As displayed in Fig. S1 (ESI[†]), PdNPs were not evenly distributed on the PdNPs@rGO nanosheets, and there is a serious aggregation of Pd particles with a particle size of approximately 9.3 nm. The above analysis further confirmed that the PdNPs were uniformly and stably dispersed on the GO nanosheets due to the introduction of QPOSS. Compared with the PdNPs@rGO catalyst without QPOSS modification, to further demonstrate the stability of the catalyst, we also presented the photographs of two samples placed at the same time and concentration. As shown in Fig. S2b (ESI[†]), PdNPs@QPOSS@rGO is still stably dispersed in water after two weeks. In contrast, a precipitate has appeared in the bottle only for two days for PdNPs@rGO without hydrophilic QPOSS modification (Fig. S2a, ESI[†]). The above results also demonstrate that the highly hydrophilic quaternized POSS plays an essential role in enhancing the dispersion and stabilization of PdNPs.

The chemical structures of GO, OAPOSS@rGO and PdNPs@ QPOSS@rGO nanohybrids were confirmed by FTIR (Fig. 2). In Fig. 2a, we can observe characteristic peaks at 3415, 1728, 1227 and 1050 cm⁻¹ which are attributed to the stretching and bending vibrations of -OH, C=O, C-O-C and C-O bonds on GO nanosheets, respectively.⁴³ In addition, the vibration peak at 1621 cm⁻¹ may be attributed to the water molecules, or caused by the vibration of the unoxidized carbon skeleton on the GO surface. It can be seen from Fig. 2b that the stretching vibration absorption peaks of C=O and C-OH appeared at 1618 and 3415 cm⁻¹ after carboxylation of GO, while the peaks of the epoxy and alkoxy groups were weakened, which proved that GO has been successfully carboxylated.44 As shown in Fig. 2c, in contrast, the OAPOSS modified GO (OAPOSS@rGO) showed a significant decrease in the carboxyl band at 1728 cm⁻¹ and a strong peak at 1102 cm⁻¹ was also observed due to the stretching vibration of the special Si-O-Si cage structure.45 The characteristic peaks observed at 2874 and 2943 cm⁻¹ are attributed to the presence of CH2 groups on the cage of OAPOSS, and a new peak appearing at 1570 cm⁻¹ could be assigned to the stretching vibrations of N-H and C-N bonds.44,46 The above result indicates that OAPOSS molecules have been successfully



Fig. 1 TEM images of (a) GO, (b) OAPOSS@rGO and (c) PdNPs@QPOSS@rGO; (d) Pd particle size distribution histogram of PdNPs@QPOSS@rGO.



Fig. 2 FTIR spectra of (a) GO, (b) GO-COOH, (c) OAPOSS@rGO, (d) QPOSS@rGO and (e) PdNPs@QPOSS@rGO.

covalently grafted onto the surface of GO sheets. As shown in Fig. 2d, the sample QPOSS@rGO showed a stronger and wider O–H absorption peak at 3415 cm⁻¹ after the epoxy ring-opening reaction of GDTMAC with OAPOSS. At the same time, a new typical peak of the quaternary ammonium groups appeared at 1640 cm⁻¹, which revealed that the nanocatalyst support of QPOSS@rGO has been successfully fabricated.⁴⁷ After loading metal Pd particles (Fig. 2e), the FTIR spectra of the as-prepared PdNPs@QPOSS@rGO nanohybrid catalyst are basically the same as those of QPOSS@rGO, which should be ascribed to the lower palladium loading on the QPOSS@rGO surface.

