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# Functional Hyper-Crosslinked Polypyrene for Reductive Decolorization of Industrial dyes and Effective Mercury Removal from Aqueous Media

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Abstract: A rigid and valuable hyper-crosslinked polymer (HCP) has been synthesized using pyrene, a polycyclic aromatic hydrocarbon (HCPPy). The HCPPy was prepared through a simple one-step Friedel-Crafts alkylation reaction that involves ZnBr2-catalyzed crosslinking in the presence of an external crosslinker, bromomethyl methyl ether (BME). Interestingly, the unreacted bromomethyl groups (-CH<sub>2</sub>Br) on the surface of HCPPy could be quantified, which later aided in modification as per our requirement. We aimed at fabricating with disulfide containing cystamine dihydrochloride (Cys-HCPPy). The Cys-HCPPy exhibited an extended  $\pi$ -conjugated system with uniform (~1 µm diameter) morphology and high porosity (specific surface area: 445 m<sup>2</sup>/g). As a fundamental application, the Cys-HCPPy composite was used as a sorbent to remove Hg<sup>2+</sup> ions from aqueous media. Thus, at pH 6, the adsorption capacity of mercury ions reached 1124.82 mg g<sup>-1</sup> after 24 h. Furthermore, the immobilization of Ag nanoparticles on the surface of Cys-HCPPy (Ag@Cys-HCPPy) enhanced the catalytic properties, which allowed for the reductive decolorization of industrial dyes such as methylene blue, methyl orange, and Congo Red in the presence of NaBH4 as a reducing agent.

#### Introduction

The substantial worldwide industrialization is one of the major threats to the environment in this century. Various industries such as textile industries, paper and pulp, plastics, cosmetics, and leather industries annually utilize huge quantities of different dyes and pigments <sup>[1]</sup>, especially azo dyes. Azo dyes are common synthetic colors that contain an azo group, in their structure. These dyes are an abundant source of colored organics originating as unwanted substances from the industry dyeing process. This widespread use of colored dyes is extremely hazardous to the environment owing to the discharge of toxic and potentially poisonous substances into aqueous systems. Color removal using Fenton reagents results in heavy sludge deposition, which also requires further separation and appropriate disposal<sup>[2]</sup>. In recent years, photocatalysis <sup>[3]</sup> and adsorption <sup>[4]</sup> have been used for wastewater treatment to effectively remove colored organics at ambient temperatures. The adsorption tactics causes the gradual transfer of effluents from wastewater to solid wastes.

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Supporting information for this article is given via a link at the end of the document.

Photocatalysis involving the use of TiO<sub>2</sub>, a well-known photocatalytic material, is the primarily used methodology for azo dye degradation. However, photocatalysts can be activated only in the presence of ultraviolet light, which limits their practical application because the UV region constitutes only 4% of the entire solar spectrum <sup>[5]</sup>. Consequently, the development of simpler and effective methodologies for the efficient degradation of azo dyes has gained much importance.

The most harmful contaminants of industrial wastewaters are mercury and its derivatives, which result in health issues and environmental pollution. Among the methods introduced for the detection of mercury in aqueous solutions, <sup>[6]</sup> the most effective one is the use of adsorbents modified by incorporating sulfurbased ligands such as thiol and thiourea groups <sup>[7]</sup>. In particular, mesoporous silica is one of the most competent adsorbents for trapping heavy metal ions because of its high specific surface area, regular and tunable pore size, etc. <sup>[8]</sup>. However, the exploration for more economically feasible and chemically stable adsorbents with easy functionalization of organic ligands for more efficient removal of Hg<sup>2+</sup> and other heavy metals is underway.

Microporous materials have recently attracted considerable attention owing to their distinctive properties such as large surface area, small pore size, and low skeletal density <sup>[9]</sup>. These materials also exhibit satisfactory chemical, thermal, and mechanical stability for application to various fields such as gas sorption and storage, heterogeneous catalysis, sensing and heavy metal removal <sup>[10]</sup>. Hyper-crosslinked polymers (HCPs) are a new subclass of porous materials synthesized from inexpensive organic monomers, and they have satisfactory stability, tunable porosity, and potential for synthetic modification. The porosity remains permanent owing to the extensive crosslinking in HCPs, which prevents the polymer chains from aggregating into a dense, nonporous state <sup>[11]</sup>. HCPs can be produced using a formaldehyde dimethyl ether crosslinker through a simple one-step Friedel-Crafts reaction, so that this approach can be extended to the synthesis of a diverse range of polymers derived from simple aromatic monomers <sup>[12]</sup>. Surface areas, pore-size distributions, and surface functionalities of HCPs are apparently tuned by changing the aromatic monomer, the reaction stoichiometry, or via the addition of functionalized aromatic comonomers.

