

Electronic Supplementary Information

One-step synthesis of magnetic iron-conducting polymer-palladium ternary nanocomposite microspheres and their use as recyclable catalyst

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Materials

Unless otherwise stated, all materials were guaranteed reagent grade. PdCl₂ (99.9 %) was obtained from Wako Chemicals. Poly(4-ammonium styrene sulfonic acid) [PASSA; nominal molecular weight 200,000; 30 wt% aqueous solution], sodium chloride (NaCl, 99.5 %), hydrated ferric chloride (FeCl₃·6H₂O), aluminum oxide (activated, basic, Brockmann 1, standard grade, ~150 mesh, 58 Å) and sodium deoxycholate (SDC, C₂₂H₃₉O₄Na) were obtained from Sigma-Aldrich and were used without further purification. Pyrrole (Py, 98 %) was also obtained by Sigma-Aldrich and purified by passing through a column of the activated basic alumina. Carbon-coated Fe (Fe/C) nanoparticles were supplied by Kurimoto Ltd. Japan, and their synthesis route is briefly described below. Deionized water (<0.06 μS cm⁻¹) was prepared using a deionized water producing apparatus (Advantec MFS RFD240NA: GA25A-0715) and used for syntheses and purification of the nanocomposite microspheres. A magnetic bar (150 mm×10 mm×30 mm, 533 mT) was obtained from NeoMag Co. Ltd.

Synthesis of carbon-coated Fe (Fe/C) nanoparticles

Fe/C nanoparticles were synthesized by an arc plasma method. The apparatus consists of an arc chamber with a tungsten cathode and an anode of Fe bulk (purity: 99.98%). A mixture gas of Ar+H₂+CH₄ was introduced into the chamber after vacuuming. The arc plasma was generated under an arc current of 200 A and an arc voltage of 65 V at a total gas pressure of 101 kPa with the gas flow rate of 100 L/min. The arc plasma method is based on a vaporization of anode metal by arc plasma and a subsequent quenching of the metal vapor. The arc plasma generated under Ar+H₂ is often used for an efficient vaporization of the anode metal [J. Noma et al., *J. Magn. Magn. Mater.*, **322**, 1868 (2010)]. The arc plasma generated under CH₄ gas has been used for synthesis of carbon encapsulated metal nanoparticles [X.L.Dong, et al., *J. Appl. Phys.*

86, 6701 (1999)]. In our arc plasma condition, the nanoparticles with 10.5 m²/g (73 nm) were obtained. Unfortunately, some of Fe nanoparticles were not completely encapsulated with carbon (partially coated with carbon shell).

Preparation of Fe/C nanoparticle aqueous dispersion

Ultrasonic treatment was carried out to prepare the colloidally-stable Fe/C aqueous dispersion. SDC, which can be applicable to assist the dispersing of carbon material [(a) A. Ishibashi, N. Nakashima *Chem. Eur. J.*, **12**, 7595 (2006) (b) H. Xu, H. Abe, M. Naito, Y. Fukumori, H. Ichikawa, S. Endoh, K. Hata, *Adv. Powder Technol.*, **21**, 551 (2010)], was used as a surfactant. Precisely weighed 1.0 g dry Fe/C nanoparticles (2.0% w/w) were added into a 50 mL glass bottle including 49.0 g dispersion medium (10% SDC aqueous solution, w/w). The glass bottle was capped, placed into a conventional ultrasonic bath (24/31 kHz, Model VS-02RD, Velvo-clear, Japan), and ultrasonically treated at 70 W. After 4 h sonication, we obtained a black dispersion of the Fe/C nanoparticles.

Synthesis of Fe/C-PPy-Pd ternary nanocomposite microspheres

Aqueous chemical oxidative polymerization was conducted at 25°C in the presence of the SDC-modified Fe/C nanoparticles with poly(4-ammonium styrene sulfonic acid) (PASSA) colloidal stabilizer for 4 days using an agitator (National baby motor SCVS50W; Matsushita Electric Industrial Co., Ltd.). Pyrrole (0.5 g, 7.45×10⁻³ mol) and PASSA (MW, 200K; aqueous solution of 30 wt%; solid content, 0 and 100 wt% with respect to pyrrole monomer) were added to the Fe/C nanoparticle aqueous dispersion (16.0 g, containing 0.1 g Fe/C nanoparticles) in a 70 mL screw-capped bottle. PdCl₂ oxidant (1.54 g, 8.68×10⁻³ mol) was dissolved in 34.0 g water containing NaCl (0.51 g, 8.72×10⁻³ mol), and then added to the aqueous dispersion of the Fe/C nanoparticles containing pyrrole. NaCl was added in order to dissolve PdCl₂ in water. Chemical oxidative polymerization of pyrrole proceeds with a reaction stoichiometry of 2.33 moles of electrons per mole of monomer [S. P. Armes, S. Gottesfeld, J. G. Beery and F. Garzon, S. F. Agnew, *Polymer*, **32**, 2325 (1991)]. The PdCl₂/pyrrole molar ratio was adjusted to 1.17: two electrons are necessary to reduce one Pd²⁺.

