



Electrostatic self-assembly of TiO₂ nanoparticles onto carbon spheres with enhanced adsorption capability for Cr(VI)

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ABSTRACT

A rapid electrostatic assembly method has been developed for deposition of highly dispersed TiO₂ nanoparticles on the surface of carbon spheres. Surface charges on carbon spheres are found to facilitate the spontaneous deposition of the TiO₂ nanoparticles, in which no additional chemicals are required in this assembling process. In the formed C/TiO₂ hybrid structure, carbon microspheres not only reduce the agglomeration of TiO₂ nanoparticles, but also allow easy separation from the reaction medium for reuse. Remarkably, the as-prepared C/TiO₂ hybrid microspheres exhibit a superior adsorption capacity for Cr(VI), which is 3.6 times greater than that of commercial Degussa P25 TiO₂ nanoparticles. The effect of pH value in solution on the adsorption capacity of the products has also been systematically investigated.

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1. Introduction

Hexavalent chromium, Cr(VI), is one of the most dangerous heavy metal ions due to its carcinogenic and mutagenic effects and its toxicity to the liver. U.S. EPA recommends that the concentration of Cr(VI) in water should be reduced to 0.05 mg L⁻¹ [1]. To meet environmental regulations, it is imperative for industries to reduce the chromium concentration in their effluents to an acceptable level before discharging into municipal sewers. Recently, a variety of treatment techniques have been developed for the removal of Cr(VI) from wastewater including electro-deposition, membrane filtration, ion exchange, biological processes, and adsorption [2–6]. However, most of these methods cannot be widely practiced due to the high capital investment and operation costs. In this regard, nanostructured metal oxides may offer some promise for wastewater treatment because they usually have large surface area and a high capacity for removing trace amount of heavy metal ions, making the treatment more economical [7].

Titanium dioxide (TiO₂), a nontoxic material, possesses high concentration of hydroxyl groups (–OH) on the surface. As a result, the pollutants in water can be adsorbed on TiO₂ surface by interacting with the –OH groups. Recently, TiO₂ nanoparticles have been used as an effective adsorbent for arsenic, showing higher removal capacities than the bulk TiO₂ material [8]. However, from a practical point of view, the application of such nanoparticles for wastewater treatment has a major drawback, that is, an additional separation step is usually required to remove the adsorbent from the solution. Moreover, pure TiO₂ nanoparticles often show lower removal efficiencies owing to the

problem of self-aggregation [9], which causes serious fast diminishment of the active surface area.

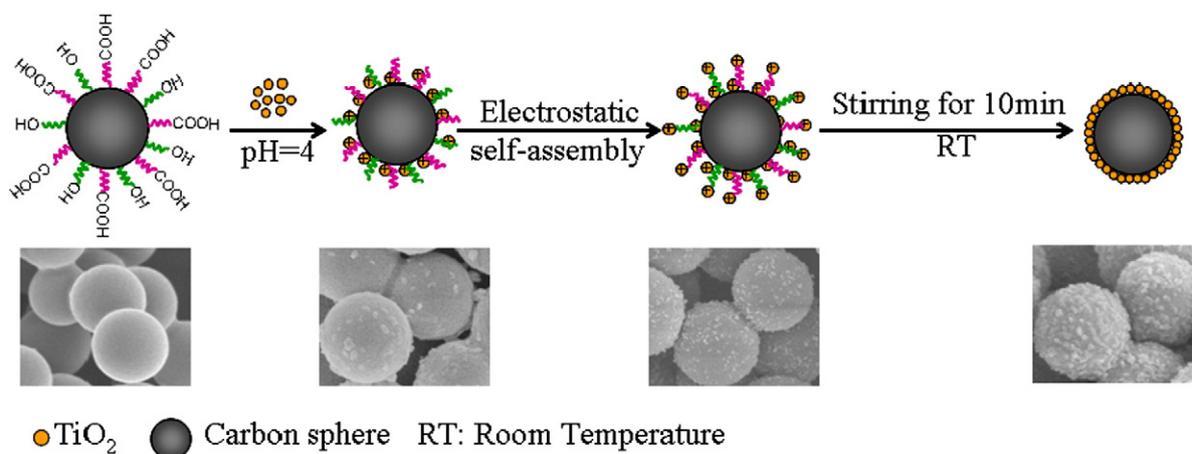
To overcome these obstacles, TiO₂ nanoparticles are frequently immobilized on supporting materials such as activated carbon, glass, and ceramics [10–13]. This would improve the stability of TiO₂, reduce the agglomeration of TiO₂, and allow the easy separation from the solution for reuse. Functional carbonaceous materials have been extensively studied because of their use in a wide range of applications such as adsorbents, catalysts, electrode materials, etc. [14]. Up to now, composites of colloidal carbon spheres and noble metals, metal oxides, or semiconducting nanoparticles have been successfully synthesized via a variety of methods [15–17].