The flexible nature of HCPs may help in moderating the environmental problems caused by poisonous heavy metals and dye molecules. Significantly, HCPs are a less explored class of porous materials for environmental pollutant removal <sup>[13]</sup>. To the best of our knowledge, the duel application of HCPs for both dye degradation and Hg<sup>2+</sup> removal from an aqueous solution has not yet been reported. Our strategy is to employ an HCP and its post-modification with a disulfide-containing chelating agent for the reductive decolorization of industrial dyes and the adsorption of

Hg<sup>2+</sup> from aqueous solutions. The HCP is synthesized via a onepot Friedel–Crafts alkylation promoted by anhydrous ZnBr<sub>2</sub>, using a low-cost pyrene monomer with an external crosslinking agent, BME. Further, the unreacted bromomethyl groups on the surface of HCPPy are simply substituted with cystamine. Furthermore, this hybrid material i.e., Cys-HCPPy, is used for the removal of Hg<sup>2+</sup> from aqueous solutions, primarily owing to the presence of disulfide-containing cystamine dihydrochloride, and for the reductive degradation of MB, MO, and CR dyes by immobilizing Ag nanoparticles (Ag NPs) on the surface of Cys-HCPPy.

#### **Results and Discussion**

#### Synthesis and modification of HCPPy

Following our previous report <sup>[14]</sup>, the HCP was obtained via simple one-pot synthesis involving crosslinking of a pyrene-like aromatic hydrocarbon in the presence of an external crosslinker. In brief, the polymer networks were prepared via Friedel-Crafts alkylation involving the condensation of BME and the pyrene monomer in the presence of ZnBr<sub>2</sub> as a Lewis acid catalyst. Anhydrous ZnBr<sub>2</sub> can induce the Friedel-Crafts crosslinking of the polypyrene with BME to construct methylene bridges that are essential for rigid aromatic network formation. The electrophilic reaction for methylene bridge formation substitution regioselectively occurred at the 1-, 3-, 6-, and 8-positions of the pyrene ring, which are more electron-rich centers. The polymer

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contains an uncrosslinked portion that exists as bromomethylated PPy. Hence, the entire bromomethylated polyaromatic networks resembling the Merrifield resin (chloromethylated polystyrene) can be widely used for the synthesis of various reactive and functional polymers that are strong and insensitive to the solvent, and the swelling problem seen for styrene-divinylbenzene resins does not exist <sup>[15]</sup>. Consequently, we found that these polymeric spherical networks serve as exceptional substrates for functionalization via simple substitution reactions <sup>[16]</sup>. This paper describes the functionalization of cystamine dihydrochloride on polypyrene spherical networks, Cys-HCPPy, and further stabilization of Ag NPs on the cystamine supported polypyrene, Ag@Cys-HCPPy, via a simple chemical reduction without any reducing agents. Previously reported synthetic methods by assembling noble metal NPs on solid surfaces based on chemical reduction have the difficulty in removing extra-reducing or protecting agents, which further affect the catalytic activity of NPs/polymer hybrid system. Interestingly, we have observed amine group present in the Cys-HCPPy directly acts as a reducing agent without applying any additional reductants or surfactants [17]. Our emphasis here is to simultaneously utilize the large surface area and high electron density of PPy, flexible structure of the cystamine moieties, and the catalytic activity of the Aq NPs. toward the degradation of industrial organic dyes and adsorption of Hg<sup>2+</sup> ions. For a better understanding of the synthesis and modification of HCPPy, we have schematically illustrated the entire synthesis process in Scheme 1.





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# Characterization of Cys-HCPPy and Ag@Cys-HCPPy hybrid materials

The functionalization of HCPPy with cystamine moieties was traced via a weight loss between 200 °C and 800 °C using TGA thermograms (Figure 1). Both HCPPy and Cys-HCPPy samples show minor weight losses around 100 °C owing to the loss of moisture and adsorbed water molecules. The degradation of amine groups and ethylene moieties covalently attached to the surface of HCPPy are observed between 200-300 °C. A sharp decrease in the temperature range between 350°C to 650 °C in HCPPy and stepwise degradation with the loss of 25% in Cys-HCPPy is due to the destruction polymer networks. Moreover, the TGA thermogram of Ag@Cys-HCPPy (Figure S1 in Supporting Information (SI)) shows the similar thermal degradation behavior with the smallest weight loss at 650 °C.

The covalent links between cystamine and HCPPy were verified via FT-IR spectroscopy (Figure 1(a)). The remaining uncrosslinked bromomethylated groups in the HCPPy provided more domains for Cys-HCPPy and were distinctly detectable from the IR spectra. The characteristic band of HCPPy was observed at 574 cm<sup>-1</sup> (C–Br stretching vibration of the CH<sub>2</sub>Br group). For Cys-HCPPy, the C-Br peak disappeared and a new peak at 1247 cm<sup>-1</sup> (C–N stretching vibrations) appeared. Furthermore, the spectrum exhibited the vibration band of N–H at 1630 cm<sup>-1</sup> <sup>[18]</sup>. FTIR spectrum of Ag@Cys-HCPPy shown in the Figure S2 in SI.