Characterization of Fe/C-PPy-Pd nanocomposite microspheres

Particle size analysis

The sizes of the nanocomposite microspheres were determined using a particle size analyzer (Malvern Mastersizer 2000) equipped with a small volume sample dispersion unit (Hydro 2000SM; ca. 150 mL including flow cell and tubing), a He-Ne laser (633 nm), and a solid-state blue laser (466 nm). The stirring rate was adjusted to 2,000 rpm. The mean microsphere diameter was taken to be the volume mean diameter (D_v). The laser diffraction microsphere size analysis results were in good agreement with those obtained by optical microscopy.

Chemical composition

The PPy-Pd nanocomposite, Pd and PPy loadings of the nanocomposite microspheres were determined by comparing the nitrogen contents determined by CHN elemental microanalysis (Yanaco CHN-Corder MT-5) among the Fe/C-PPy-Pd nanocomposite

microspheres, PPy–Pd and PPy bulk powders. The PPy–Pd and PPy bulk powders were prepared by precipitation polymerization as reported previously [S. Fujii, S. Matsuzawa, Y. Nakamura, A. Ohtaka, T. Teratani, K. Akamatsu, T. Tsuruoka and H. Nawafune, *Langmuir*, **26**, 6230 (2010)]. Sulfur content microanalyses were carried out at an independent laboratory (Sumika Chemical Analysis Service, Japan) by ion chromatography with an oxygen-flask-combustion method.

Density measurements

The solid state densities of the dried samples were determined by helium pycnometry using a Micromeritics AccuPyc 1330 instrument. Typical reproducibility is within 0.02% of the nominal full-scale volume on clean, dry, thermally equilibrated samples.

Observation of the ultrathin cross sections of microspheres using transmission electron microscope (TEM)

The ternary nanocomposite microspheres were first suspended in a high viscous aqueous solution containing sucrose (concentration / 2M). A drop of the suspension was put on a sample holder and immediately immersed in liquid nitrogen to be frozen. The frozen suspension was cut to an ultrathin specimen at 77 K using a microtome (UCT, Leica, Germany). The ultrathin specimen was transferred on a carbon coated TEM grid, and the sucrose was removed by washing with distilled water at room temperature. TEM image, high resolution TEM (HRTEM) image and selected area electron diffractions (SAEDs) were taken on a JEM-2100F operated at 200kV.

TEM images of ultrathin cross section of the nanocomposite microspheres show heterogeneous character, which is composed of a more transparent PPy matrix, with incorporated Pd and Fe/C nanoparticles that have a higher absorbance for TEM electrons (dark elements dispersed in the PPy matrix). Nanoparticles with an average diameter of *ca.* 5 nm were identified as Pd from HRTEM image and SAED pattern. The average diameter accorded well with that of Pd nanoparticles observed in PPy–Pd nanocomposites reported previously [H. Hamasaki, N. Fukui, S. Fujii, S. Yusa, Y. Nakamura, *Colloid Polym. Sci.*, **1**, 223 (2013)]. The spherical particles with an average diameter of *ca.* 100 nm were identified as the magnetic particles. Unfortunately, the thin specimen was broken into small fragments and it was difficult to investigate in detail a space distribution of Fe/C and Pd nanoparticles inside the microspheres. As mentioned earlier, some of the Fe nanoparticles were not completely encapsulated with carbon shell, and the fraction of completely carbon-coated Fe nanoparticles observed in the PPy matrix was about 70%. The oxidized Fe phase was observed for the insufficient carbon-coated Fe nanoparticles.

BET study

The specific surface area (SSA) was determined by nitrogen gas adsorption based on the BET method (micromeritics ASAP 2010, Shimadzu, Japan). In the BET measurements, the sample was degassed for 2 h at 200°C under a vacuum to remove adsorbed molecules. The equivalent diameter, d_s , was calculated using the following equation.

$$d_s = 6 / (\rho_p \times \text{SSA})$$

where a density, ρ_p , was 7850 kg/m³ for the bulk iron.

