

# Rapid and Efficient Removal of Heavy Metal Ions from Aqueous Media Using Cysteine-Modified Polymer Nanowires

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**ABSTRACT:** We report the development of a novel, simple, and highly effective polymeric material with nanoscale dimensions for use in removal of heavy metal ions from aqueous media. The nanomaterial was  $\sim 200$  nm in diameter and several microns long and was fabricated in the form of nanowires via template-directed electrochemical polymerization. The nanowires were covalently modified by cysteine, a nonessential amino acid with very high binding constants for selected toxic heavy metal ions, such as,  $\text{As}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cu}^{2+}$ . We demonstrated rapid and efficient removal of  $\text{As}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cu}^{2+}$  ions from natural water samples. The arsenic removal capacity was found to be  $\sim 160$  mg  $\text{As}^{3+}$  per gram of the material,

a substantially greater removal capacity than other materials reported to date. The removal capacity of other heavy metals ions was also rapid and effective, their concentrations becoming undetectable in a matter of minutes after treatment with the nanowires. These nanowires have demonstrated potential that could lead to a low cost, novel, and highly effective technique for use in treatment of drinking water and for other environmental remediation purposes. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 308–313, 2010

**Key words:** conducting polymers; nanowires; heavy metals; remediation; removal; treatment; polypyrrole

## INTRODUCTION

The removal of toxic heavy metal ions from the environment continues to attract much attention due to their intrinsically persistent nature and their adverse effects on humans and other species.<sup>1</sup> Most heavy metals are released into the environment due to inadequate treatment of industrial discharges, and in some cases, due to industrial accidents. An example of accidental industrial waste discharge is the 5 million cubic meters of acidic waste containing high concentrations of heavy metals that was discharged into an area surrounding the Coto de Do'ana, a World Heritage Site, and Europe's biggest natural park in southwest Spain.<sup>2</sup> Recently, a report released by Jiangsu Environment Monitoring Center indicated that almost 40% of fish in Jiangsu's Province (Eastern China) were contaminated with heavy metals, such as, Hg, Cd, Pb, and Cr.<sup>3</sup> Currently, circa 100 million people worldwide consume water with

arsenic concentrations up to 100 times above the 10 ppb limit guideline of the World Health Organization.<sup>4,5</sup> The increasingly restrictive regulations of allowable levels of heavy metals discharge and the accelerated requirements for the remediation of contaminated sites necessitates the development of highly efficient technologies for heavy metal removal.

Some methods being explored for heavy metal ion removal involve using materials, such as, modified glassy carbon spheres,<sup>6</sup> modified graphite powder,<sup>7</sup> tunable biopolymers,<sup>8,9</sup> resins,<sup>10–12</sup> crown ethers,<sup>13</sup> and zeolites.<sup>14</sup> Although these materials may be effective in heavy metal ion removal, they harbor several drawbacks. For example, ion-exchange resins lack selectivity and target specific metal ions with difficulty. They also have weak binding characteristics.<sup>15</sup> Glassy carbon spheres require extreme physical and chemical conditions for their synthesis,<sup>16</sup> and crown ethers are often toxic.<sup>15</sup> Biopolymers are not only costly but also biodegradable, thus hindering their potential for reusability.

In this article, we report the development of a novel and highly effective nanoscale polymeric material for rapid and efficient removal of heavy metal ions from aqueous solutions. The polymeric material was fabricated in the form of nanowires that were subsequently modified by cysteine, a nonessential

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amino acid with a very high binding constant for some toxic heavy metal ions like  $\text{As}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cu}^{2+}$ . We demonstrated the removal of these metal ions from aqueous solutions using these modified polymer nanowires. Because of the high surface area of the polymer nanowires and their ability to bind large amounts of cysteine, their heavy metal ion removal capacity greatly exceeds any other material reported to date. Thus, this construct could lead to a low cost and highly effective material for use in treatment of drinking water in particular and for other environmental remediation purposes in general.