Figure 1. FTIR spectra (a) and TGA profiles (b) of HCPPy and Cys-HCPPy.

For further confirmation of the surface functionalization of HCPPy with cystamine, we carried out XPS and EA of the assynthesized Cys-HCPPy. The weight percentages of different elements are shown in Table 1. The presence of nitrogen and sulfur was attributed to the functionalization of cystamine. More information was obtained by observing the high-resolution spectra of C1s, N1s, and S2p (Figure 2(a)). The XPS spectrum of HCPPy shows the Br3d at 72.5 eV that is considerably reduced after the functionalization. The C1s spectrum of Cys-HCPPy could be deconvoluted into two peaks centered at 284.4, and 285.5 eV, which corresponded to  $sp^2$  C and C–N bonds, respectively <sup>[19]</sup> (Figure 2(b)). As seen in Figure 2(c), the N1s peak could be fitted into two curves with binding energies of 399.4 and 401.8 eV, which attributed to the formation of a primary amine (–CH<sub>2</sub>–NH<sub>2</sub>) and a secondary amine (–NH–CH<sub>2</sub>–) <sup>[20]</sup>. The lower energy peak

at position of 163.6 eV was observed for S–S bond in the cystamine (Figure 2(d)). Overall, the XPS data confirmed the functionalization of cystamine on the HCPPy surface <sup>[21]</sup>. Figure S3 in SI shows the wide-scan XPS spectrum of Ag@Cys-HCPPy and its core-level XPS spectrum for Ag 3d. Two clear peaks can be observed due to Ag  $3d_{5/2}$  (368.8 eV) orbit and Ag  $3d_{3/2}$  (374.9 eV) orbit, which is associated to the formation of Ag<sup>0</sup>.

Table 1. Elemental composition of Cys-HCPPy							
Cys-HCPPy	C (wt %)	H (wt %)	N (wt %)	S (wt %)			
XPS data report	93.53		3.11	3.08			
EA data report	90.21	4.65	2.95	2.55			



Figure 2. Wide-scan XPS spectrum of Cys-HCPPy (a); core-level spectra of C1s (b), N1s (c), and S2p (d).

For the structural morphology analysis of polymeric system, as-synthesized samples were subjected to FE-SEM and TEM characterization. From the FE-SEM images (Figure 3), spherically self-assembled HCPPy could be observed, which was interestingly obtained within 30 min of polymerization. Uniform microspheres with a particle size of approximately 1 µm could be intrinsically fabricated without using any templates. Postmodification with cystamine on HCPPy did not lead to any morphological variation (Figure 3(b)). Figures 3(c) and (d) demonstrate the formation of Ag NPs on the Cys-HCPPy microsphere surface after modification with silver nitrate solution. The TEM images of Ag@Cys-HCPPy (Figures 3(g) and (h)) indicated that Ag NPs are immobilized on the surface of Cys-HCPPy, revealing the formation of the Ag@Cys-HCPPy composite. The existence of Ag NPs on the surface of the Cys-HCPPy was also confirmed using an EDS detector coupled to SEM system, which demonstrated the presence of C, O, and Ag in Figure 4 (d). The sample was coated with Au before the

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analysis, so the presence of this element was also indicated in the EDS mapping.

The surface porosity parameters of HCPPy and Cys-HCPPy were investigated via nitrogen adsorption analysis at 77.3 K. As shown in the Figure 4(a), the isotherm of the polymer exhibits a type I character, with a sharp nitrogen gas uptake at low  $P/P_0$  with a large microporous structure; the significance of broad hysteresis in the HCPPy isotherm suggests the presence of mesopores <sup>[22]</sup>. After the functionalization, the hysteresis loop was decreased as shown in the isotherm of Cys-HCPPy. The broadness between the desorption and adsorption branches at low relative pressures might be due to the swelling of the porous

polymer networks.<sup>[23]</sup> The BET surface area calculated for HCPPy is 520 m<sup>2</sup> g<sup>-1</sup> at a low relative pressure ( $P/P_0 < 0.001$ ), whereas the calculated surface area of Cys-HCPPy is 445 m<sup>2</sup> g<sup>-1</sup>. The slight decrease in the surface area is due to the functionalization by Cys. Based on pore size distribution analysis (Figure 4(b)), as determined by NLDFT, micropores with width of ca. 0.86 nm and minor mesopores peaked around 2.08 nm are confirmed for HCPPy. The micropore volume and total pore volume are 0.6841 cm<sup>3</sup>/g and 0.9528 cm<sup>3</sup>/g, respectively, where the micropore volume was determined using the t-method. After the functionalization, mesopore peak decreases gradually and a minor peak appears around 2.2 nm.