Inductively coupled plasma measurement

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) studies were performed using ICPS-8100 (Shimadzu Co., Kyoto, Japan). Dried Fe/C-PPy–Pd

nanocomposite microspheres (1.7 mg) were placed in a screw-capped vial and then 13 M nitric acid (5 mL) was added. The mixture was heated at 80 °C for 20 h in order to dissolve Pd component. After cooling to room temperature, the aqueous solution was adjusted to 50 g by adding water and then the amount of Pd metal was measured by ICP-AES analysis (16.2 ppm). In order to check Pd dissolution into reaction media during catalytic reactions, the supernatant of the nanocomposite microsphere aqueous dispersion (1.0 g) was adjusted to 10 g by adding nitric acid. The amount of Pd was measured to be <0.1 ppm, which indicates there is no/little leaching of Pd metal component from the nanocomposite microspheres.

Scanning electron microscopy and energy dispersive X-ray spectroscopy studies

Scanning electron microscopy (SEM) studies and elemental analysis of the microspheres were performed using a JSM-7001FA field emission scanning electron microscope (FE-SEM) equipped with an energy dispersive X-ray (EDX) microanalyzer operating at 15 kV.

X-ray photoelectron spectroscopy study

XPS measurements were carried out at an independent laboratory (Sumika Chemical Analysis Service, Japan) using an XPS spectrometer (Thermo Fisher Scientific, VG Theta Probe) with a monochromated Al K α X-ray gun. The base pressure was 1.0×10^{-8} Torr. Pass energies of 80 and 20 eV were employed for the survey spectra and elemental core line spectra, respectively. Quantification of the atomic percentage composition was obtained from high-resolution spectra according to the manufacturer sensitivity factors. Spectra were aligned to the hydrocarbon component of the C 1s peak set at 284.6 eV.

Magnetization measurement

Room temperature magnetization (hysteresis loops) for Fe/C nanoparticles and Fe/C-PPy-Pd nanocomposite microspheres was measured as a function of the magnetic field, H using a vibrating sample magnetometer (VSM; Toei Scientific Industrial Co., Ltd.). The magnetic saturation value was obtained by linear extrapolation about 2 T past to $H=0$.

Percentage transmittance measurements

Transmittances of the aqueous dispersions of Fe/C-PPy-Pd nanocomposite microspheres were recorded on an Agilent 8453 spectrophotometer with visible light (600 nm wavelength) using a 1.0 cm path length quartz cell at various time intervals. The magnet bar was set under the quartz cell. The measurements were conducted at an elevated position in the sample: in this way, when the microspheres in aqueous media settled down to the bottom of the quartz cell, high %T values were recorded.

Suzuki-Miyaura cross-coupling reaction in aqueous media using Fe/C-PPy-Pd nanocomposite microspheres as a catalyst

To a screw-capped vial were added 0.5 mmol of *p*-bromoacetophenone, 0.75 mmol of *p*-methylphenylboronic acid, Fe/C-PPy-Pd nanocomposite microsphere aqueous dispersion (0.23 wt%, 17 μ L, 0.03 mol% of Pd based on *p*-bromoacetophenone), and 1.5 mol L $^{-1}$ aqueous K $_2$ CO $_3$ solution (1 mL). After shaking with a Peti-Syzer (HiPep Laboratories) at 80 °C for 3 h, the nanocomposite microspheres were collected using a magnetic bar and the aqueous phase containing no catalyst was removed. The collected microspheres were washed with water (5 \times 1.5 mL) and diethyl ether (5 \times 1.5

mL), which were then gathered with the aqueous phase removed previously. The 4-acetyl-4'-methyl-1,1'-biphenyl was extracted five times from the aqueous phase with diethyl ether. The diethyl ether containing 4-acetyl-4'-methyl-1,1'-biphenyl dissolved was dried over MgSO_4 and then under reduced pressure. The resulting dried product was weighed and analyzed by ^1H nuclear magnetic resonance spectroscopy (NMR; CDCl_3 , Varian UNITY 300). The recovered microspheres were dried in vacuo and reused as a catalyst. The amount of Pd metal in the aqueous phase determined by ICP-AES analysis was less than 0.1 ppm. UV-Vis measurements for diethyl ether solution of 4-acetyl-4'-methyl-1,1'-biphenyl confirmed that Fe impurities could not be detected.