## EXPERIMENTAL

### Materials and instruments

Pyrrole (99%), ethyl acetate (99.6%), acrylonitrile (99+%), and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC, 98+%) were purchased from Fisher Scientific (Fair Lawn, NJ). *N*-hydroxysuccinimide (NHS) was acquired from Pierce Biotechnology, (Rockford, IL).  $\text{l}$ -Cysteine (99.5%) was purchased from Acros Organics (NJ). Benzyltrimethyl ammonium hydroxide (40 wt % solution in methanol) was obtained from Aldrich (St. Louis, MO). Gold plating solution, Orotemp 24 TRU Rack was purchased from Technic, (Cranston, RI). Anodic alumina membranes (Anodisc 13), having 200 nm pore size and 13 mm diameter, were obtained from Whatman, (Florham Park, NJ).

Electrodeposition was performed using a multi-channel VMP3 potentio/galvanostat (Ametek Princeton Applied Research, Oak Ridge, TN). Scanning electron microscopy (SEM) images were recorded with a JEOL JSM-840A scanning electron microscope at 7 kV acceleration potential. Metal removal analysis was performed by a Liberty 150 AX Turbo ICP Emission Spectrometer (Varian, Palo Alto, CA). Fourier transform infrared (FTIR) spectroscopy was executed using a FTS 7000 from Thermo Corporation. The spectrometer was equipped with a DTGS KBr detector in the region  $400\text{--}4000\text{ cm}^{-1}$ . An average of 20 scans ( $4\text{ cm}^{-1}$  resolution) were obtained and then averaged.

### Synthesis of pyrrolepropylic acid

Pyrrolepropylic acid (PPA) was prepared according to a literature protocol (Scheme 1).<sup>17</sup> Briefly, 55 mmol of pyrrole was added to 1.7 mmol of benzyltrimethylammonium hydroxide. Subsequently, acrylonitrile (55 mmol) was added gradually to the reaction mixture and stirred overnight. The resulting mixture was hydrolyzed using potassium hydroxide followed by overnight refluxing. After cooling, the

reaction mixture was acidified to pH 3.0 using hydrochloric acid. The aqueous layer was extracted four times with ethyl acetate. The combined organic layer was washed with brine, dried with magnesium sulfate, and evaporated to yield solid PPA [proton nuclear magnetic resonance spectroscopy in deuterated chloroform ( $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )) gave the following peaks: 2.83 (t, 2H,  $J = 7.2$  Hz), 4.20 (t, 2H,  $J = 7.2$  Hz), 6.14 (t, 2H,  $J = 2.1$  Hz), 6.67 (t, 2H,  $J = 7.2$  Hz), 9.00 ppm (s, bd peak, 1H)].

### Electrochemical deposition of poly(PPA) nanowires

Fabrication of poly(PPA) nanowires was accomplished using an electrochemical template-directed method.<sup>17,18</sup> Before the electrodeposition process, one side of the alumina template was sputtered with a thin gold film, which also acted as the seed layer. The template was mounted on an electrode and immersed in gold plating solution (Orotemp 24 RTU solution). A potential of  $-0.9$  V versus Ag/AgCl was applied to effectively seal the pores in the template. A platinum gauze was used as a counter electrode. The electrode containing the template was sequentially rinsed with water and acetonitrile before immersion in a solution containing the 0.2M of PPA monomer in 0.1M solution of lithium perchlorate ( $\text{LiClO}_4$ ) in acetonitrile. Application of positive potential ( $+0.9$  V) enabled the growth of poly(PPA) nanowires on the gold layer. The gold layer was later dissolved in aqueous 0.2M  $\text{KI}/\text{I}_2$  solution. The alumina template was dissolved in 0.5M NaOH, leaving the suspended poly(PPA) nanowires. The resultant poly(PPA) nanowires were centrifuged at 13,000 rpm, and the solution phase was discarded. Subsequently, the nanowires were washed with water and centrifuged. This process was repeated several times until the suspension solution achieved a neutral pH, after which the nanowires were separated and air dried. The resultant poly(PPA) nanowires (poly(PPA) NWs) possessed numerous carboxyl groups that were used for covalent attachment of various chelates and other molecules.