Figure 3. FE-SEM [(a)–(d)] and TEM [(e)–(h)] images of HCPPy (a), Cys-HCPPy (b, e and f), and Ag@Cys-HCPPy (c, d, g and h) under low- and high-magnifications.



**Figure 4.** Nitrogen adsorption/desorption isotherm of HCPPy and Cys-HCPPy (brown filled symbols for adsorption branch and green filled symbols for desorption branch) (a); pore size distribution curves calculated via NL-DFT (b); XRD patterns of HCPPy, Cys-HCPPy, and Ag@Cys-HCPPy (c); and SEM-EDS spectrum of Ag NPs. The peak at 3 keV confirms the presence of Ag (d).

Figure 4 (c) shows the XRD patterns of the pure HCPPy, Cys-HCPPy, and corresponding nanocomposites with Ag NPs. The representative Bragg diffraction peaks for Ag at  $2\theta = 37.88^{\circ}$ , 44.19°, 64.14°, and 77.28° were observed in the XRD pattern of Ag@Cys-HCPPy, which corresponded to the face-centered cubic (fcc) phase of Ag (111), (200), (220), and (311), respectively <sup>[24]</sup>. The sharp diffraction peaks distinctly indicated the existence of Ag NPs on the polymer surfaces. Moreover, a broad band centered at  $2\theta = 22.71^{\circ}$  was present, which was characteristic of the amorphous nature of the polymer networks.

Considering the simulated polymerization method can be to mimic complicated polymerization tailored systems accompanied by crosslinking in multistep processes, a computational methodology for structure generation of HCPPy polymers was studied, consisting of a crosslinking simulation script using Forcite - an atomistic molecular dynamics module within BIOVIA's Materials Studio [25]. For the simulation, amorphous cell is constructed by a random packing of repeat units into a box under periodic boundary conditions at an initial density, 0.8 g/cm<sup>3</sup>. The chemical structures of the repeat units are defined as shown in Figure 5(a) and 100 units of 1-(bromomethyl)pyrene, 67 units of 1,6-bis(bromomethyl)pyrene and 22 units of 1,3,6-tris(bromomethyl)pyrene are packed in a unit cell as illustrated in Figure 5(b). Then, a polymerization step is performed so that close contacts between the pair of reactive atoms (R1 and R2 in Figure 5(a)) that meets all bonding criteria

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can be selected. After a new bond is formed between predefined R1 and R2, and side product, HBr, is removed from the box, an energy minimization is performed to relax the newly formed bond. If no pair meeting all bonding criteria is found, a molecular dynamics simulation is performed and a polymerization step is attempted again. This is repeated until the targeted conversion is achieved. As shown in Figure 5(b), a segment of a line of the periodic box bearing 200 monomers is 47.13 Å before polymerization. However, it sharply decreases to 41.64 Å even at very low conversion (X) of 4.8%, then, it decreases monotonously according to X value to yield 40.04 Å at X = 100%. The degree of conversion are easily identified by the decrease of the number of red balls representing bromine atoms.

At low degree of conversion, crosslinked networks would not be formed and the polymers are essentially nonporous, since the flexible and mobile nature of growing polymer chains prevents pores from forming. As the degree of conversion increases to a specific degree inducing gelation, expected micropores are formed. Figure 5(b) display the variation of pore volumes as defined by the solvent-accessible surface <sup>[26]</sup> with respect to the degree of conversion from X=0.0% to 100%. A solvent-accessible surface area (SASA) was calculated for each cell with a solvent diameter set to 3.681 Å (the kinetic diameter of nitrogen). The amorphous cells for the 200-unit cluster with solvent-accessible surfaces (in blue) are shown in Figure 5(b). The surface area is calculated from the center of the probe molecule for the accessible surface and the accessible solvent-accessible surface



Figure 5. Bromomethylated PPy monomers to build networks and simplified flow chart to obtain HCPPy network (a), and snapshots of molecular simulation boxes of HCPPy networks taken at various degrees of conversion showing the solvent-accessible surface areas (blue areas). For amorphous cells construction, 200 units of monomer consisting of 100 units of M1, 67 units of M2 and 33 units of M3 were used. Dark blue areas represent the micropore surface, grey balls and sticks represent newly formed crosslink sites, and red balls represent unreacted bromine groups (b).

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area describes the surface area of pore structures more accurately in terms of real physical sorbent-sorbate interactions and is also related to the entropy of the adsorbed molecules <sup>[25]</sup>.

