Supporting Information

3D Graphene/Nylon Rope as Skeleton of Noble Metal Nanocatalysts for Highly Efficient Heterogeneous Continuous-Flow Reaction

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Experimental

Synthesis of graphene oxides. GO nanosheets were synthesized from natural graphite powers according to a modified Hummers' method.[1] Typical, 3.0 g graphite and 1.5g $NaNO_3$ were added to 70 mL of 98% concentrated sulfuric acid under stirring at room temperature, and then the mixture was cooled at 0 °C. Under vigorous stirring, 9.0 g $KMnO_4$ was added slowly to keep the temperature of the suspension lower than 20 °C. Later, the mixture was transferred to a 35-40 °C water bath for 0.5 h, forming a thick paste and then 140 mL water was added. The solution was stirred for another 15 min at the temperature of 90 °C. 500 mL water was added and followed by a slow addition of 20 mL of 30% H_2O_2. The mixture was filtered and washed with 1:10 HCl aqueous solution (250 mL) to remove metal ions, followed by repeated washing with water and centrifugation to remove the extra acid (pH=6). The resulting solid was dispersed in water by ultrasonic for 1 h to make a GO aqueous dispersion (1 wt %). The obtained brown dispersion was centrifugation at 4000 rpm for 0.5 h to remove the aggregates. Finally, it was purified by dialysis for 1 week to remove the remaining salt impurities for the following experiments.

Synthesis of noble metal/graphene/nylon rope (NMGN) catalysts. PdGN catalysts were synthesized by one-step hydrothermal at 120 °C of a mixed solution containing clean nylon rope, graphene oxides, Na_2PdCl_4 and glucose. In a typical process, glucose (1.5 g) and Na_2PdCl_4 (27 mg) were added to 35 mL graphene oxide suspension (1 mg/mL) with a stirring for 30 min. Then, the mixture was transferred into a 50 mL Teflon-lined stainless-steel autoclave. 50 cm of clean nylon rope was then immersed in the solution and hydrothermally at 120 °C for 20 h. After hydrothermal treatment, the PdGN catalysts were washed with copious of water and stored for continuous-flow reactions.

The synthesis of PtGN, AuGN, and AgGN was performed under similar conditions as PdGN, except the $NaPdCl_4$ was replaced by H_2PtCl_6, $HAuCl_4$ and $AgNO_3$, respectively.

General procedure for continuous-flow Suzuki-Miyaura cross-coupling reaction. A DMF solution of iodobenzene (0.25 M) and benzeneboronic Acid (0.30 M) was mixed with isopyknic aqueous solution of K_2CO_3 (0.75 M). The mixture was pumped into the reactor with a controllable flow velocity. The reactor integrated with PdGN catalysts was pre-heated to 90 °C in an oil bath. The products of the reaction were extracted with ethyl acetate and purified by a microcolumn filled with silica gel. The conversion of iodobenzene and yield of biphenyl were determined by GC-MS (Agilent 7890A GC and 597C MS, the column is HP-5MS) with an internal label dodecane.

General procedure for continuous-flow reduction 4-nitrophenol reaction. A aqueous solution of 4-nitrophenol (1 mM) and $NaBH_4$ (50 mM) were pumped into the reactor with a controllable flow velocity. The reactor integrated with different noble metal/graphene/nylon rope catalysts was kept at room temperature. The conversion of 4-nitrophenol was determined by UV-vis spectrophotometer.

Characterization. The phase evolution of as-synthesized nanostructures was monitored by powder X-ray diffraction (XRD). The XRD patterns with diffraction intensity versus 2θ were recorded in a Shimadzu X-ray diffractometer (Model 6000) using Cu Kα radiation. Scanning electron microscopy (SEM) was performed on Zeiss Merlin system operating at 5 kV. Transmission electron microscopy (TEM) studies were conducted on a Hatchie HT-7700 field-emission transmission electron microscope with an accelerating voltage of 120 kV. Specific surface areas were measured on an ASAP 2020 HD 88 (Micromeritics Co.) apparatus by nitrogen physisorption method based on the Brunauer-Emmett-Teller (BET) method. Raman measurements were carried out on LabRAM HR800 (Horbia Jobin Yvon) at 633 nm. The Pd content was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis (Agilent 7500ce)

