Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supporting Information

Atomic Layer Deposition of Palladium Nanoparticles on a Functional Electrospun Poly-Cyclodextrin Nanoweb as a Flexible and Reusable Heterogeneous Nanocatalyst for Reduction of Nitroaromatic Compounds

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Experimental.

Adsorption Studies. The Pd@poly-CD nanoweb (2.2 mg) was put into a 20 mL glass vial containing 5 mL MB solution (c= 50 mg/L)). The solution was shaken at 150 rpm at the horizontal position at 25 ^{o}C. At different time intervals, 100 μL sample was taken from the solution and 100 μL water was added to the solution to keep the volume constant. Before UV-vis measurements, the sample volume was completed to 1 mL with distilled water and disposable PMMA UV cuvettes were used for the measurements. As a control, a Pd-free poly-CD nanoweb was treated with an identical concentration of MB. The reusability of the Pd@poly-CD nanoweb was evaluated

using the same nanoweb two times more with the identical concentration of MB. In this regard, after the adsorption test, the Pd@poly-CD nanoweb was treated with methanol for 5 h to remove the adsorbed MB from the fiber surface, and the nanoweb retreated with the MB solution of the identical concentration for 5 h. During these experiments, the amounts of adsorbed and desorbed MB were determined by UV-vis measurements.

The sorption capacity (Q_e) of the Pd@poly-CD nanoweb was calculated with the following formula;

$$Q_e \text{ (mg/g)} = (c_0 - c_e) \text{ x } (V/w) \quad (1)$$

Where c_0 and c_e are the initial and equilibrium concentrations of the MB in the test solution (mg/L), V is the volume of the testing solution in L, and w is the nanoweb weight in g.

The kinetics models (pseudo-first and pseudo-second-order) are used to find the kinetic behavior of the sorption as given in Eqs. 2 and 3, respectively.

$$\log(Q_e - Q_t) = \log Q_e - k_1 t/2.303 \quad (2)$$

$$t / Q_t = 1 /k_2 Q_e^2 + t/Q_e \quad (3)$$

where Q_e and Q_t are the adsorption capacity at time t and equilibrium, respectively. The rate constants (k_1 and k_2) for the removal of MB were calculated from the equations above.

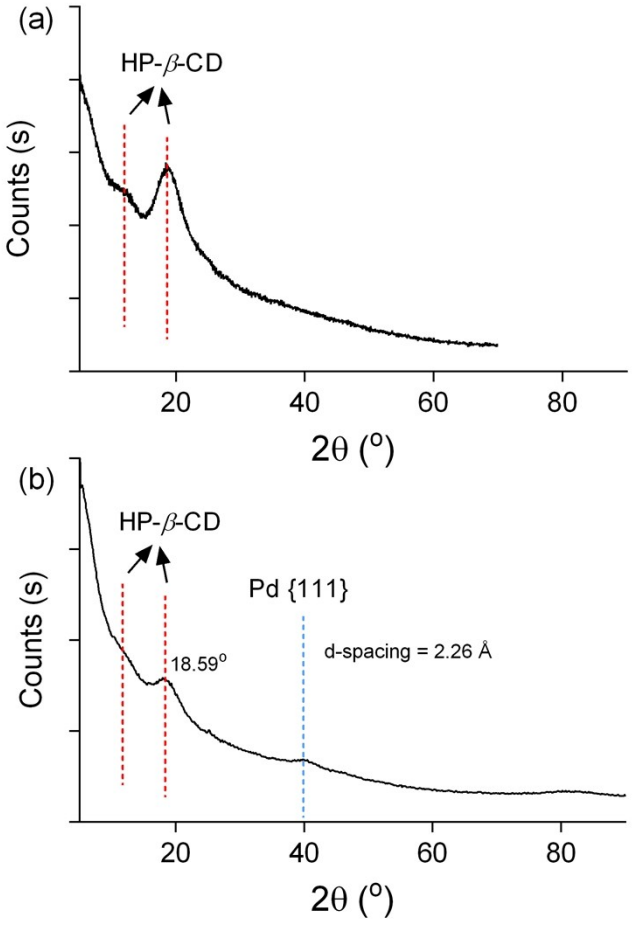

Figure S1. XRD patterns of (a) the poly-CD and (b) Pd@poly-CD nanowebs.