At low degree of conversion, X=4.8% to 38.7%, the solvent accessible area is around 50 m<sup>2</sup>/g, which is variable upon simulation conditions, since the growing polymer chains are flexible and movable until gelation occurs. The SASA sharply increases to 245.2 m<sup>2</sup>/g at X=52.0%, demonstrating the formation of micropores by the primary gelation; however, it decreases to 28.6 m<sup>2</sup>/g at X=88.6%, most probably due to the secondary gelation inside of crosslinking networks. The SASA value increases to 480.8 m<sup>2</sup>/g at X=92.2%. Even though the simulated geometric and BET surface areas are fundamentally different and should be compared with care, and strict trend of the variation of SASA according to the degree of crosslinking is not observed, considering the experimental BET surface area of HCPPy is 520 m<sup>2</sup>/g, the calculated solvent-accessible surface areas show reasonable agreement with the experimental BET value as measured by N<sub>2</sub> sorption. The origination of discrepancies between BET surface area and SASA have been well described in the literature [27].

#### Catalytic reduction of MB, MO, and CR

To explore the promising competency of Ag@Cys-HCPPy to remove impurities from wastewater, the catalytic activity of Ag NP-immobilized polymer microstructures was evaluated with respect to the reduction of MB, MO, and CR in the presence of NaBH<sub>4</sub> as a reducing agent. Experiments were conducted in both the presence and absence of the catalyst. The reduction of MB solution (0.313 mol L<sup>-1</sup>) catalyzed by Ag@Cys-HCPPy (1 mg) was conducted in the UV cuvette and monitored via time-varied absorbance spectral changes at 664 nm with the addition of freshly prepared 50  $\mu$ L of 0.1 M NaBH<sub>4</sub>.

As shown in Figure 6(a), the absorption spectra evidently demonstrated a continuous decrease in the absorption intensity of the blue colored MB solution, indicating the reduction of MB. The absorption intensity was unaffected in the absence of the catalyst or NaBH<sub>4</sub> even after 150 min. Figure 6(b) shows the degree of degradation of MB versus reaction time for Ag@Cys-HCPPy. The degree of degradation was calculated using the expression  $(I_0 - I)/I_0 \times 100$ . The degree of degradation increased linearly with time and reached 90.7% after 40 min in the presence of the catalyst and NaBH<sub>4</sub>. In the absence of the catalyst, the degree of degradation only reached up to 15% in 150 min (Figure 6(g)).

The decolorization experiments were also conducted on other azo dyes such as MO and CR, which contain diazo chromophores. The Ag@Cys-HCPPy (1 mg) was used to treat MO solution (0.305 mol L-1) with the addition of 50  $\mu$ L freshly prepared 0.1 M NaBH<sub>4</sub>. The degradation was monitored in situ by UV/Vis spectroscopy. Fig. 6(c) shows the variation in the UV/Vis absorbance spectra as a function of time; the prime absorption peak for MO appears at 467 nm, which decreases and flattens after 12 min. The degree of degradation reached 99.9% after 12 min (Figure 6(d)) in the



As shown in Figure 6(e), CR (0.143 mol L<sup>-1</sup>) exhibited the typical absorption peak at 494 nm and degradation as a function of reaction time. After 40 min, the color of the CR solution disappeared, indicating degradation resulting from the cleavage of azo bonds of this dye, similar to MO. It was observed that 98.1% of CR was degraded, but this required a longer time than of MO (Figure 6(f)), this might be due to the presence of two azo groups in CR. The degree of degradation only reached 14.5% in 150 min in the absence of the catalyst (Figure 6(g)). Generally, the reductive decolorization of a metal hydride on the catalyst surface after the adsorption of NaBH<sub>4</sub>. Subsequently, desorption results in the formation of a vacant space for further dye adsorption, so that the reduction continues <sup>[28]</sup>.

In the reductive dye-decolorization study, we found that the large redox potential barrier between donor (BH<sub>4</sub>-) and acceptor (dyes) hinders rapid degradation. However, in the presence of the catalyst, the high surface area and the interconnected large pores within the frameworks of Ag@Cys-HCPPy hybrid significantly favor double electron transfer to adsorb the dyestuffs owing to the electrostatic force of attraction, and the required reactions are terminated within a short time <sup>[29]</sup>. Excess NaBH<sub>4</sub> (reaction equivalent) does not affect the reduction rate; thus, the reaction is considered to follow pseudo-first-order kinetics based on the straight line obtained in the (Figure 6(h)) plot of  $ln(A_t/A_0)$  verses time.