Table S1 XPS data of Fe/C-PPy-Pd nanocomposite microspheres

	Binding energy / eV	Atomic ratio
Fe2p3	710.6	0.2
N1s	400.0	8.0
Pd3d5	335.8	2.9
	338.2	2.0
S2p	168.0	4.3

Fig. S1 TEM images of carbon-coated magnetic Fe (Fe/C) nanoparticles. Figs S1b and S1c show magnified image of Fig. 1a: (b) carbon-coated Fe nanoparticle and (c) oxide film-coated Fe nanoparticle.

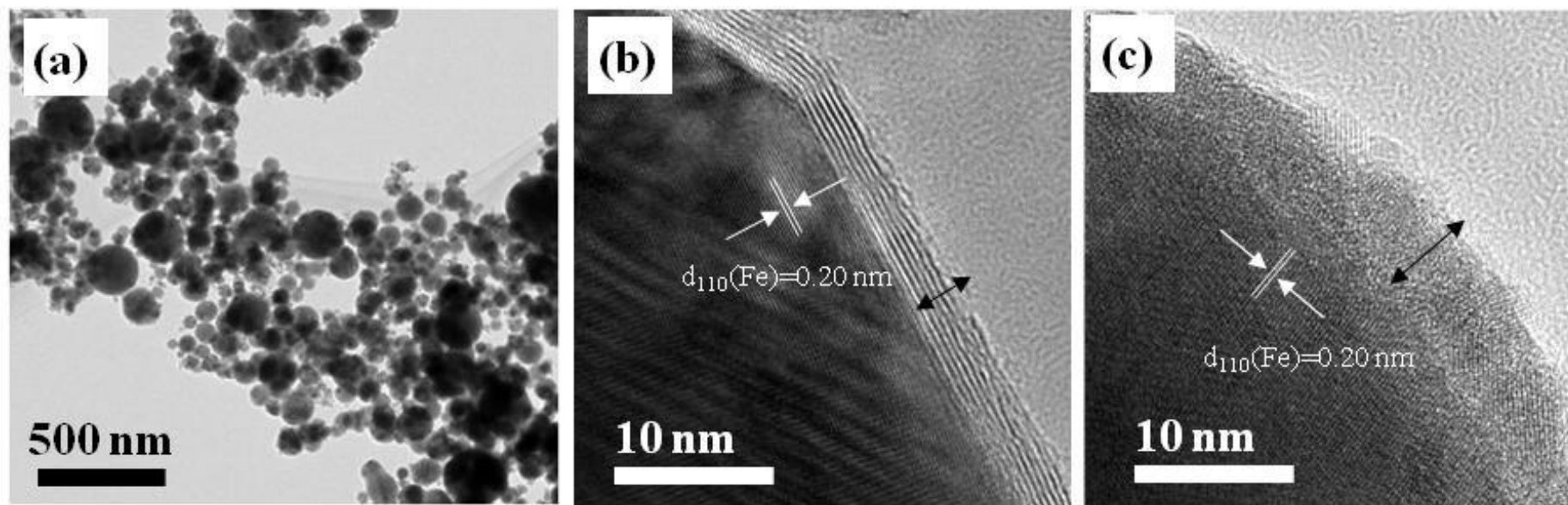


Fig. S2 Laser diffraction particle size distribution curves of (a) Fe/C nanoparticles, (b) PASSA-Fe-PPy-Pd nanocomposite microspheres and (c) Fe-PPy-Pd nanocomposite bulk powder.

