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Highly Efficient Degradation of Organic Dyes by Palladium Nanoparticles Decorated on 2D Magnetic Reduced Graphene Oxide Nanosheets

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Chemicals

Graphite flake, PEI (Mr: 25000), DIB, $PdCl_2$, Iron(III) acetylacetonate ($Fe(acac)_3$), benzylether, and oleylamine were purchased from Sigma-Aldrich. Sulfuric acid (H_2SO_4, 98%), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2, 30%), hydrogen chloride (HCl, 37%), and sodium borohydride ($NaBH_4$) were obtained from Tianjin Med.

Instrumentation

X-ray powder diffraction patterns of the as-prepared samples were characterized by a Bruker AXS D8 Advance diffractometer using CuKα radiation (λ = 1.5418 Å). Transmission electron microscopy (TEM) were conducted on a JEM-2100 system with an accelerating voltage of 200 kV. The samples for TEM characterization were prepared by the deposition of hexane or ethanol dispersions of the nanomaterials on amorphous carbon-coated copper grids at room temperature. X-ray photoelectron spectroscopy (XPS) spectra were determined using a PHI-5702 multifunctional spectrometer with AlKα radiation. Magnetization measurements were obtained using a Lakeshore 7404 high-sensitivity vibrating sample magnetometer (VSM) with fields up to 1.5 tesla at room temperature. A Nicolet FT-170SX spectrometer was used to demonstrate the chemical nature of the products in KBr pellets. The contents of the iron and palladium in the sample were determined using inductively coupled plasma (ICP).

Preparation of PEI-RGO (1a)

Graphene oxide (GO) was prepared from graphite flake powder according to a modified Hummers method[1]. PEI-RGO was obtained according to the literature with a little modification[2]. In our experiment, 100 mL of the GO dispersion (0.1 mg/mL) was dispersed into a solution that contained PEI (1 g) in distilled water (100 mL) by sonication for 60 min. Subsequently, the reaction solution was kept at 60 °C for 12 h. The product was collected by centrifugation and washed several times with ethanol and diethyl ether (1:4 v/v). The as-prepared intermediate was then redispersed into ethanol (100 mL).

Preparation of DIB-PEI-RGO (1b)

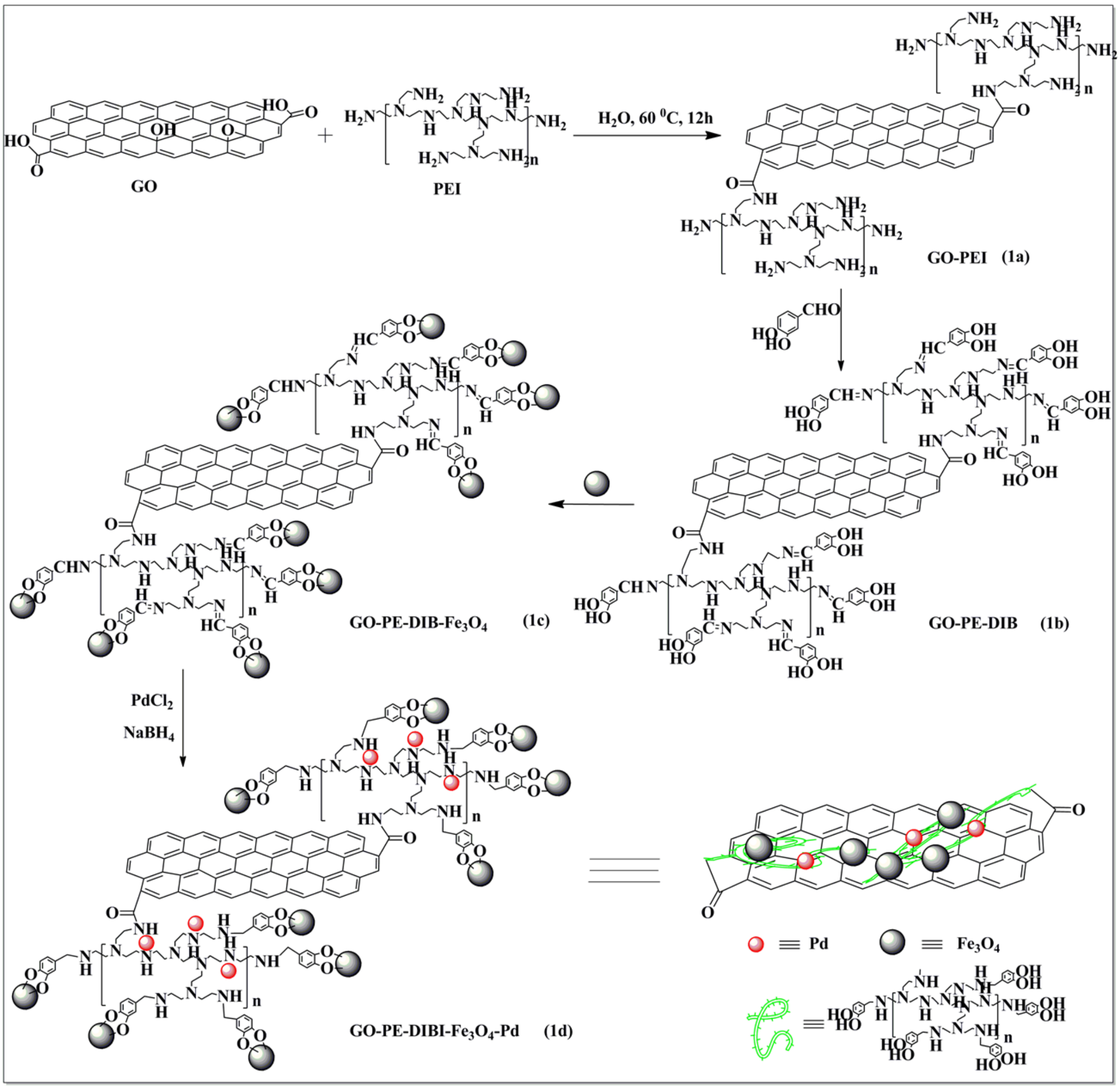
DIB (55 mg, 0.4 mmol) in ethanol (20 mL) was added dropwise into the above dispersion. After stirring for 12 h at room temperature, the product was separated via centrifugation, washed thoroughly with ethanol and diethyl ether (1:4 v/v) and then dispersed into ethanol (15 mL) as a stock solution.