The XRD patterns of OAPOSS, GO, QPOSS@rGO and PdNPs@QPOSS@rGO are shown in Fig. 3. As expected, GO showed a major peak at a low diffraction angle $(2\theta = 11.41^{\circ})$ in Fig. 3b, indicating the successful synthesis of graphene oxide with a certain degree of aggregation.⁴⁸ Pure OAPOSS showed a number of sharp diffraction peaks corresponding to the presence of cage-type structures and amine-substituted isomers of the POSS inorganic segment at $2\theta = 6.8^{\circ}$, 11° , 19.1° , 21.8° , 23.3° , 26.9° , 33.1° and 38.7° (Fig. 3a), indicating the formation of a typical crystalline structure.⁴⁹ As shown in Fig. 3b, after QPOSS was covalently functionalized on GO nanosheets, the typical peak of GO shifted to a lower scattering angle at $2\theta = 7.4^{\circ}$ because the introduction of QPOSS increases the layer spacing between GO sheets, which is consistent with the literature report.50,51 The amorphous QPOSS on GO exhibited a weak broad diffraction peak at $2\theta = 20^{\circ}$. But the characteristic peak of GO disappeared in PdNPs@OPOSS@rGO, showing that the ordered graphitic stacking of GO has been converted to welldisordered structures. When Pd particles were further formed on QPOSS@rGO, as illustrated in Fig. 3d, four typical peaks appeared at $2\theta = 80.4^{\circ}$, 66.7°, 46.4° and 39.2° which are ascribed to the (311), (220), (200), and (111) diffraction planes of PdNPs, respectively.⁵² These results also proved that PdNPs have been successfully loaded on QPOSS@rGO hybrid nanosheets.

The chemical structures of GO, OAPOSS@rGO, QPOSS@rGO, PdNPs@QPOSS@rGO were further characterized by XPS. As expected, only C 1s and O 1s peaks were observed in the XPS spectrum of GO (Fig. 4a), but the peaks of N 1s (398.9 eV), Si 2p (101.8 eV) and Si 2s (154.3 eV) appeared in the XPS spectrum of OAPOSS@rGO (Fig. 4b). As shown in Fig. 4c, we can clearly



Fig. 3 XRD patterns of (a) OAPOSS, (b) GO, (c) QPOSS@rGO and (d) PdNPs@QPOSS@rGO.



Fig. 4 XPS survey scans of (a) GO, (b) OAPOSS@rGO, (c) QPOSS@rGO and (d) PdNPs@QPOSS@rGO.

observe that the contents of nitrogen and silicon elements in QPOSS@rGO have decreased due to the introduction of GDTMAC. After loading the Pd nanoparticles, additional peaks of Pd 3d at 335.7 and 560.5 eV appeared in Fig. 4d. The C 1s spectrum of GO in Fig. 5a showed four peaks at 288.6, 287.3, 286.8 and 284.8 eV, representing the carbon bonds of O=C-C, C=O, C-O, and C-C, respectively. This is attributed to the rich oxygen-containing functional groups on the GO sheets. Compared with GO, the high-resolution C 1s XPS spectrum for OAPOSS@rGO in Fig. 5b clearly revealed that the peak intensities of C-O (286.9 eV) and C=O (287.2 eV) were significantly reduced and that of C-C became dominant, together with the new appearance of the C-Si peak (283.6 eV).⁵³ This is because the OAPOSS was successfully grafted onto the surface of GO by the amidation reaction and most of the GO was reduced to rGO. The N 1s XPS spectrum (Fig. 5c) of OAPOSS@rGO clearly indicated that the peak of nitrogen appeared at 399.2 (C-N), 398.7 (N-H) and 401.1 eV (-NH-CO-), demonstrating the formation of an amide bond, again indicating that POSS-NH₂ is covalently anchored to GO.⁴⁹ For the Pd 3d XPS



Fig. 5 High-resolution C 1s spectra of GO (a), high-resolution C 1s and N 1s spectra of OAPOSS@rGO (b and c), high-resolution Pd3d spectrum of PdNPs@QPOSS@rGO (d).

spectrum in Fig. 5d, two signal peaks of Pd $3d_{3/2}$ and Pd $3d_{5/2}$ were observed at 340.9 and 335.4 eV. The appearance of the Pd²⁺ peaks (337.6 and 342.8 eV) indicated that some Pd atoms are bonded with their carriers.²³ The above analysis confirmed the formation of PdNPs on the surface of QPOSS@rGO.