### Covalent modification of poly(PPA) nanowires with cysteine

Dry poly(PPA) nanowires (100 mg) were suspended in a solution containing 0.1M 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) and a 0.1M of NHS in 0.1M acetate buffer (pH 5.5). The reaction was allowed to continue for 1 h when stirring with a magnetic stir bar. The nanowires were centrifuged at 13,000 rpm and the solution phase was discarded after several washings with deionized water (18 M $\Omega$ ). Subsequently, the nanowires were then suspended in a solution containing 0.1M



Scheme 1 Electropolymerization of PPA.

cysteine in acetate buffer for 1 h. Once again, the nanowires were centrifuged at 13,000 rpm, and the solution phase was discarded. The nanowires were washed with deionized water and centrifuged several times. The water was discarded and nanowires dried at ambient atmosphere and stored in the refrigerator. The cysteine-modified poly(PPA) NWs are referred to as poly(PPA)-Cys NWs in this document.

#### Heavy metal ion removal and detection

Poly(PPA)-Cys NWs (10 mg) were added to 10 mL of water sample. The water sample was buffered to pH 5.5 with 0.1M acetate buffer and spiked with various concentrations of heavy metal ions. The mixture was immediately sonicated for  $\sim 5$  s followed by stirring for a predetermined time (0–180 min). After stirring, the nanowires were separated from the solution by centrifugation at 13,000 rpm, and the concentration of remaining heavy metal ions in the spent solution was determined by inductively-coupled plasma atomic emission spectrometry. Each experiment was performed at least four times.

### RESULTS AND DISCUSSION

Figure 1 shows a typical SEM image of the poly(PPA)-Cys NWs. The average diameter of the poly(PPA)-Cys NWs was about 175–225 nm. The lengths of the nanowires depended on the amount of charge passed. SEM images indicate that the nanowires were sufficiently dispersed and aggregation was not an issue. Figure 2(a) shows the FTIR of poly(PPA). The peak at about 1750 indicates presence of carbonyl group (C=O stretch). The broad peak at about 3200–3600  $\text{cm}^{-1}$  is due to O–H stretch. Figure 2(b) demonstrates an FTIR spectrum of poly(PPA)-Cys NWs. Cysteine attachment on the poly(PPA) NWs introduces unique amide and thiol groups that are absent in naked poly(PPA) NWs. This modification is reflected by the emergence of a characteristic secondary amine peak at about 1550  $\text{cm}^{-1}$  and the thiol peak at about 2500  $\text{cm}^{-1}$ . Additionally, the stretching vibrations of N–H range from 3300 to 3500  $\text{cm}^{-1}$ , thus overlapping with carboxylic O–H stretches. The carboxylic C=O stretch in poly(PPA)-Cys appears at  $\sim 1750$   $\text{cm}^{-1}$ . The above observations

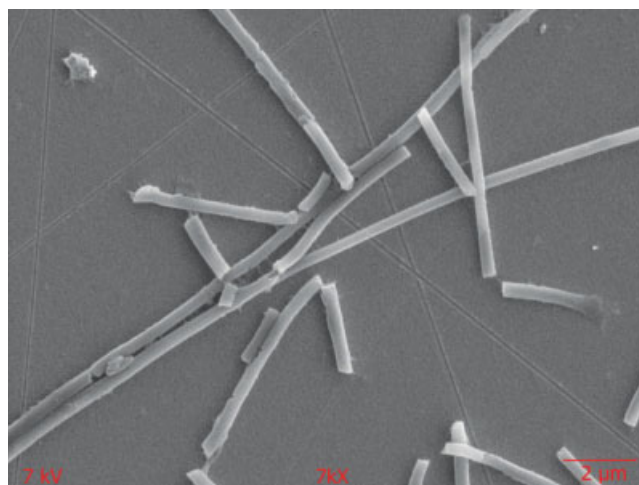


Figure 1 SEM image of poly(PPA)-Cys nanowires. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

confirmed that cysteine was covalently bound on poly(PPA) NWs to form poly(PPA)-Cys NWs.