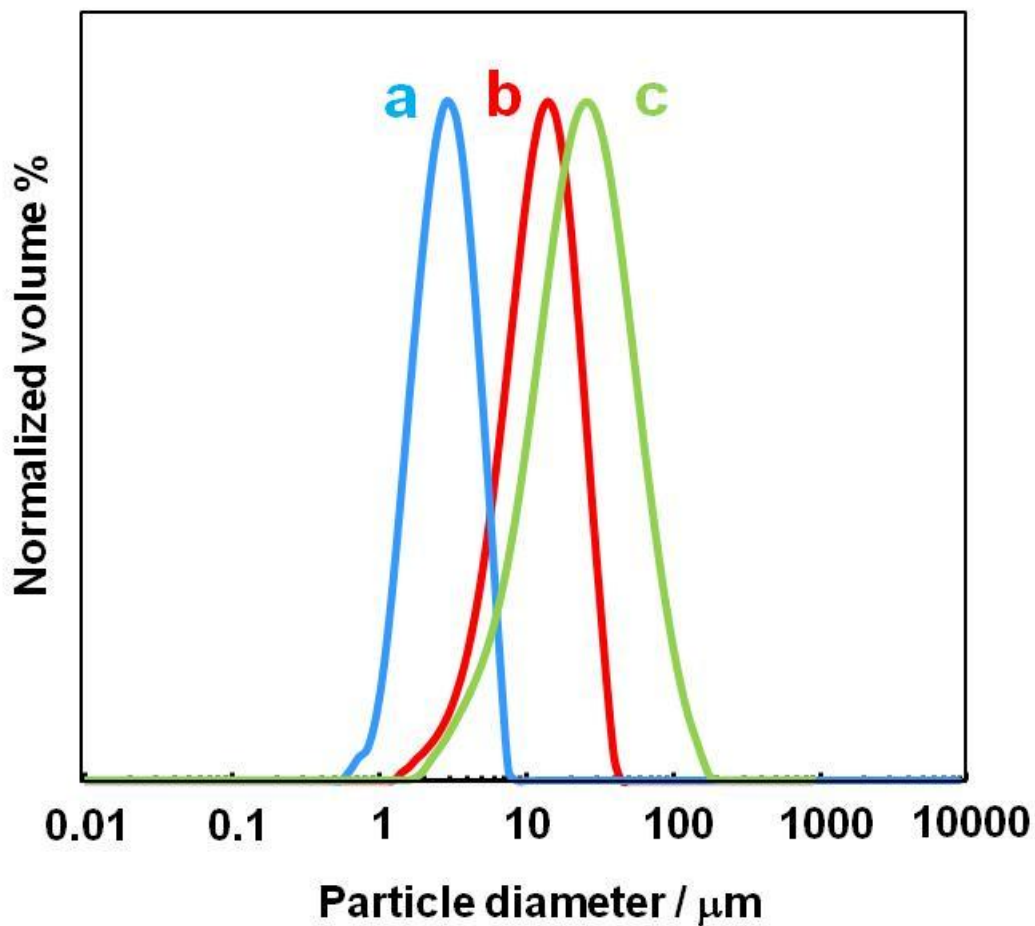


Fig. S3 SEM image of Fe/C-PPy-Pd nanocomposite bulk powder synthesized by chemical oxidative precipitation polymerization in the absence of PASSA

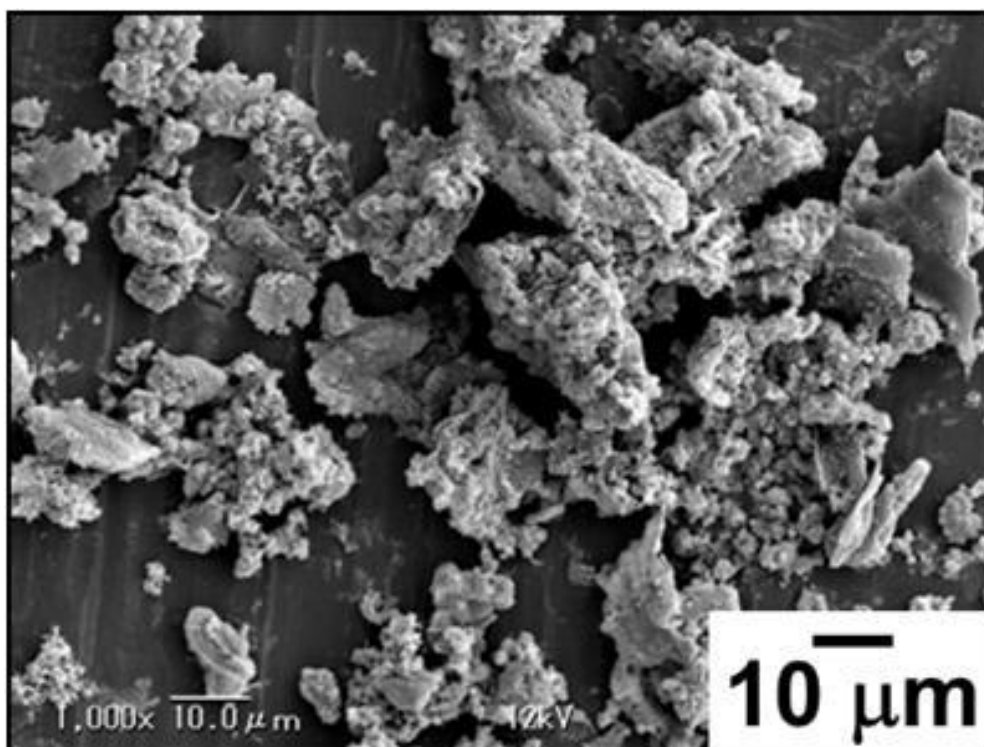


Fig. S4 (a) SEM image and (b, c, d) EDX images of PASSA-Fe-PPy-Pd nanocomposite microspheres. Corresponding elements: (b) iron, (c) palladium and (d) sulfur.