As we all know, the thermal decomposition behavior of particular structures is different, so we studied the thermal stabilities of GO-COOH, QPOSS@rGO, and PdNPs@QPOSS@rGO by TGA (Fig. 6). GO-COOH displayed two stages of weightlessness in Fig. 6a. The first stage weight loss occurred from 100 to 230 °C, mainly caused by the loss of the hydroxyl groups of GO and the evaporation of water adsorbed by the surface layer. The weight loss in the second stage occurred between 600 and 700 °C, mainly attributed to the loss of more stable oxygen-related groups.54 In Fig. 6b, the final complete weight loss observed for QPOSS@rGO at 700 °C is 54.6% and the total mass loss is only 5% below 200 °C, whereas pure POSS loses all weight at around 300 $^\circ C$ due to thermal evaporation, indicating that GO as a carrier is very important for the stable presence of POSS.^{53,55} Due to the loading of Pd NPs (Fig. 6c), the residual amount of PdNPs@QPOSS@rGO (67.7%) is larger than that of QPOSS modified GO (54.6%) because of PdNPs and carbon residues,²² which further illustrates the improvement of the thermal stability of the PdNPs@QPOSS@rGO nanocomposites.

The catalytic activity of the PdNPs@QPOSS@rGO nanohybrid catalyst for organic dye MB was monitored by UV-vis absorption spectroscopy. As displayed in Fig. 7a, after the amount of PdNPs@QPOSS@rGO added to the reaction solution is 20 µL, it was clearly seen that the maximum absorption peak at 662.7 nm for methylene blue (MB) disappeared instantaneously and the indicative absorption peak of leucomethylene blue (LMB) appeared at 291.2 nm and the solution quickly changed from blue to colorless within only 20 s, which also indicates that MB was successfully reduced to LMB. When adding the PdNPs@ QPOSS@rGO catalyst (10 µL) to the reaction system, the MB characteristic peak continued to decrease and after 40 s a new LMB absorption peak appeared (Fig. 7b), indicating that PdNPs@ QPOSS@rGO as a catalyst has significant catalytic activity. Under the same conditions, the same amount (0.25 mg mL⁻¹) of catalysts GO, OAPOSS@rGO, and PdNPs@rGO was used to catalyze MB as a comparative experiment (Fig. S4, ESI⁺). We can observe that GO and OAPOSS@rGO showed almost no catalytic effect on the degradation of MB (Fig. S4a and b, ESI†).



Fig. 6 TGA curves of (a) GO-COOH, (b) QPOSS@rGO, and (c) PdNPs@ QPOSS@rGO.



Fig. 7 UV-vis spectra for the reduction of MB to LMB utilizing various volumes of catalyst aqueous solutions: (a) PdNPs@QPOSS@rGO (20 µL), (b) PdNPs@QPOSS@rGO (10 µL). The concentration of the catalyst was fixed at 0.1 mg mL⁻¹. (c) Plots of $ln(C_t/C_0)$ vs. time in the reduction of MB using various catalysts. (d) Reusability of the PdNPs@QPOSS@rGO nanohybrid catalyst for MB reduction.

Although the PdNPs@rGO has catalytic activity (Fig. S4c, ESI†), the catalytic efficiency is much lower than that of PdNPs@ QPOSS@rGO, which proves that compared to the above control samples, PdNPs@QPOSS@rGO as a new nanocatalyst exhibits higher catalytic activity.

Since excess NaBH₄ is used, the catalytic reduction of MB is considered to be a pseudo first order reaction, assuming that the catalytic rate is not associated with the NaBH₄ concentration for the reduction reaction. Based on the above kinetics, we determined the catalytic reduction rate associated with the concentration to evaluate the apparent rate constant k_{app} for the reduction of MB, expressed as $\ln(C_t/C_0) = -kt$ (Fig. 7c and Fig. S4f, ESI[†]).²³ According to the linear relationship between the reaction time and $\ln(C_t/C_0)$, the k_{app} values were calculated to be approximately 0.03, 0.01, 0.13, 5.95 and 11.69 min^{-1} corresponding to GO (20 µL), OAPOSS@rGO (20 µL), PdNPs@rGO (20 µL), PdNPs@QPOSS@rGO (10 µL) and PdNPs@QPOSS@rGO (20 µL) respectively. The rate constant of the PdNPs@QPOSS@rGO catalyst was much higher than those of the control samples. This also showed that upon synergy of QPOSS and GO, the nanocatalyst showed an excellent catalytic effect, and the hydrophilic QPOSS cage structure had a positive influence on the catalytic reaction.