Preparation of Fe_3O_4-DIB-PEI-RGO (1c)

Fe_3O_4 nanoparticles were prepared according to a previous work[3]. In our experiment, Fe_3O_4 NPs (4 mg) in a fresh mixture of ethanol and chloroform (4 mL, 2:1 v/v) was added dropwise into the stock solution of **1b** and stirred at room temperature for about 24 h. This product were thus obtained by adding hexane and collected by means of an exogenous magnet. The residual solid was repeatedly washed with hexane. The resulting solid was then redispersed into ethanol and chloroform (40 mL, 2:1 v/v).

Preparation of Pd /Fe_3O_4-DIB-PEI-RGO (1d)

1d was prepared by the literature method[4]. Briefly, the stock solution of **1c** was dispersed into 40 mL of ethanol by sonication for 30 min to form a suspension, followed by the addition of $PdCl_2$ (4.0 mg, 0.023 mmol) in ethanol (5 mL). The reaction solution was stirred for 2 h at room temperature to ensure the metal ions thoroughly bound to the N atoms of PEI. Then freshly dissolved $NaBH_4$ (5.2 mg, 0.14 mmol) in ethanol (2 mL) was added dropwise under an N_2 atmosphere into the above solution over 10 min and stirred for another 2 h. The black product was obtained by centrifugation and washed several times with excess amounts of ethanol and hexane. Finally, the solid product was dried under a vacuum at ambient temperature. For comparison, the Pd-PEI-RGO were synthesized using the same procedure, but without the addition of Fe_3O_4 NPs.



Scheme S1. Synthetic routes of Pd /Fe_3O_4-DIB-PEI-RGO (**1d**).

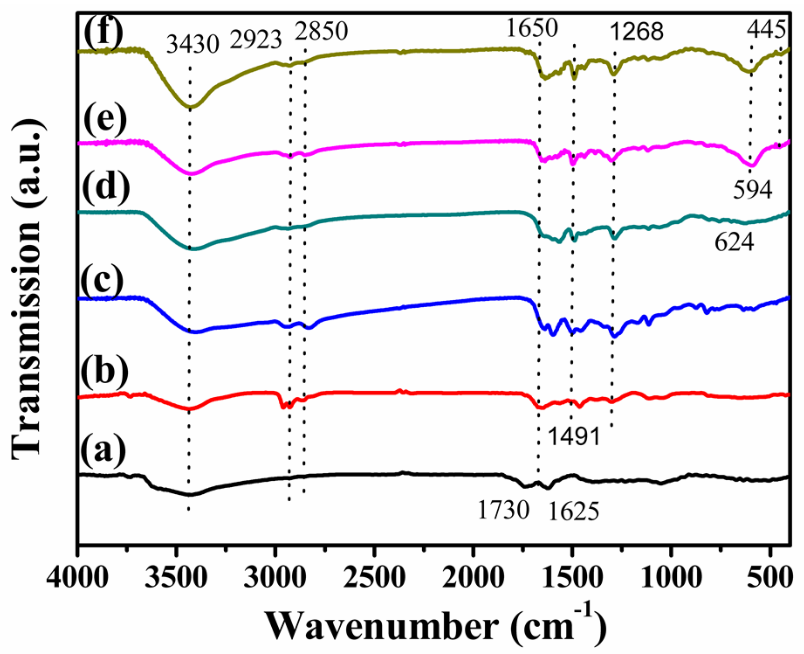


Fig. S1. IR spectra of (a) the GO, (b) the PEI-RGO, (c) the DIB-PEI-RGO, (d) the Pd-DIB-PEI-RGO, (e) the Fe_3O_4-DIB-PEI-RGO, and (f) the Pd/Fe_3O_4-DIB-PEI-RGO nanohybrids, respectively.