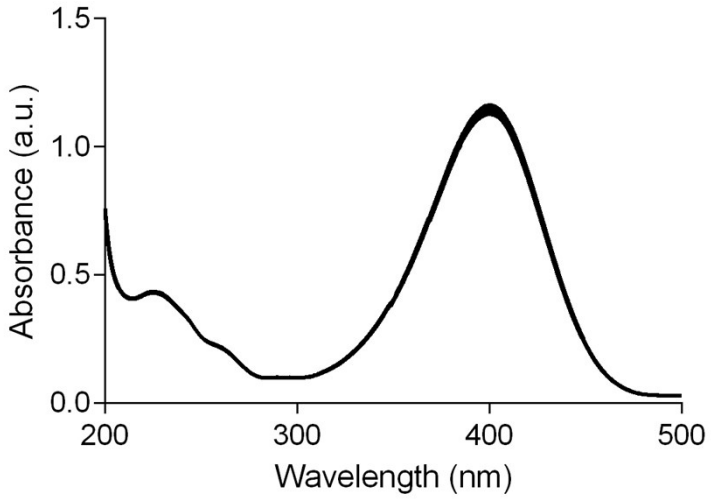

Figure S2. The catalytic conversion of 4-NP by the medium as a function of time (time interval is 5 min) after the removal of the Pd@poly-CD nanoweb.

Removal of Methylene Blue by the Electrospun Pd@Poly-CD Nanoweb. The cavity of CD molecules is ideal for complexation with dye molecules, and thus, a material composed of CD molecules can be exploited as a high-performance adsorbent for the scavenging of dyes from aqueous solutions.[1] Furthermore, the interactions between polycarboxylic-CD polymers and MB were previously studied in detail.[2, 3] In this study, we explored the adsorption performance of the Pd@poly-CD nanoweb over the scavenging of MB dye from water. In this regard, we previously studied the affinity of MB to form inclusion-complexation with the poly-CD molecules in the nanofiber form, which could sequester a significant amount of MB from aqueous solutions.[4] The UV-vis spectra of the MB solution on the course of treatment with the Pd@poly-CD nanoweb were shown in Figure S3a. The respective spectra show a clear decrease in peak intensity during the treatment with the nanoweb as a result of MB adsorption on the CD molecules. The UV-vis spectra of MB solutions at various concentrations were also measured to plot a calibration curve for MB to able determine MB content removed by the nanoweb (Figure S4). The adsorption of MB on the Pd@poly-CD nanoweb was very rapid and nearly >90% MB was removed in just 15

min (Figure S3b). The equilibrium sorption capacity was found to be 104.05 ± 6.27 mg/g. After 5 h, the color of the MB solution turned to sky blue from dark blue, suggesting a significant decrease in the MB content (Figure S3a, inset). Likewise, the time-dependent changes in the solution color were clearly observed (Figure S3c). The kinetics of the adsorption process was studied by using the pseudo-first-order and pseudo-second-order kinetic models (Figure S3d, e). The sorption kinetics fitted well with a pseudo-second-order model with the respective R^2 of 0.9999 and theoretical adsorption capacity of 102 mg/g while the respective values were calculated as 0.8634 and 57.41 mg/g according to the pseudo-first-order kinetic model (Table S1). This high sorption capacity can mostly be attributed to the inclusion-complexation with functional CD molecules. Additionally, electrostatic interactions between MB and CD molecules can also take place.[5] This sorption performance suggests the use of such materials as an adsorbent in addition to their catalytic use in the reduction of hazardous nitroaromatic compounds.[4] The reusability of the Pd@poly-CD nanoweb for the scavenging of MB was also explored. Prior to its reuse, the nanoweb was treated with a certain volume of methanol for 5 h to get rid of all adsorbed MB molecules from the nanoweb. Thereafter, the nanoweb retreated with an identical concentration of MB for 5 h. Figure S3f shows the performance of the electrospun nanoweb during its reuse for 2 times. A slight decrease in the removal performance was observed, which could be attributed to that not all adsorbed MB molecules were released to the methanol solution during the desorption process. The sorption performance of the Pd@poly-CD nanoweb was compared with the pristine Pd-free poly-CD nanoweb using the identical concentration of MB for 5 h treatment. The respective UV-vis spectra of the MB solutions show that the ALD process slightly decreased the MB-sorption performance of the poly-CD due to the partial blocking of some CD cavities by the Pd decoration (Figure S5). Overall, the MB-adsorption capacity of the Pd@poly-CD nanoweb was

very high and suggests the use of the nanoweb as an adsorbent for the removal of dyes from water in addition to its use as a catalyst (Table S2). SEM analysis on the nanoweb showed no morphological change after MB-sorption tests (Figure S6).