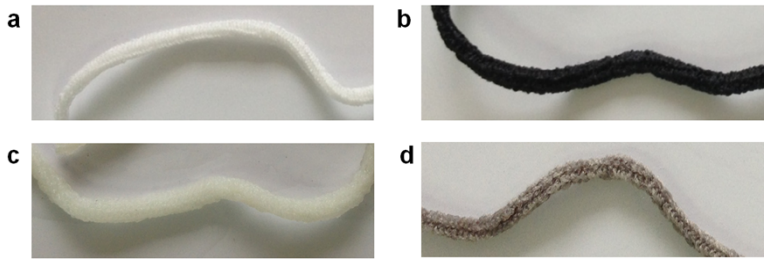


Fig. S1 The optical images of different samples. (a) clean nylon rope. (b) Pd/graphene/nylon rope. (c) Nylon rope after hydrothermal treatment in the absence of graphene and Pd precursor. (d) Synthesis of Pd/nylon rope in the absence of graphene.

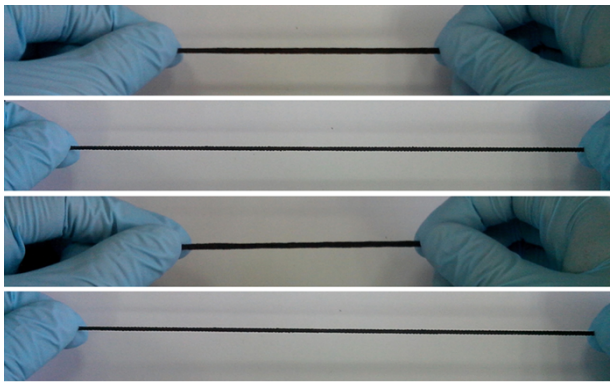


Fig. S2 The macroscale images of stretching the PdGN catalysts.

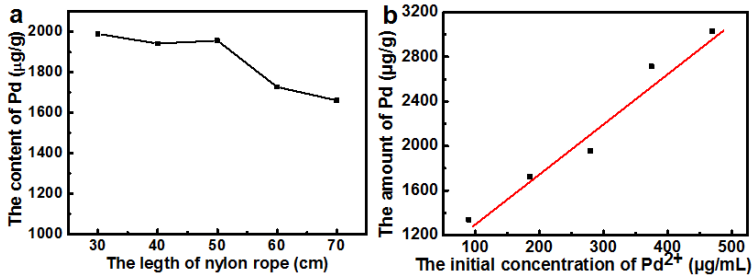


Fig. S3 The effect of the various amount of Pd in Pd/graphene/nylon rope catalysts.

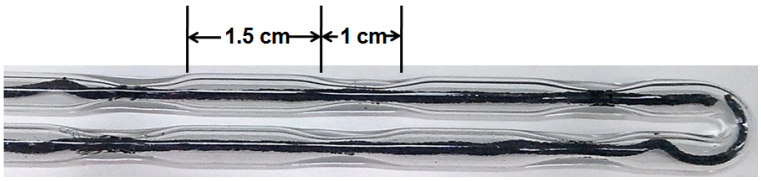


Fig. S4 The photography image of home-made U-shaped reactor loaded with PdGN catalysts.

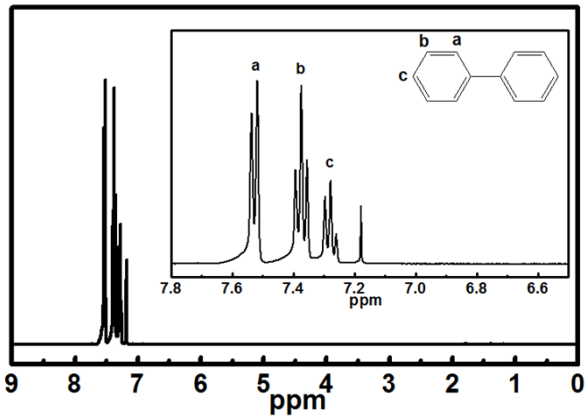


Fig. S5 ^{1}H-NMR spectra of product. We can see that the product is biphenyl without any other impurity.

