Palladium nanoparticles-anchored dual-responsive SBA-15-PNIPAM/PMAA nanoreactor: a novel heterogeneous catalyst for a green Suzuki-Miyaura cross-coupling reaction

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Experimental section

Materials

Triblock copolymer (Pluronic P123), tetraethyl orthosilicate (TEOS), 3-(trimethoxysilyl) propyl methacrylate (TMSPM), N-isopropyl acrylamide (NIPAM), methacrylic acid (MAA), potassium persulfate (KPS), sodium borohydride (NaBH\textsubscript{4}), potassium tetrachloro palladate (K\textsubscript{2}PdCl\textsubscript{4}), bromobenzene, chlorobenzene, 4-bromobenzaldehyde, 3-bromobenzaldehyde, 2-bromobenzaldehyde, 4-bromoaniline, tetrabutylammonium bromide (TBAB), anhydrous ethanol (99.8%), phenylboronic acid, sodium sulfate (Na\textsubscript{2}SO\textsubscript{4}) and potassium carbonate (K\textsubscript{2}CO\textsubscript{3}) were purchased from Sigma-Aldrich. Iodobenzene and 4-bromotoluene were purchased from Alfa Aesar. Hydrochloric acid (HCl) and ethyl acetate (EA) were obtained from Daejung Chemical Co. Ltd (Korea). All the chemicals were used as received. Double deionised (DI) water was used throughout the experiment.
Fourier-transform infrared (FTIR, JASCO FTIR-4100) spectroscopy was used for the analysis of surface functional groups within a scanning range 400–4000 cm\(^{-1}\) using potassium bromide (KBr) pellets. Small-angle X-ray scattering (SAXS) analysis of the samples was conducted using the synchrotron X-ray source of the Pohang Accelerator Laboratory (PAL, Pohang, Korea) with Co K\(\alpha\) (\(\lambda = 1.608\) Å) radiation at an energy range 4–16 keV (energy resolution \(\Delta E/E = 50 \times 10^{-4}\), photo flux = \(10^{10}–10^{11}\) ph/s, and beam size < 1 mm). X-ray diffraction (XRD, Bruker AXN) was performed using Cu-K\(\alpha\) radiation in the 2\(\theta\) range 10–80\(^\circ\). The surface morphology of the samples was studied by field-emission scanning electron microscopy (FE-SEM, ZEISS SUPRA 25 VP), which was conducted at an accelerating voltage of 20 kV, and field-emission transmission electron microscopy (FE-TEM, JEM-2011) was performed at an accelerating voltage of 200 kV, combined with energy-dispersive X-ray spectroscopy (EDX). Elemental mapping was carried out on the FE-TEM images with a high-angle annular dark-field (HAADF) detector. The samples for FE-SEM measurement were coated with platinum prior to the measurement. Conversely, the samples for the FE-TEM measurements were dispersed in ethanol, followed by loading on a copper grid and drying in air. Thermogravimetric analysis (TGA, Q50 V6.2, Build 187, TA instrument, US) was used to check the thermal stability of the material at a heating rate of 10 min\(^{-1}\) under nitrogen atmosphere. The surface area, pore volume, and pore size distribution of the synthesised material were measured using nitrogen adsorption-desorption isotherms (MICROMERETICS ASAP 2020 V3.04G), which were calculated using Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) methods, respectively. X-ray photoelectron spectroscopy (XPS) was used to examine the chemical composition of the synthesised material. The XPS spectra were obtained using a Theta Probe AR-XPS system (Thermo Fisher Scientific, UK) employing monochromated Al K\(\alpha\) X-rays (\(h\nu = 1486.6\) eV) at an electron take-off angle of 45\(^\circ\). The base pressure of the spectrophotometer was \(10^{-9}\) mbar. The X-ray gun was operated at 15 kV (power 100 W). The analyser was operated in a fixed analyser transmission mode with a pass energy of 300 eV (survey) and 50 eV (narrow). The hydrodynamic diameter of the sample was measured by dynamic light scattering (DLS, Zeta sizer NANO-S90, Malvern) at a series of different pH at room temperature and at different temperatures at pH 6. Gas chromatography (GC) (DS Science IGC 7200) with flame ionisation detector was used to measure the conversion and selectivity for the coupling reaction.
**Fig. S1** Wide angle XRD patterns of SBA-15-PNIPAM/PMAA and PdNPs-SBA-15-PNIPAM/PMAA.