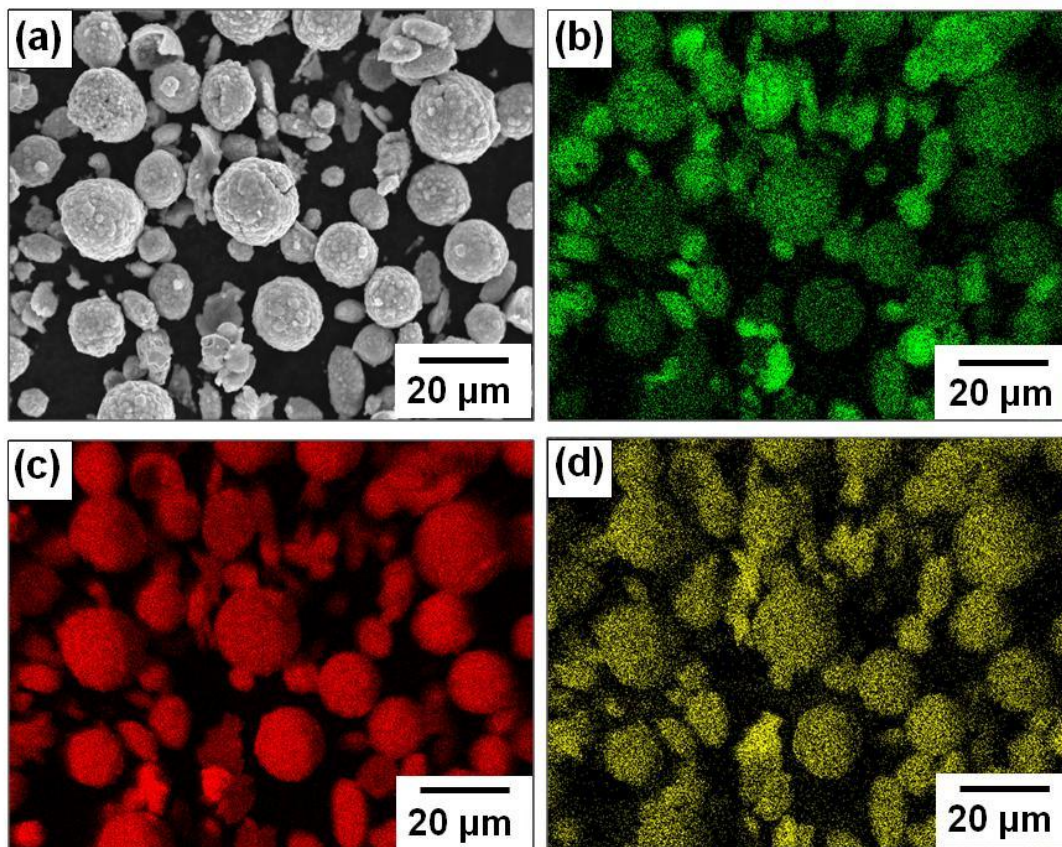


Fig. S5 Survey XPS spectra of (a) PPy-Pd nanocomposite bulk powder and (b) PASSA-Fe-PPy-Pd nanocomposite microspheres.