Herein, we report a facile and rapid electrostatic self-assembly process to deposit TiO₂ nanoparticles onto the monodisperse colloidal carbon spheres at room temperature. The strategy used to obtain C/TiO₂ core-shell hybrid spheres is illustrated in Scheme 1. First, high quality TiO₂ nanoparticles are synthesized via a nonaqueous sol–gel route at a low temperature [18]. Second, TiO₂ nanoparticles are assembled onto negatively charged amorphous carbonaceous spheres in ultrapure water by adjusting the pH value of the TiO₂ sol suspension to 4.0 using 0.1 M HCl solution under continuous stirring for 10 min. These hybrid spheres are subsequently used as an adsorbent for Cr(VI) removal from its aqueous solution. The as-prepared sample exhibits rapid adsorption kinetics for Cr(VI), approaching to 94.8% of the maximum adsorption capacity in a short period. It also shows an adsorption capacity that is 3.6 times greater than that of Degussa P25 TiO₂ nanoparticles.

2. Materials and methods

In a typical preparation, 1 mL of TiCl₄ was slowly added to 20 mL of anhydrous benzyl alcohol in a round flask under vigorous stirring

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Scheme 1. Schematic illustration of electrostatic assembly of TiO₂ nanoparticles on the surface of carbon microspheres.

at room temperature. The reaction vessel was heated to 80 °C for 24 h, and the solution was then cooled to room temperature. Subsequently, the white precipitate was collected by centrifugation and washed with ethanol and tetrahydrofuran (THF) for three times, and redispersed in ultrapure water for further use [18]. Monodisperse carbon (C) spheres were synthesized following a previously reported method [16]. 0.1 g of C spheres was dispersed in 20 mL of ultrapure water by ultrasonication for 10 min. Then, 2 mL of colloidal TiO₂ aqueous suspension, with the pH value adjusted using 0.1 M HCl or NaOH, was slowly added into the above carbon spheres suspension. The mixture was continuously stirred for 10 min at room temperature. The samples were washed with ethanol before being dried in an oven at 60 °C for 6 h. In addition, experiments with different time durations and pH values of the TiO₂ sol solution were also carried out, while the other conditions remain unchanged.

Powder X-ray diffraction (XRD) measurements of the samples were performed with a Philips PW3040/60 X-ray diffractometer using Cu K α radiation at a scanning rate of 0.06 deg s⁻¹. Scanning electron microscopy (SEM) was performed with a Hitachi S-4800 scanning electron micro-analyzer with an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) was conducted using a JEM-2100F field emission TEM. For the adsorption measurement, K₂Cr₂O₇ is used as the source of Cr(VI) for the preparation of standard and working solutions with different concentrations. Then, 0.025 g of the as-prepared samples and Degussa P25 TiO₂ nanoparticles was added to 12.5 mL of the above solution under stirring. After a certain time, the solid and liquid were separated. Inductively Coupled Plasma-Optical Emission Spectroscopy (Optima 5300DV) was used to measure the chromium concentration in the remaining solutions. The adsorption isotherm was obtained by varying the initial Cr(VI) concentration and stirring for 2 h at room temperature. After the equilibration time, the adsorbents were separated from the aqueous solutions by centrifugation.

3. Results and discussion

The XRD pattern of as-prepared C/TiO₂ hybrid spheres obtained by electrostatic self-assembly process is shown in Fig. 1. From the XRD pattern, all the identified diffraction peaks are in good agreement with the body-centered tetragonal TiO₂ (JCPDS standard card no.89-4921) with a cell constant of $a_0 = 0.3777$ nm, and $c_0 = 0.9501$ nm. No other impurity phases are detected in any of these products. The average crystallite size of TiO₂ nanoparticles calculated using the Debye-Scherrer equation based on the full width at half maximum of the diffraction peaks is ~ 4.7 nm.

To investigate the electrostatic self-assembly process of the C/TiO₂ hybrid microspheres, we carried out time-dependent experiments during which samples were collected at different time intervals from the reaction medium. Fig. 2a displays a typical SEM image of nearly monodisperse carbon spheres with smooth surface and about 1 μ m in diameter. Fig. 2b–d shows the SEM images of products collected at different stirring time intervals of 2, 5 and 10 min, respectively. As expected, TiO₂ nanoparticles are uniformly deposited on the surface of the carbon microspheres. With the increasing time, more TiO₂ nanoparticles are assembled on the surface of carbon spheres by electrostatic attraction while keeping their dispersion state. The TEM image (inset in Fig. 2d) of the as-prepared C/TiO₂ hybrid spheres displays clearly a layer of TiO₂ nanoparticles loaded on the surface of the carbon spheres after stirring for 10 min. From these images, it can be seen that the as-prepared hybrid structures preserved the good dispersibility and uniformity of the initial carbon spheres, which may endow the hybrids a high specific surface area and the application potential as the adsorbent for Cr(VI) ions. The TEM image and XRD pattern of as-prepared TiO₂ nanoparticles are shown in Fig.S1 and Fig.S2, and SEM images of samples obtained under various pH conditions of the TiO₂ sol solution are shown in Fig. S3.