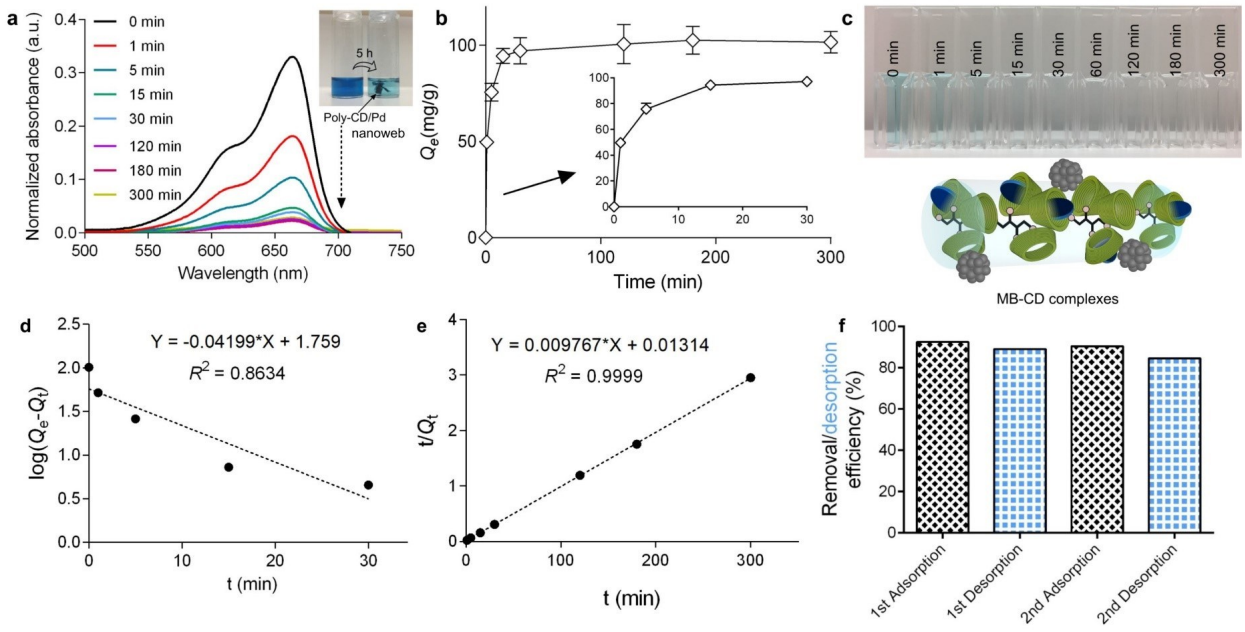

Figure S3. The removal of MB dye by the Pd@poly-CD nanoweb. (a) UV-vis spectra of the MB solution during the treatment with the Pd@poly-CD nanoweb at different time intervals. Inset photo shows the aqueous solution of MB before and after treatment with Pd@poly-CD nanoweb for 5 h. The initial MB concentration was 50 mg/L. However, the sample taken from this solution was diluted 10 times with water for UV-vis measurements. (b) Sorption capacity of the Pd@poly-CD nanoweb as a function of time. Inset shows the initial change in the respective plot. (c) The optical photos of aqueous MB solutions, which were diluted with water by ten-fold, show a clear decrease in MB content by the decolorization of the solution. (d) The pseudo-first-order kinetic and (e) pseudo-second-order kinetic plots for MB dye removal. (f) The removal/desorption efficiency of MB by the Pd@poly-CD nanoweb during its repetitive use. The treatment time for adsorption and desorption was 5 h.

Table S1. Kinetic parameters for the adsorption of MB dye by the Pd@poly-CD nanoweb.

	Experimental	Pseudo-first order model			Pseudo-second order model		
	Q_{exp} (mg/g)	Q_e (mg/g)	k_1 (min^{-1})	R^2	Q_e (mg/g)	k_2 ($g \cdot mg^{-1} min^{-1}$)	R^2
MB	104.05 ± 6.27	57.41	0.0182	0.8634	102.4	9.76×10^{-3}	0.9999