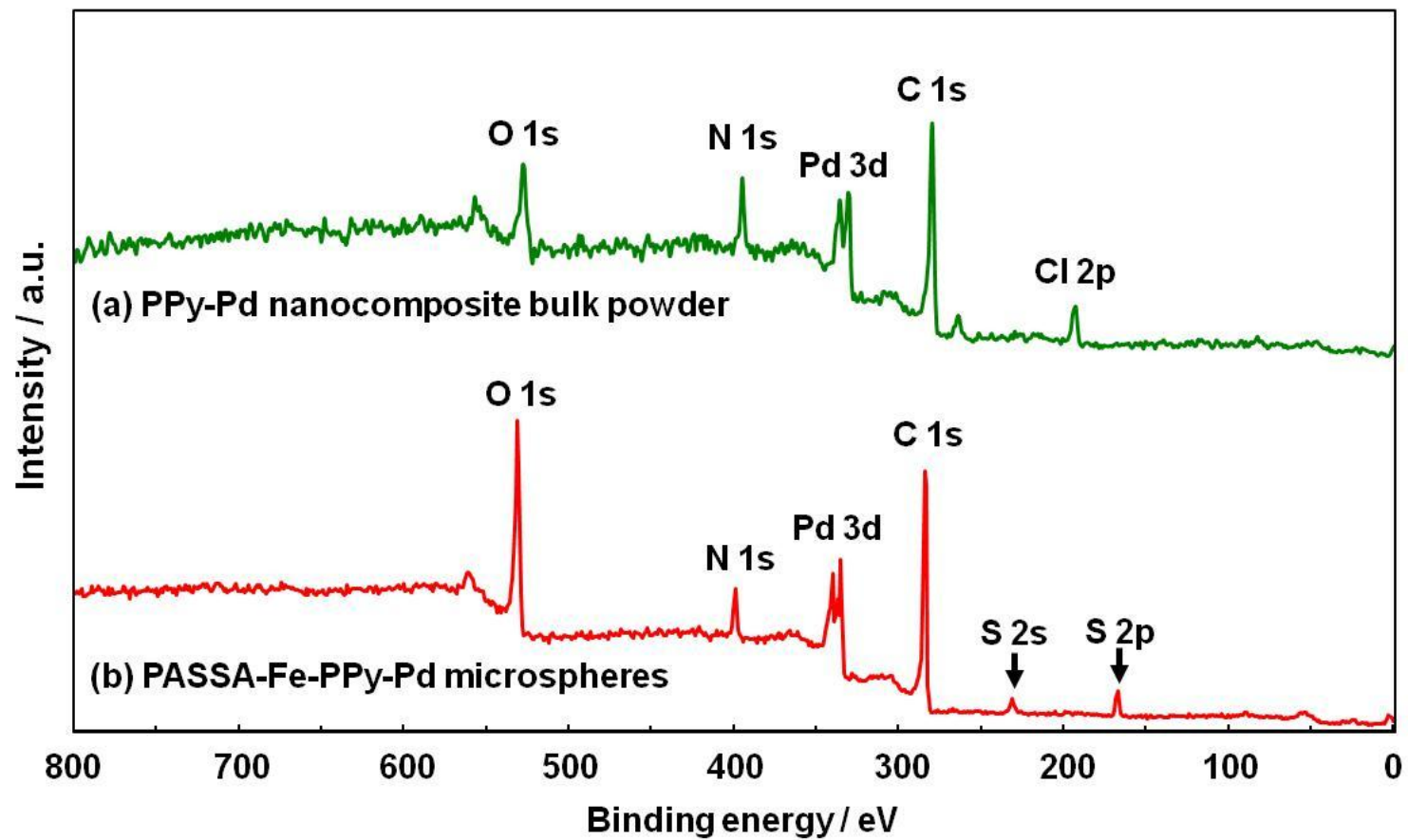
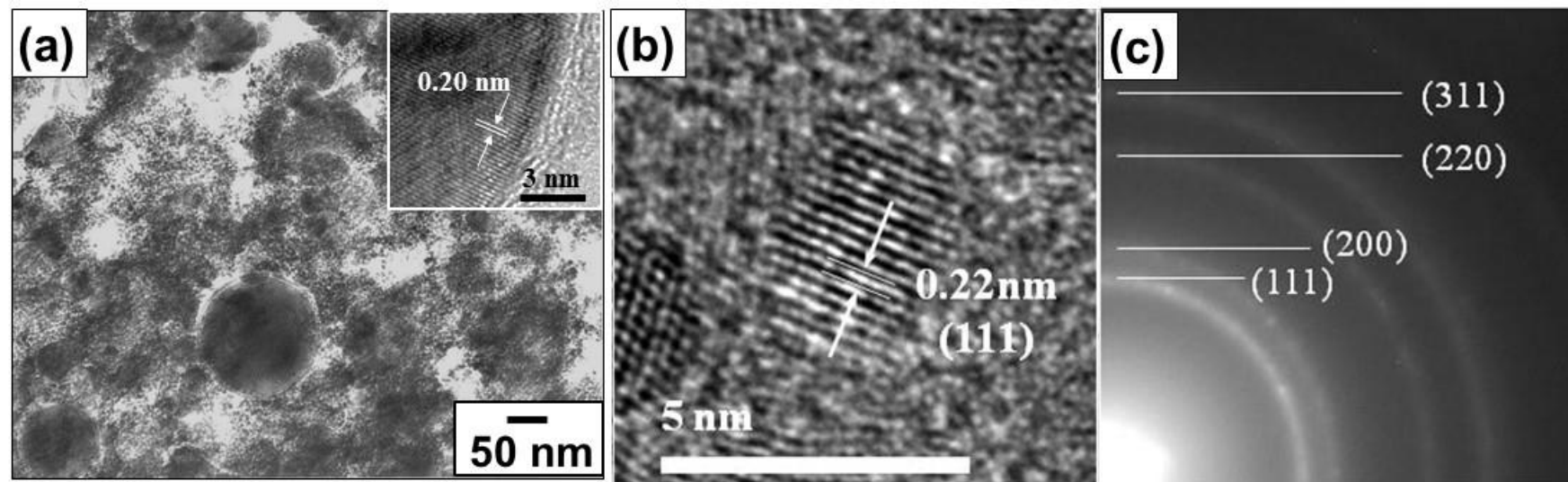