We first investigated the removal of metal ions from a bottled water sample. Before the determination of metal removal from this water sample, the bottled

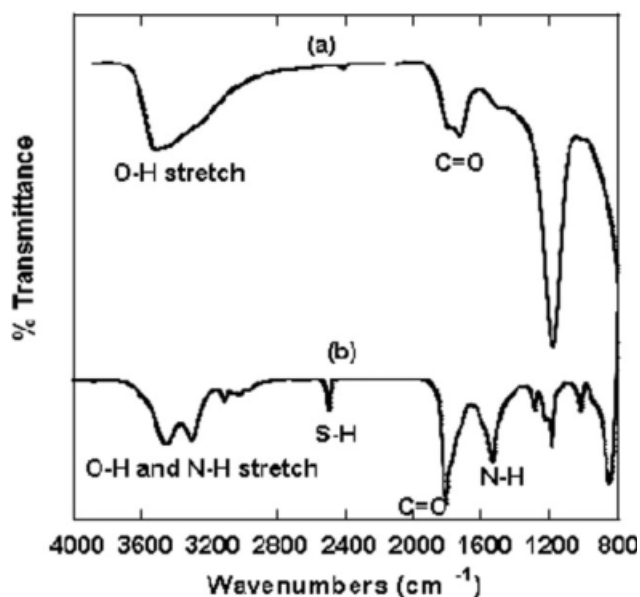
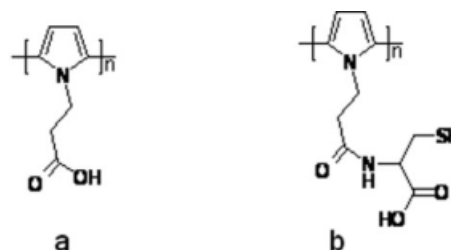
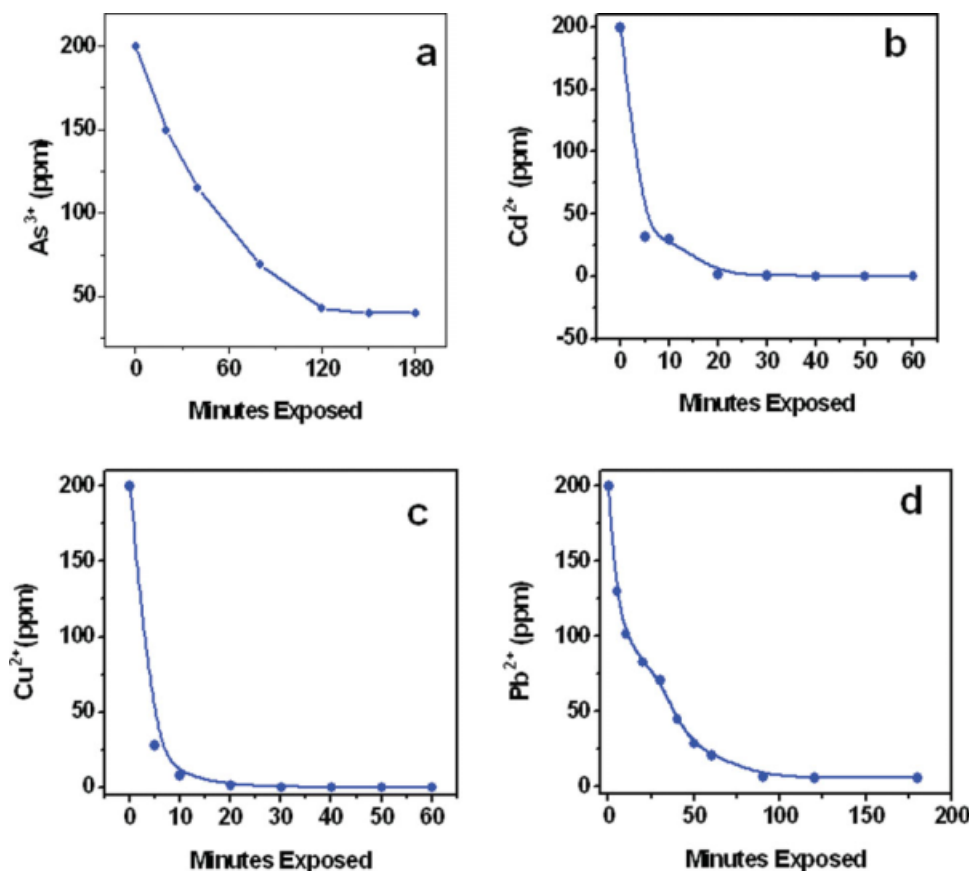