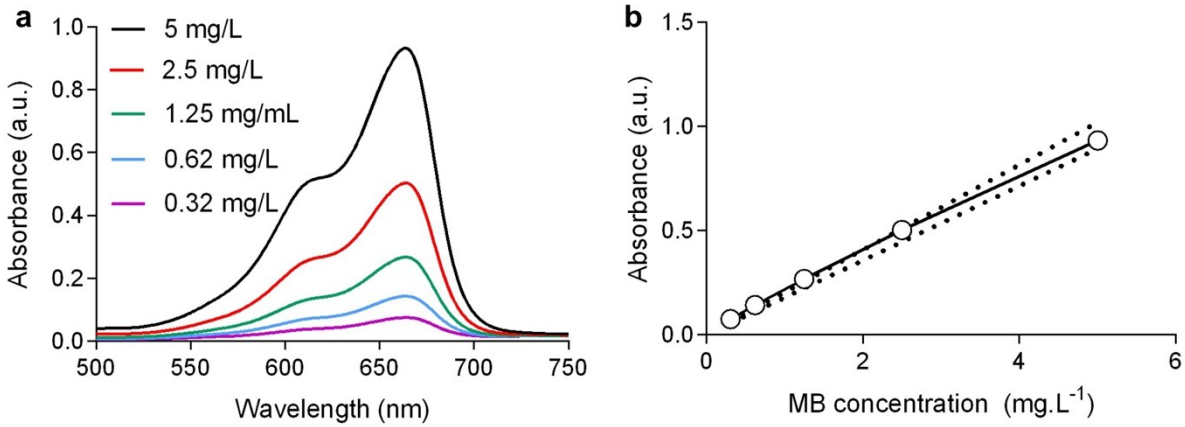

Figure S4. (a) UV-vis spectra and (b) the respective calibration curve of MB solutions prepared at various concentrations.

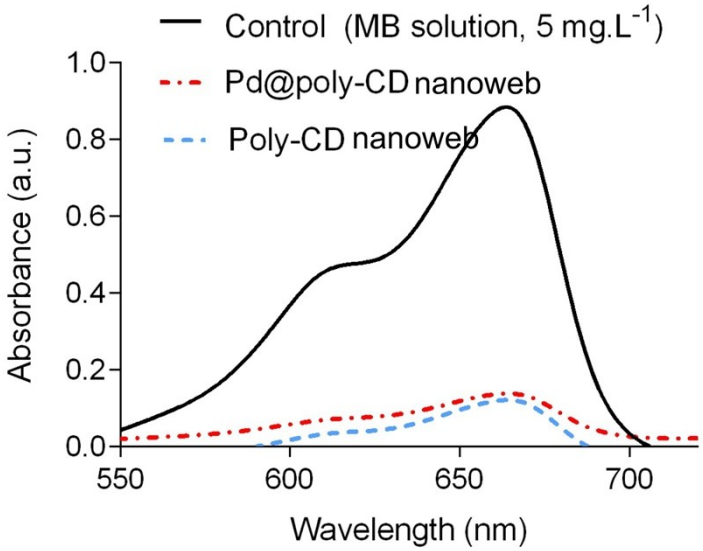

Figure S5 The UV-vis spectra of MB solutions treated with the Pd@poly-CD and Pd-fee poly-CD nanowebs for 5 h.

Table S2. Comparison of equilibrium adsorption capacity of different electrospun adsorbents for MB removal.

Adsorbent	**Equilibrium adsorption capacity ($mg.g^{-1}$)**	**Equilibrium time (min)**	**Reaction kinetic model**	**References**
Graphene oxide/polyurethane NF	~ 11	60	Pseudo-second order	[6]
Graphene oxide/gum Arabic/poly(vinyl alcohol) NF	46.4	60	Pseudo-second order	[7]
Plasma-etched PLLA NF	1.10	30	Pseudo-second order	[8]
Pd@poly-CD NF	104.05 ± 6.27	180	Pseudo-second order	This study
Polyimide (PI)-based carbon nanofibers (CNFs)	138.46	1250	Pseudo-second order	[9]
Poly-CD NF	100 (at pH = 7) 120 (at pH = 9)	180	Pseudo-second order	[4]

NF: Nanofibers

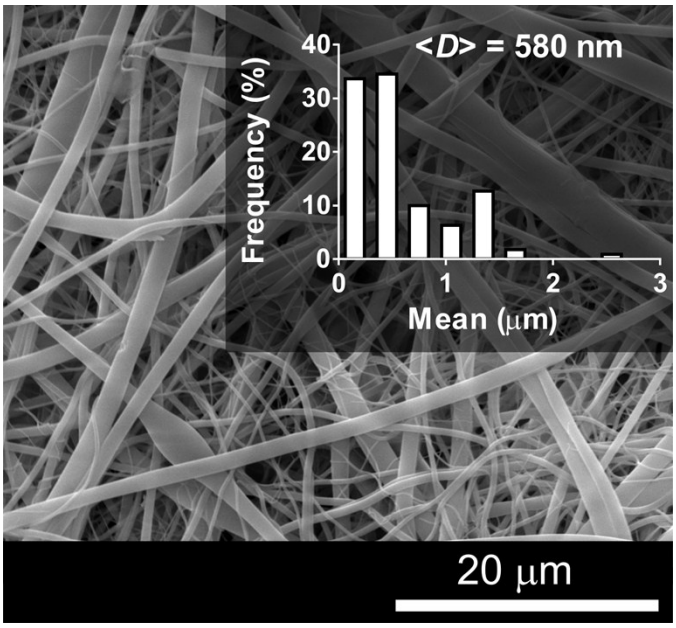

Figure S6. Scanning electron micrograph of the Pd@poly-CD nanoweb after its use in the MB removal. Inset shows the size distribution of the nanofibers.

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