Fig. S6 (a) TEM image of ultrathin cross-section of Fe/C-PPy-Pd nanocomposite microspheres. Inset shows HRTEM image of Fe/C nanoparticle. (b) HRTEM image of single Pd nanoparticle embedded in PPy matrix and (c) Debye-Scherrer rings obtained by electron diffraction study of Pd nanoparticles.



The Fe/C nanoparticles with an average diameter of *ca.* 100 nm have a lattice spacing (d_{110}) of 0.20 nm. The Pd nanoparticles with an average diameter of *ca.* 5 nm have a lattice spacing (d_{111}) of 0.22 nm.

Fig. S7 Magnetization curves of Fe/C nanoparticles and Fe/C-PPy-Pd nanocomposite microspheres

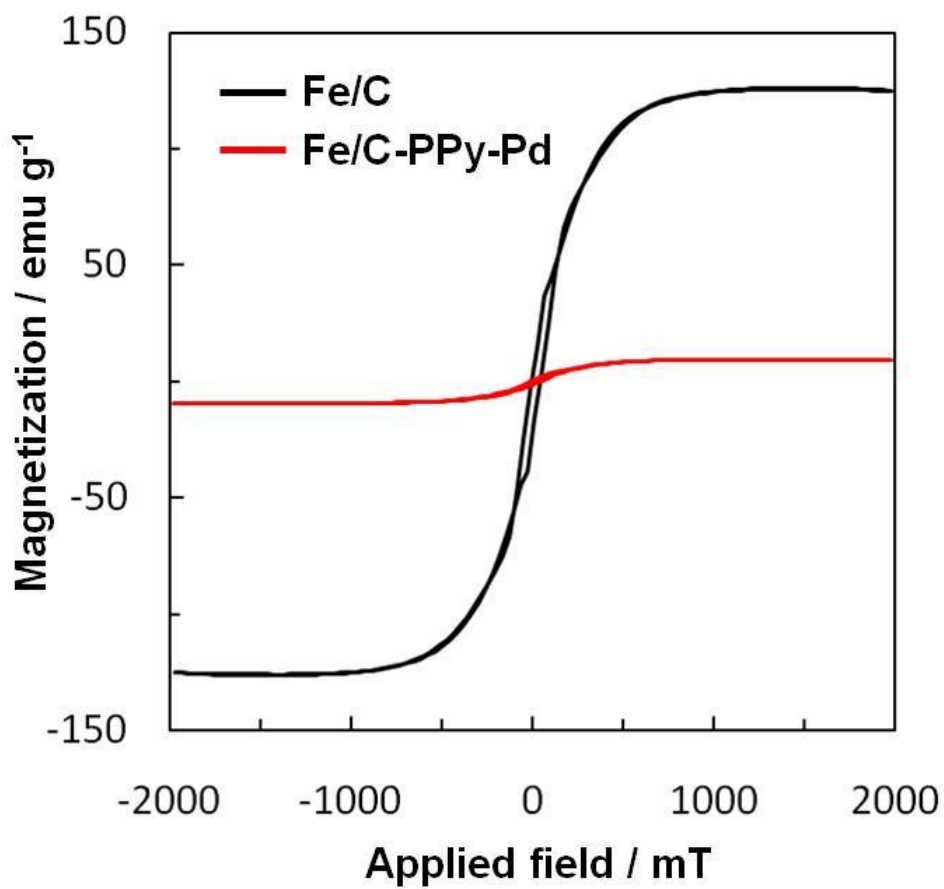


Fig. S8 Suzuki-Miyaura cross-coupling reaction using nanocomposite microspheres in aqueous media.