The rate constant (k) for the reaction is calculated using  $ln(A_t/A_0) = -kt$ , where k is the pseudo first order rate constant;  $A_t$ and A<sub>0</sub> are the absorbance for the initial concentration of the dye and that at a specific time, respectively. The kinetic constants A<sub>0</sub>, At, and k for MB, MO, and CR degradation were obtained via exponential regression from the experimental data. The k value for MB is 0.0491 min-1 and that for MO with one azo group is 0.4788 min<sup>-1</sup>. Because CR has two azo groups, the k value is much smaller, 0.0227 min<sup>-1</sup>, under similar conditions. After the catalytic reactions under the NaBH<sub>4</sub> environment, the Ag@Cys-HCPPy material characterized using SEM, confirming that Ag NPs are bound on the surface of polymer networks and no significant changes are observed (Figure S4 in SI). Based on the experimental results of catalytic reduction of MB, MO and CR displayed in the Figure 6 and associated schemes given in the Figure S5 in SI, a possible mechanism for reductive decolorization of dye molecules can be described. Ag NPs stabilized on the Cys-HCPPy help the electron relay from the donor species to the acceptor substrate. Then, a redox mechanism occurs where the Ag NPs catalyze the transfer of electrons from donor BH<sub>4</sub><sup>-</sup> ions to the acceptor dye molecule. This type of electron conducting phenomenon is called as "electron relay effect" in which metal NPs perform as a redox catalysts <sup>[30]</sup>.



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Figure 6. UV–visible spectra recorded during MB (a), MO (c), and CR (e) degradation over Ag@Cys-HCPPy, degree of degradation versus time profiles of MB (b), MO (d), and CR (f), degree of degradation versus time profiles (g) in the absence of any catalysts, and pseudo-first-order kinetic plots (h) for the degradation of MB, MO and CR using Ag@Cys-HCPPy.

#### Adsorption of Hg<sup>2+</sup> from aqueous solution

After identifying the structural stability, porosity, and sulfur content of the chelating groups of Cys-HCPPy, we studied their capability to adsorb Hg<sup>2+</sup> from aqueous solutions. To measure the overall ability of Cys-HCPPy for Hg<sup>2+</sup> adsorption, the equilibrium data were collected after effective treatment of Hg<sup>2+</sup> aqueous solutions with initial concentrations of 1294.34 ppm at pH 6. As previously reported, metal hydrolysis might occur above pH 6 and the resultant Hg(OH)<sub>2</sub> slightly inhibits the adsorption capacity of the adsorbent <sup>[31]</sup>. The metal ion concentration of all post-filtered aliquots was obtained by ICP-OES analysis. After treatment with the metal ion-containing aqueous solution using HCPPy and Cys-HCPPy, the initial concentration of Hg<sup>2+</sup> in the solution reduced to 1059.89 ppm and 169.52 ppm. The adsorption capacity of the adsorbent for divalent mercury per gram (qe, in mg g<sup>-1</sup>) was determined. In the presence of unmodified HCPPy, very less adsorption capacity for the Hg<sup>2+</sup> species (234 mg g<sup>-1</sup>) was observed in 24 h, which might be due to the presence of surface porosity. Simultaneously, Cys-HCPPy exhibited significant adsorption capacity of 1124.82 mg g<sup>-1</sup>. This observation is

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certainly favored with respect to the coordination reaction between Hg and disulfide-containing cystamine ligands.

The Hg<sup>2+</sup> adsorption capacity of Cys-HCPPy, in comparison with that of other micro- and mesoporous materials, is shown in Table 2. Compared with thiol-functionalized non-silicate adsorbents, the

Table 1. Systematic literature survey of materials used for $\mathrm{Hg}^{2+}$ adsorption							
Entry	Adsorbent	Supporting material	Ligands	<i>q<sub>e</sub></i> <sup>[a]</sup> (mg g⁻¹)/h	Ref.		
1	γ-PGA	Extracellular biopolymer	γ-Glutamic acid	96.8	[32]		
2	Thiol- CNT/Fe <sub>3</sub> O <sub>4</sub>	MWCNT/ Fe <sub>3</sub> O4 <sup>[b]</sup>	Thiol	65.5	[33]		
3	SH-HMS	Silica	Thiol	140.1/12	[34]		
4	COF- LZU8	COF <sup>[c]</sup>	Thiol	236	[35]		
5	SH-SBA- 15	Silica	Thiol	429	[36]		
6	PAF-1	POP <sup>[d]</sup>	Thiol	1000/8	[37]		
7	CBAP-1 (EDA)	POP	EDA	181/1	[38]		
8	CBAP-1 (AET)	POP	AET	232/1	[38]		
9	Cys- HCPPy	HCP	Cystamine	1124.8/24	This work		

[a] Adsorption capacity/time. [b] Multiwall carbon nanotube/magnetite nanocomposites. [c] Covalent organic framework. [d] Porous organic polymer.

disulfide-containing cystamine-functionalized Cys-HCPPy material demonstrated significantly higher adsorption capability for Hg<sup>2+</sup> ions. The ge value was higher than those of g-glutamic acid-functionalized biopolymers and thiol-functionalized CNT/Fe<sub>3</sub>O<sub>4</sub>, as well as those of thiol-functionalized mesoporous silica and microporous COF-LZU8, as described in the literature. Generally, the high adsorption capacity of mesoporous materials is attributed to the unimpeded and easy diffusion of Hg<sup>2+</sup> ions to the adsorption sites (Entries 5 and 6). Recently, ethylenediamine (EDA)- and 2-aminoethanethiol (AET)-functionalized microporous polymers were used as adsorbents with excellent adsorption capacity (Entries 7 and 8). Thus, we expect that the synergetic effect of the micro- and mesoporous nature of HCP might enhance the adsorption capacity for Hg<sup>2+</sup> in aqueous solutions.