Figure 2 Structures of (a) poly(PPA) and (b) poly(PPA)-Cys together with their corresponding FTIR spectra.



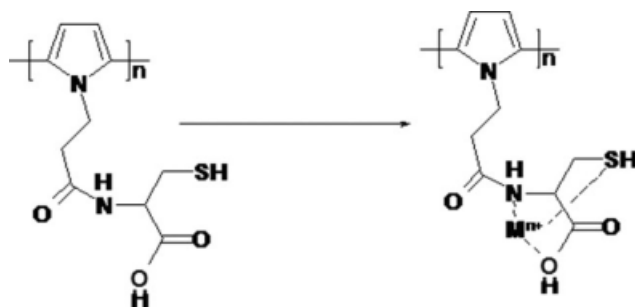
**Figure 3** Removal of (a)  $\text{As}^{3+}$ , (b)  $\text{Cd}^{2+}$ , (c)  $\text{Cu}^{2+}$ , and (d)  $\text{Pb}^{2+}$  by 10 mg of poly(PPA)-Cys NWs from a 10 mL lake water spiked to 200 ppm. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

water sample was tested initially for  $\text{As}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cu}^{2+}$ ; none of these metals were detectable in the bottled water sample by ICP emission spectrometry. Poly(PPA)-Cys NWs (10 mg) were then added to 10 mL of bottled water that was spiked to 300 ppb  $\text{Pb}^{2+}$ , 20 times the United States Environmental Protection Agency (U.S. EPA) maximum contaminant limit of 15 ppb  $\text{Pb}^{2+}$ .<sup>19</sup> It required <5 min to remove  $\text{Pb}^{2+}$  to undetectable levels (detection limit = 10 ppb). We obtained similar results when the water samples were separately spiked to 200 ppb  $\text{As}^{3+}$  and 100 ppb  $\text{Cd}^{2+}$ . These concentrations are 20 times the WHO<sup>20,21</sup> and U.S. EPA<sup>19</sup> maximum contaminant limits for  $\text{As}^{3+}$  and  $\text{Cd}^{2+}$ . These toxic heavy metal ions were removed to undetectable levels in a few minutes. In contrast, the amount of metals removed by control poly(PPA) NWs (not modified with cysteine) was not substantial.

After demonstrating the efficacy of this material in the treatment of water meant for human consumption, our next investigation was to investigate its potential in the treatment of hazardous waste. Figure 3(a) shows the rate of removal of  $\text{As}^{3+}$  by 10 mg of poly(PPA)-Cys NWs from a 10 mL natural water sample from Lake Springfield (Springfield, MO) spiked to 200 ppm  $\text{As}^{3+}$  to simulate environmental

contamination. Approximately 55% of  $\text{As}^{3+}$  was removed from the water sample after 1 h by 10 mg of poly(PPA)-Cys NWs. Extending the exposure of the poly(PPA)-Cys NWs to 3 h resulted in almost 80% removal of  $\text{As}^{3+}$ . This translates to 160 mg removal of  $\text{As}^{3+}$  per gram of poly(PPA)-Cys NWs. These preliminary results suggest a far greater removal rate of  $\text{As}^{3+}$  by poly(PPA)-Cys NWs than by other previously reported materials including glassy carbon spheres,<sup>6</sup> dried roots of the water hyacinth plant,<sup>22</sup> zirconium resin,<sup>10</sup> iron (III)-loaded chelating resin,<sup>12</sup> nanocrystalline  $\text{TiO}_2$ ,<sup>23</sup> and hybrid (polymer/inorganic) fibrous sorbent.<sup>24</sup> However, the composition of different waters and industrial effluents can vary greatly, and other factors, such as, initial metal ion concentration, must be considered for an objective comparison of metal ion removal capacity. We performed additional experiments for the purpose of investigating the removal capacity of other metal ions by these nanowires. Figure 3(b) shows the progress of removal of  $\text{Cd}^{2+}$  by 10 mg of poly(PPA)-Cys NWs from a 10 mL natural water sample from Lake Springfield spiked to 200 ppm  $\text{Cd}^{2+}$ . In this case, it required only 5 min for the nanowires to remove 84% of the  $\text{Cd}^{2+}$  from the lake water. The concentration of  $\text{Cd}^{2+}$  after 40 min was found to be