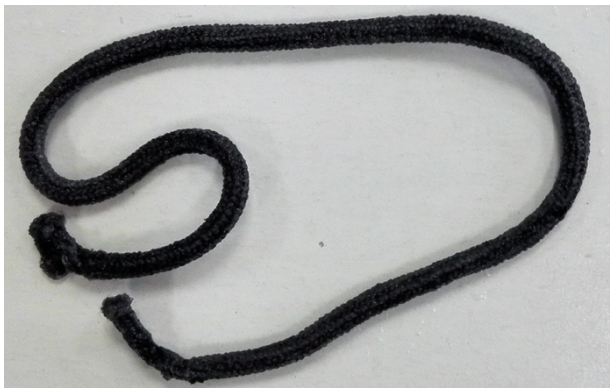


Fig S6. The macroscale images of the PdGN catalysts after finishing three cycles of continuous-flow SMC reaction with a duration of 6-hour for each cycle.

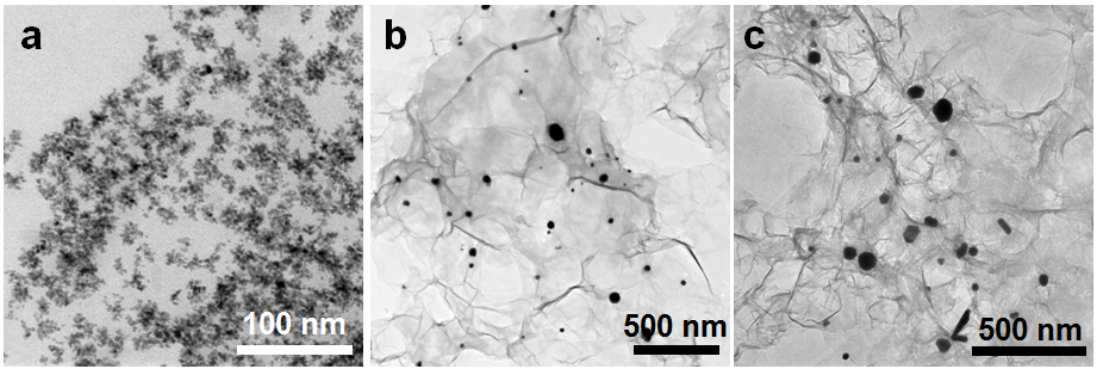
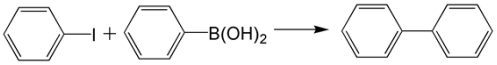


Fig. S7 TEM images of graphene anchored with (a) Pt, (b) Au and (c) Ag nanoparticles form PtGN, AuGN and AgGN catalysts, respectively.

Table S1. SMC reaction activity of different catalysts in batch reaction*



Entry	Catalysts	Loaded (Pd) **(μg)**	Conversion (%)	Yield (%)
1	Pd/graphene	500	89.8	88.9
2	Pd/graphene/rope	489	80.3	79.6

* **Reaction condition:** iodobenzene (2 mmol), phenylboronic acid (2.4 mmol), K_2CO_3 (6 mmol), H_2O (4 mL), DMF (4 mL), 1 h and 90 ^oC

Table S2. The ICP-OES results of noble metal graphene nylon rope and noble metal nylon rope

Sample	**Loaded Pd (μg/g)**	**Bleaching (ppb)**
Pd/graphene/nylon rope	1956	5.99
Pd/nylon rope	631	
Pt/graphene/nylon rope	1766	10.79
Pt/graphene rope	400	
Au/graphene/nylon rope	1236	2.3
Au/nylon rope	310	
Ag/graphene/nylon rope	2465	2.35
Ag/nylon rope	390	

The calculation on the loaded graphene:

The calculate equation of loading reduced graphene oxide in the 3D noble metal/graphene/rope:

m(rGO)=m(noble metal/graphene/nylon rope)-m(nylon rope)-m(noble metal nanoparticles) (1)