**Fig. S2** The effect of the catalyst amount on the SMC reaction between bromobenzene and phenylboronic acid. Reaction conditions: bromobenzene = 1 mmol, phenylboronic acid = 1.3 mmol, TBAB = 0.5 mmol, K$_2$CO$_3$ = 3 mmol, solvent (water-ethanol (4:1)) = 5 mL. The conversion was determined by GC.
Fig. S3 The TEM-EDX elemental mapping of the PdNPs-SBA-15-PNIPAM/PMAA catalyst after the fifth cycle.

$^1$H NMR spectra of products

Biphenyl
4-Phenyltoluene

4-Phenylbenzoic acid
4-Phenylbenzaldehyde

3-Phenylbenzaldehyde
2-Phenylbenzaldehyde

\[ \text{Biphenyl: } ^1\text{H NMR (500 MHz, CDCl}_3\text{) } \delta 7.62 - 7.58 \text{ (m, 2H), 7.44 (t, } J = 7.6 \text{ Hz, 2H), 7.35 (t, } J = 7.4 \text{ Hz, 1H). (Table 2, entry 1-3)} \]

\[ \text{4-Phenyltoluene: } ^1\text{H NMR (500 MHz, CDCl}_3\text{) } \delta 7.48 \text{ (dd, } J = 8.1, 0.9 \text{ Hz, 2H), 7.40 (d, } J = 8.1 \text{ Hz, 2H), 7.32 (t, } J = 7.7 \text{ Hz, 2H), 7.22 (t, } J = 7.4 \text{ Hz, 1H), 7.15 (d, } J = 7.9 \text{ Hz, 2H), 2.30 (s, 3H). (Table 2, entry 5)} \]

\[ \text{4-Phenylbenzoic acid: } ^1\text{H NMR (500 MHz, DMSO) } \delta 13.11 \text{ (s, 1H), 8.06 (d, } J = 8.2 \text{ Hz, 1H), 7.89 (d, } J = 8.4 \text{ Hz, 2H), 7.82 (t, } J = 8.3 \text{ Hz, 2H), 7.74 (d, } J = 9.3 \text{ Hz, 2H), 7.39 (dd, } J = 30.7, 12.1 \text{ Hz, 2H). (Table 2, entry 6)} \]

\[ \text{4-Phenylbenzaldehyde: } ^1\text{H NMR (500 MHz, CDCl}_3\text{) } \delta 10.03 \text{ (s, 1H), 7.93 (d, } J = 8.4 \text{ Hz, 2H), 7.73 (d, } J = 8.2 \text{ Hz, 2H), 7.62 (d, } J = 7.1 \text{ Hz, 2H), 7.46 (t, } J = 7.5 \text{ Hz, 2H), 7.40 (t, } J = 7.3 \text{ Hz, 1H). (Table 2, entry 7)} \]

\[ \text{3-Phenylbenzaldehyde: } ^1\text{H NMR (500 MHz, CDCl}_3\text{) } \delta 9.99 \text{ (s, 1H), 8.01 (s, 1H), 7.76 (dd, } J = 7.6, 1.6 \text{ Hz, 2H), 7.52 (dd, } J = 14.8, 7.4 \text{ Hz, 3H), 7.38 (t, } J = 7.6 \text{ Hz, 2H), 7.33 - 7.28 \text{ (m, 1H). (Table 2, entry 8)} \]
2-Phenylbenzaldehyde: $^1$H NMR (500 MHz, CDCl$_3$) δ 9.99 (s, 1H), 8.03 (d, $J = 7.8$ Hz, 1H), 7.64 (t, $J = 8.2$ Hz, 1H), 7.50 (dd, $J = 13.4$, 6.1 Hz, 2H), 7.45 (d, $J = 9.4$ Hz, 3H), 7.41 – 7.35 (m, 2H). (Table 2, entry 9)