**Scheme 2** Chelation of metal ions by the poly(PPA)-Cys nanowires.

200 ppb, which indicated that 99.9% of  $\text{Cd}^{2+}$  had been removed from the water sample. We also performed similar experiments to investigate the progress of removal of  $\text{Cu}^{2+}$  [Fig. 3(c)]. After 5 min, the nanowires removed 86.0% of the  $\text{Cu}^{2+}$  from the lake water. The concentration of  $\text{Cu}^{2+}$  after 50 min was found to be 130 ppb, indicating that 99.9%  $\text{Cu}^{2+}$  had been removed from the lake water within that time. The  $\text{Cu}^{2+}$  removal was so efficient that the concentration of  $\text{Cu}^{2+}$  in the lake water decreased below the U.S. EPA maximum contaminant limit of 1.3 ppm  $\text{Cu}^{2+}$ .<sup>19</sup> Similar experiments were executed to monitor the removal of  $\text{Pb}^{2+}$  [Fig. 3(d)]. The  $\text{Pb}^{2+}$  removal rate was substantially less than that for the other metal ions tested. Only 35% of  $\text{Pb}^{2+}$  was removed by 5 min, yet this amount increased to 97.0%  $\text{Pb}^{2+}$  removal after 2 h.

These results demonstrate a rapid and efficient removal of heavy metals from aqueous media, putatively due the high surface area-to-volume ratio of the poly(PPA)-Cys NWs that permits exposure of numerous carboxyl groups to covalent binding with cysteine. As a consequence, a very high concentration of cysteine molecules are available to bind with metal ions. The chelation probably occurs via the interaction of nitrogen, sulfur, and oxygen atoms of the cysteine molecule as shown in Scheme 2. Unlike other materials, the poly(PPA)-Cys NWs have numerous advantages. For example, their electrochemical fabrication procedure is facile and rapid and can be performed at ambient conditions. Moreover, the diameter of the nanowires can be further reduced (or modulated) by using anodic alumina templates with various pore sizes during the electrochemical fabrication process. Furthermore, the length of the nanowires can be tailored by precise control of the charge passed during the electrodeposition process.

## CONCLUSIONS

In summary, novel Poly(PPA)-Cys NWs were electrochemically fabricated and covalently modified with cysteine. These nanowires were utilized for

rapid and efficient removal of heavy metal ions from simulated and naturally contaminated waters. The efficient removal is hypothetically due to the apparent high surface area of the nanowires that enables the extensive attachment of cysteine. These nanowires could lead to the production of a low cost and highly effective material for use in treatment of drinking water and for environmental remediation purposes in general. However, the composition of different waters and industrial effluents can vary greatly and, therefore, further studies are underway in our laboratory to determine various factors like pH, initial metal ion concentration, nanowire dimension, material regeneration, and other factors, such as, the thermodynamics of sequestration, that may affect metal ion removal. Although the concept has been demonstrated within the context of removal of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cd}^{2+}$ , it could readily be designed for the removal of other metals or toxins by the modification of polymer nanowires with appropriate chelates or other specific molecules. Finally, the potential to modify the poly(PPA) NWs with multiple molecules with different selectivities toward various contaminants suggests that these nanoscale polymeric materials offer great promise toward the versatile removal of numerous toxins from the environment.

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