The turnover frequency (TOF) value is frequently utilized to more accurately evaluate the catalytic activity. The TOF value is described as the number of substrate molecules (MB) per mole of metal (Pd) per hour or minute and the corresponding unit is h^{-1} or min⁻¹. The method for determining the TOF value is given in the ESI† (see eqn (S1)). When compared to the formerly reported nanocatalysts for the catalytic reduction of MB, it can be stated that the PdNPs@QPOSS@rGO nanohybrid catalyst with a TOF value of 2431.5 min⁻¹ exhibits excellent catalytic activity for the reduction reaction compared with the control samples (Table S1, ESI†). The recycling of nanocatalysts is also critical for practical applications, so we tested the reusability of the nanocatalysts. As shown in Fig. 7d, the PdNPs@QPOSS@rGO nanocatalyst maintains almost the high conversion rate after 5 cycles, which is sufficient to prove that the new nanocomposite has excellent stability.

As shown in Scheme 2, the excellent catalytic activity of the PdNPs@QPOSS@rGO nanocatalyst for reducing MB probability is attributed to the synergistic effect of functionalized GO and the outstanding hydrophilicity of nanohybrids: (i) rGO nanosheets have a high adsorption capacity for MB. Due to the layered structure GO, a larger specific surface area is imparted to the nanocatalyst and the reactant MB is rapidly adsorbed by the π - π stacking and van der Waals forces.⁵⁶ (ii) The synergy between QPOSS and GO accelerates the electron transfer among the PdNPs and MB. This is beneficial for MB molecules to absorb electrons thereby increasing the catalytic activity.⁵⁷ (iii) Highly hydrophilic quaternized POSS plays a vital role in enhancing the dispersibility of the nanocatalyst in the catalytic system, and excellent hydrophilicity also results in the efficient contact of the catalyst with MB.²¹ (iv) Functionalization of GO with QPOSS effectively prevents aggregation and overgrowth of PdNPs, resulting in higher interaction efficiency between PdNPs and MB molecules, which improves catalytic activity.^{22,57} In particular, compared to PdNPs@rGO, the hydrophilicity of the QPOSS modified catalyst can further ameliorate the catalyst dispersibility in pure water, maximizing the amount of surface exposed to metal atoms, thereby enhancing the accessibility of the reactants to the metal active center.^{58,59} These characteristics are beneficial for the wide applicability of the nanocatalyst in heterogeneous catalysis.

The degradation properties of different nitrophenol derivatives (*m*-NP, *o*-NP, and *p*-NP) were also investigated to further evaluate the catalytic performance of the as-prepared PdNPs@OPOSS@rGO nanohybrid.10 The UV-visible spectra in Fig. 8a-c show the reduction process and reaction time of p-NP, o-NP, and m-NP catalyzed by the PdNPs@QPOSS@rGO nanohybrid catalyst respectively. It can be seen that after the addition of the catalyst, the maximum absorption peaks of *m*-, *p*- and *o*-NPs at 392, 400 and 414 nm were observed to decrease and disappear completely after about 0.5, 4.0, and 2.5 minutes, respectively. As shown in Fig. 8d, the rate constants (k_{app}) for m-, o- and p-NPs are determined to be 3.69, 1.31 and 0.95 min⁻¹, respectively. The excellent catalytic activity of the PdNPs@QPOSS@rGO nanocatalyst for the reduction of nitrophenol is also demonstrated. For comparison with the as-designed PdNPs@QPOSS@rGO nanocatalyst, we used control catalysts PdNPs@rGO, OAPOSS@rGO and GO to evaluate the reducing ability of p-NP under the same conditions. As shown in Fig. S5 (ESI⁺),



 $\label{eq:scheme 2} \begin{array}{l} \mbox{Catalytic reduction mechanism of MB with PdNPs@QPOSS@rGO as the catalyst.} \end{array}$



Fig. 8 Successive UV-vis absorption spectra for the catalytic reduction of (a) *o*-NP, (b) *m*-NP, and (c) *p*-NP utilizing PdNPs@QPOSS@rGO as a catalyst. (d) Plots of $\ln(C_t/C_0)$ versus reaction time for the reduction of three isomeric nitrophenols catalyzed by the PdNPs@QPOSS@rGO catalyst.

the rate constants of these control catalysts are determined to be 0.025, 0.008, and 0.003 min⁻¹, which are significantly lower than that of the PdNPs@QPOSS@rGO nanocatalyst. PdNPs@ QPOSS@rGO showed different TOF values for *m*-, *o*- and *p*-NP, which are determined to be 244.8, 49.0 and 30.6 min⁻¹ respectively. In addition, the nanocatalyst for the catalytic reduction of *p*-NP maintained high conversion rates after five cycles in Fig. S6 (ESI†). Therefore, the PdNPs@QPOSS@rGO nanocatalysts designed by us exhibited high catalytic activity and stability, and presented significant advantages over other reported catalysts for the reduction of *p*-NP (Table S2, ESI†).