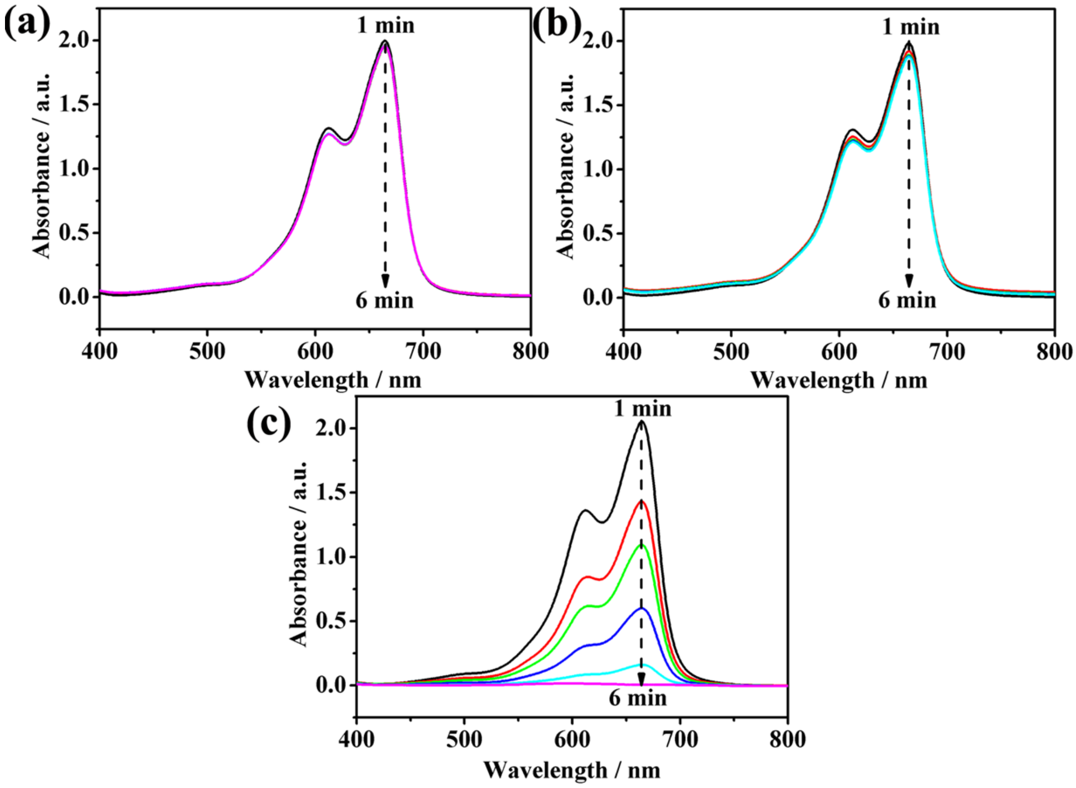


Fig. S2. UV-vis spectral changes of MB (50 μM) aqueous solution with $NaBH_4$ (1 μM) using (a) the PEI-RGO, (b) the Fe_3O_4-PEI-RGO nanohybrids, and (c) the Pd-PEI-RGO nanohybrids as catalysts at 1 min intervals.

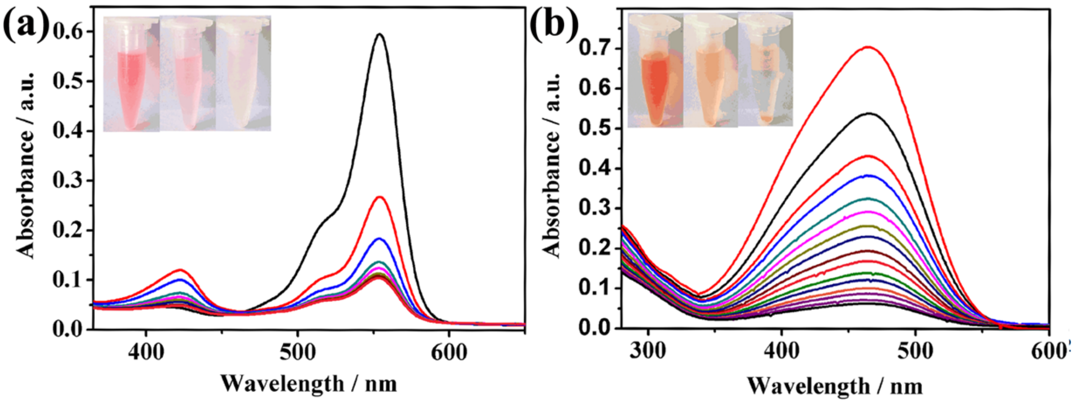


Fig. S3. (a) UV-vis spectral changes of RB (30 μM) aqueous solution with $NaBH_4$ (1 μM) using the Pd/Fe_3O_4-PEI-RGO nanohybrids as catalysts. (b) UV-vis spectral changes of MO (30 μM) aqueous solution with $NaBH_4$ (1 μM) using the Pd/Fe_3O_4-PEI-RGO nanohybrids as catalysts.

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