### Conclusions

In summary, we have developed a HCP using pyrene monomer through a simple one-step Friedel-Crafts alkylation involving ZnBr<sub>2</sub>-catalyzed crosslinking in the presence of BME. Further chemical modification of the -CH<sub>2</sub>Br moiety on the periphery of HCPPy via cystamine dihydrochloride was successfully achieved, and the resulting material was well characterized. As discussed in the results, Cys-HCPPy has a reasonably large specific surface area, extended  $\pi$ -conjugated system, and microporous structure, which make it an effective material for use in adsorption and

catalysis. In the preliminary study, Cys-HCPPy was used as the potential adsorbent for the removal of Hg<sup>2+</sup> from aqueous solutions. The ligand nature of the Cys-HCPPy surface significantly enhanced the Hg<sup>2+</sup> adsorption capacity. Furthermore, we demonstrated the reductive degradation of MB, MO, and CR dyes after immobilization of Ag NPs on the surface of Cys-HCPPy. The findings of this study indicate that these types of rigid and cost-effective post-modified microporous polymers will propel research in the area of environmental remediation.

### **Experimental Section**

#### Materials

The aromatic monomer, pyrene (98%), and cystamine dihydrochloride (96%, Sigma-Aldrich) were used without further purification. Other chemicals, including the bromomethyl methyl ether (BME) crosslinker (95%, TCI, Japan), ZnBr2 (98%, TCI, Japan), silver nitrate (AgNO<sub>3</sub>, ACS reagent,  $\geq$ 99.0%, Sigma-Aldrich), and mercury (II) nitrate hydrate, (Hg(NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O, ACS, 98.0%, Alfa Aesar) were also used as received. Congo Red (CR), methylene blue (MB), methyl orange (MO), 1,2-dichloroethane (DCE), and dichloromethane (DCM) were procured from Daejung Chemical Co. (Korea). DCE and DCM were distilled before use.

#### Instrumentation

The functional groups of the polymers were analyzed using a Fourier transform infrared (FT-IR) spectrometer (Nicolet iS5, Thermo Scientific) and a PHI 5400 X-ray photoelectron spectroscope (XPS, Physical Electronics, Mg Ka source). The surface morphologies of the samples were investigated using a field emission scanning electron microscope (FESEM, ZEISS Supra 40VP SEM) and transmission electron microscope (TEM). The surface areas were analyzed using a NOVA 3200e surface area and pore size analyzer. The Brunaeur-Emmett-Teller (BET) surface areas were determined using the BET theory. The total pore volumes  $(V_t)$ . estimated from the amount of nitrogen adsorbed at a relative pressure  $(P/P_0)$  of ~0.997 at 77 K, were measured using a Nova 3200e system (Quantachrome Instruments, USA). Pore size distribution was analyzed using the nonlocal density functional theory (NLDFT) method combined with nonnegative regularization and medium smoothing. Thermogravimetric analysis (TGA) was performed using a TGA N-1000 (Scinco, Korea) instrument. X-ray diffraction (XRD) analysis was performed using an automatic Philips powder diffractometer with nickelfiltered Cu Kg radiation. The diffraction patterns were collected in the 20 range of 0-80° in steps of 0.02° and at counting times of 2 s step<sup>-1</sup>. Elemental analysis was conducted on a GmbH elemental analyzer and Energy-dispersive X-ray spectroscopy (EDS) coupled with SEM. The Hg<sup>2+</sup> concentrations were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES, ACTIVA, JY HORIVA).

#### Synthesis of HCPPy

BME (0.60 g, 4.8 mmol) was added dropwise to the DCE (15 mL) solution containing ZnBr<sub>2</sub> (0.54 g, 2.4 mmol) and pyrene (0.50 g, 2.4 mmol) under nitrogen atmosphere, and subsequently, the mixture was stirred for 12 h at 40 °C. The resulting precipitate was thoroughly washed with water and methanol until the filtrate became clear. After Soxhlet extraction with methanol for 24 h, the spherical HCPPy was collected (60% yield) and dried overnight in a vacuum oven at 110 °C. The concentration of unreacted  $-CH_2Br$  was assayed via colorimetric estimation <sup>[16]</sup>. The bromine content of HCPPy was 4.7 mmol g<sup>-1</sup>.