We further studied the catalytic performance of PdNPs@ QPOSS@rGO as an environmentally benign nanohybrid catalyst for Suzuki coupling reactions. We chose the most common phenylboronic acid and bromobenzene as the basic reaction model to optimize the Suzuki coupling reaction conditions including solvent, temperature and reaction time (Table 1).

Table 1 Influence of solvents and reaction conditions on Suzuki cross-coupling reactions catalyzed by the PdNPs@QPOSS@rGO nanocatalyst $(0.3 \text{ mol}\% \text{ Pd})^a$

R ₁ -	-	}—x	+ - B(C	$DH)_2 \xrightarrow{\text{Catalyst, K}_2CO_3} R_1$ Reaction Conditions	
Entry	R_1	х	Solvent	Reaction conditions	Conversion ^c (%)
1	Н	Br	H_2O	RT, 12 h	24.5
2	Н	Br	H_2O	RT, 24 h	98.5
3	Н	Cl	H_2O	RT, 24 h	37.0
4	Н	Ι	H_2O	RT, 24 h	98.5
5	Н	Br	H_2O	60 °C, 2 h	40.8
6	Н	Br	H_2O	60 °C, 4 h	97.3
7	Н	Br	$EtOH/H_2O^b$	60 °C, 4 h	99.9
8	Н	Br	H ₂ O	80 °C, 2 h	98.9
9	Н	Br	EtOH/H ₂ O	80 °C, 2 h	99.9

^{*a*} Reaction conditions: bromobenzene (0.5 mmol), chlorobenzene (0.5 mmol), iodobenzene (0.5 mmol), phenylboronic (0.6 mmol), and K_2CO_3 (1.5 mmol), water (5.0 mL). ^{*b*} Volume ratio of EtOH/H₂O is 1:1. ^{*c*} Conversion was measured by GC analysis.

Paper

We used K₂CO₃ as a base to investigate the effect of different solvents on the model reaction, and it was observed that the best yield was obtained in both EtOH/H₂O ($v_1/v_2 = 1:1$) and pure water (Table 1, entries 6-9). From the perspective of environmental protection, we finally chose water as the green solvent. In addition, the effect of temperature and time (Table 1, entries 1, 2 and 5-9) was also investigated and it was found that the yield was the highest at 80 °C for 2 h. Although the conversion rate at room temperature for 24 h (Table 1, entries 2 and 4) was as high as 98.5%, under the same conditions, the reaction effect of the catalyst on iodobenzene and phenylboronic acid was not satisfactory (Table 1, entry 3). According to the above comparison conditions, we found that the catalyst PdNPs@OPOSS@ rGO (0.3 mol% Pd) showed the best conversion rate in the presence of water at 80 °C for 2.0 h. This optimal condition serves as a basis for subsequent investigation of the Suzuki coupling reaction.

Under the optimal reaction conditions, we also evaluated the applicability of PdNPs@QPOSS@rGO catalysts for Suzuki coupling reactions of phenylboronic acid and various aryl halides. In general, most of the reactants have achieved good conversion rates in the Suzuki reaction. The PdNPs@QPOSS@rGO catalyst showed excellent catalytic activity in the presence of aryl iodide with phenylboronic acid (Table 2, entries 9–12), followed by a slight decrease in aryl bromide (Table 2, entries 4–8), whereas for the reaction of aromatic chlorides, the related coupled product conversions were relatively low (Table 2, entries 1–3), which was basically consistent with previous studies.^{60–63} Interestingly, it was found that the reaction of a substituted aryl halide having electronwithdrawing groups (–CN, –CHO) afforded satisfactory yields (96.1–98.8%) (Table 2, entries 7, 8, and 12).