#### Functionalization of HCPPy with cystamine dihydrochloride

HCPPy (0.1 g) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) in a 25 mL flask, and cystamine dihydrochloride 0.47 mmol (0.074 g) was added slowly at room temperature (r.t.). The mixture was stirred for 12 h at r.t. The resulting cystamine-functionalized polymer (Cys-HCPPy) was centrifuged, washed with CH<sub>2</sub>Cl<sub>2</sub> (10 mL), and dried at 80 °C for 4 h.

#### Fabrication of Ag NPs on Cys-HCPPy (Ag@ Cys-HCPPy)

Cys-HCPPy (50 mg) was dispersed in de-ionized water upon sonication in a 100 mL two-neck round bottom flask. To the solution, 10 mL of 0.01 M AgNO<sub>3</sub> solution was added dropwise, and the mixture was stirred for 5 h. The obtained light pink colored solution was filtered, washed thrice with water, and dried under vacuum to yield Ag@Cys-HCPPy.

#### Dye degradation study

For dye degradation study, a stock solution of 100 mg L<sup>-1</sup> of the industrial dyes (MB, MO, and CR) were prepared in milli Q water. For each decolorization study, 1 mL of stock solution was treated with 50  $\mu$ L of 0.1 M NaBH<sub>4</sub> and 1 mg of catalyst inside the UV cuvette. The decrease in absorbance of the supernatant solution was frequently monitored via spectrophotometric measurements at 664 nm, 467 nm, and 494 nm on a UV-1650PC spectrophotometer (Shimadzu, Kyoto, Japan). The degree of degradation of the samples was determined using the relation ( $I_0 - I$ ) ×100 /  $I_0$ , where  $I_0$  is the initial absorbance of the sample and *I* is the absorbance at time t.

#### Hg<sup>2+</sup> adsorption using Cys-HCPPy adsorbents

The conventional method was employed to study the adsorption of Hg<sup>2+</sup> from aqueous solutions onto the unmodified and modified HCPPy. The adsorbent (10 mg) was suspended in 10 mL of aqueous solution containing Hg(NO<sub>3</sub>)<sub>2</sub>-H<sub>2</sub>O at pH 6, and the mixture was stirred for 24 h at r.t. The initial concentration of mercury in the adsorption mixture was 3.7 mmol (1294.34 mg L<sup>-1</sup>). The solid was separated via filtration using a 0.45 µm PTFE syringe filter. The quantity of residual Hg<sup>2+</sup> ions in the solution was measured via ICP-OES <sup>[36]</sup>. The amount of divalent mercury species per gram of adsorbent was calculated based on the difference between the initial and final concentrations of the solution. The adsorption capacity (*q<sub>e</sub>*, in mg g<sup>-1</sup>) of the metal ions onto Cys-HCPPy was calculated based on the following mass balance equation: *q<sub>e</sub>* = [(*C<sub>0</sub> - C<sub>e</sub>*)/*m*] × *V*, where *C<sub>0</sub>* is the initial concentration of metal ions in solution, *C<sub>e</sub>* is the concentration at equilibrium after adsorption (mg L<sup>-1</sup>), *m* is the mass (g) of adsorbent, and *V* is the initial volume of the solution (L).

#### Molecular simulations of condensation polymerization of pyrene

Molecular models for the crosslinked polymer networks of pyrene polymerization were generated using the BIOVIA Materials Studio 5.0 software package (Dassault Systemes, BIOVIA Corp., San Diego, CA) with the polymer consistent force field (COMPASS II) <sup>[39]</sup>. Molecular simulations were performed with the Forcite module, using a time step of 1 fs, the Nosé-Hoover thermostat with a Q ratio of 0.01, and the Andersen barostat with a time constant of 1 ps. Pre-defined monomers are packed into a periodic cell using Amorphous Cell module in Materials Studio. The enclosed script implemented for a crosslinking simulation using Forcite was adapted to join monomer units via a condensation polymerization based on a set of predetermined connectivity rule with the removal of generated simple molecules by condensation (see Fig. 5). Packing monomers and defining their reactive atoms and crosslinking sites, the crosslinked structure can be generated with any degree of crosslinking.

Default user parameters were used to run the script. Close contact exclusion rules were applied during the condensation polymerization.

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**Keywords:** dye degradation • hyper-crosslinked polymers • mercury absorption • polypyrene • silver nanoparticles.

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Hyper-crosslinked and porous polypyrenes synthesized by Friedel-Crafts alkylation of pyrene are effectively functionalized with cystamine and allow to immobilize Ag nanoparticles. The highly uniform spherical materials are useful for the absorption of  $Hg^{2+}$  ions from aqueous media as well as for the reductive decolorization of industrial dyes.



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Functional Hyper-Crosslinked Polypyrene for Reductive Decolorization of Industrial dyes and Effective Mercury Removal from Aqueous Media