However, for the aryl halide having electron-donating groups $(-CH_3, -OCH_3)$, the yield dropped significantly as expected (Table 2, entries 2, 3, 5, 6, 10, and 11). It is worth noting that the catalytic performance of the PdNPs@QPOSS@rGO nanocatalyst is more outstanding than those previously reported for

 Table 2
 Substrate study for the PdNPs@QPOSS@rGO-catalyzed Suzuki cross-coupling reaction^a

R ₁ -	x +	B(OH)2	Catalyst, K ₂ CO ₃	
Entry	R ₁	Х	Time (h)	Conversion ^{b} (%)
1	Н	Cl	2	90.5
2	$4-CH_3$	Cl	2	73.5
3	4-OCH ₃	Cl	2	<10
4	Н	Br	2	99.8
5	$4-CH_3$	Br	2	90.8
6	$4-OCH_3$	Br	2	38.9
7	4-CN	Br	2	96.1
8	4-CHO	Br	2	96.6
9	Н	Ι	2	99.5
10	$4-CH_3$	Ι	2	75.9
11	4-OCH ₃	Ι	2	70.3
12	4-CN	T	2	98.8

^{*a*} Reaction condition: aryl halide (0.5 mmol), phenylboronic (0.6 mmol), K₂CO₃ (1.5 mmol), water (5.0 mL), and the PdNPs@QPOSS@GO catalyst (0.3 mol% Pd). ^{*b*} Conversion was determined by GC analysis.



Fig. 9 The reusability of PdNPs@QPOSS@rGO catalysts for the Suzuki coupling reaction of bromobenzene with phenylboronic acid at 80 $^\circ\text{C}$ for 2 h.

Suzuki coupling reactions (Table S3, ESI[†]). On the whole, the above results reveal that our PdNPs@QPOSS@rGO nanohybrid catalyst has excellent catalytic efficiency in the Suzuki coupling reactions.

In order to investigate the recyclability of the PdNPs@ QPOSS@rGO catalyst, we chose phenylboronic acid and bromobenzene as a model for the Suzuki coupling reaction at 80 °C for 2 h. After each reaction was completed, the recovered catalysts finally were washed with ethanol and dried for the next reaction cycle. It is apparent from Fig. 9 that there was no significant loss in the catalytic reaction conversion after five cycles. Moreover, we tested and calculated the loss of the metal in the catalyst after five cycles via ICP analysis. The results clearly indicate that there is less leakage (about 0.39 ppm metal Pd) in the reaction system and the loss of Pd was calculated to be 0.367% in the total catalyst content in Table S4 (ESI⁺). This can be attributed to the highly hydrophilic cage QPOSS modified GO which allows the PdNPs to be stably dispersed in water. In general, this clearly indicates that PdNPs@QPOSS@rGO shows high catalytic activity and excellent stability as a green nanocatalyst.

Conclusions

In summary, we fabricated QPOSS modified rGO supported PdNPs (PdNPs@QPOSS@rGO) for the first time via a convenient and effective route. The as-designed PdNPs@QPOSS@rGO nanohybrid has high catalytic activity due to the synergistic catalysis of QPOSS and GO. The highly hydrophilic QPOSS as a stabilizer for PdNPs significantly improved the dispersibility and stability of PdNPs@QPOSS@rGO in aqueous solution. In addition, the pure QPOSS cage size is small and inconvenient to recycle and reuse, but covalent grafting of QPOSS onto the high specific surface area of GO makes the catalytic reaction recyclable. Therefore, PdNPs@QPOSS@rGO with good stability and reusability exhibited superior catalytic activity for the reduction of MB and nitrophenol isomers, and the Suzuki-Miyaura reactions in green solvent water. Obviously, QPOSS plays a crucial role in the preparation of PdNPs@QPOSS@rGO nanocomposites with high catalytic activity and good stability. Therefore, our strategy for fabricating POSS-based nanohybrid catalysts with highly active metal nanoparticles has potential value in the field of

heterogeneous catalysis, and the results of this research lay a good foundation for the development of multifunctional nanohybrid materials in a wide range of catalytic applications.

Conflicts of interest

There are no conflicts of interest to declare.

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