The surface of the carbon spheres is known to be strongly hydrophilic with abundant –OH and C=O groups [15]. Surface charges on carbon spheres can facilitate the electrostatic deposition of the TiO₂ nanoparticles, and no assistance from other chemical agents is required during the process. The electrostatic assembly offers a unique approach for formation of hybrid nanomaterials with better interaction between individual components and improved compatibility with lateral patterning [19]. For example, Li et al. reported electrostatic self-assembly of TiO₂ nanoparticles onto carbon nanotubes by simply mixing oleic acid-capped TiO₂ nanoparticles and carbon nanotubes in toluene [20]. The Zeta potentials of the as-prepared C/TiO₂ under various pH values are shown in Table S1.

To investigate the use of the products for heavy metal ion removal, we applied the as-prepared C/TiO₂ hybrid microspheres, Degussa P25 TiO₂ nanoparticles and pure carbon microspheres as adsorbents to remove Cr(VI) ions. Fig. 3a shows the adsorption of Cr(VI) on different adsorbents at different initial concentrations of Cr(VI). The as-prepared C/TiO₂ hybrid microspheres possess a much higher adsorption capacity for Cr(VI) than the Degussa P25 TiO₂ nanoparticles. For example, when the initial concentration of Cr(VI) is 40.0 ppm, the adsorption capacity of the C/TiO₂ hybrid microspheres is 18.1 mg g⁻¹, while Degussa P25 and pure carbon microspheres can only achieve 5.0 and 4.5 mg g⁻¹ under the same conditions, respectively. This result suggests that these C/TiO₂ hybrid microspheres exhibit a superior adsorption capacity

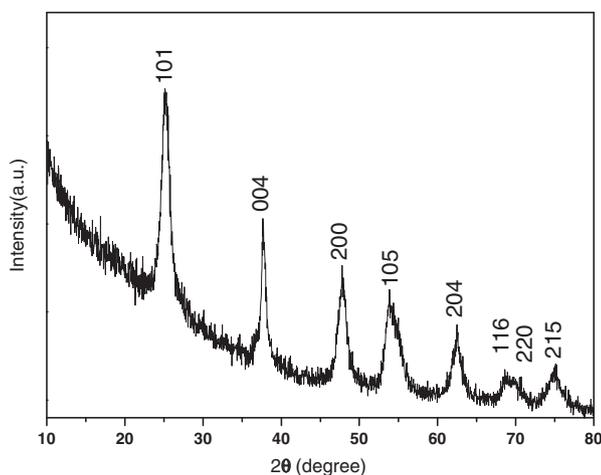


Fig. 1. XRD pattern of the as-prepared C/TiO₂ hybrid spheres.

for Cr(VI) which is ~3.6 times greater than that of Degussa P25. The adsorption rate of Cr(VI), with an initial concentration of 10.0 ppm, using different adsorbents is shown in Fig. 3b. The result indicates that about 94.8% of Cr(VI) could be removed in 5 min using the as-prepared C/TiO₂ hybrid microspheres, while only 64.6% and 18% could be removed by Degussa P25 TiO₂ nanoparticles and pure carbon spheres in the same period. The XRD patterns of different size of TiO₂ nanoparticles are shown in Fig. S4, and the adsorption isotherms of Cr(VI) using different samples as adsorbents is shown in Fig. S5. The TGA curve (Fig. S6) shows a total of 5.6% weight of TiO₂ nanoparticles on the surface of carbon microspheres.

To investigate the effect of pH value on the adsorption capacity of the as-prepared products, a set of measurements was carried out at various pH conditions. Fig. 3c depicts the effect of initial solution pH value on the removal of Cr(VI) using different adsorbents at a fixed initial Cr(VI) concentration of 10.0 ppm. It is clear that the as-prepared C/TiO₂ hybrid microspheres possess a nearly constant adsorption capacity

of about 94.8% in a wide range of pH values from 2.0 to 10.0, which then decreases dramatically from 94.8% to 21.0% as the initial pH value increases to 12.0. As compared to C/TiO₂ hybrid microspheres, Degussa P25 TiO₂ nanoparticles exhibit a much lower removal capacity for Cr(VI), which is about 61.3% at the pH value of 2.0 and decreases gradually with the increasing pH value. The mechanism for the removal of Cr(VI) is proposed to be through the formation of bidentate binuclear surface complexes between TiO₂ and Cr(VI) species in the solution [8]. Thus, the C/TiO₂ hybrid microspheres are advantageous for efficient removal of Cr(VI) because of the high active area endowed by the TiO₂ nanoparticles on the surface and the facile mass transport between the microspheres and the medium. As the pH value increases, the TiO₂ surface becomes increasingly deprotonated so that the amount of positive surface charges is significantly decreased, leading to a reduction in the adsorption capacity for Cr(VI) [21]. Additionally, another factor affecting the adsorptive ability in different pH may be the adsorption free energy of various Cr species (HCrO₄⁻, H₂CrO₄ and CrO₄²⁻) existing at different pH. At lower pH, the predominant Cr(VI) species mainly exists in the monovalent HCrO₄⁻ form, which is then gradually converted to the divalent CrO₄²⁻ form as pH increases. The adsorption free energy of HCrO₄⁻ is lower than that of CrO₄²⁻, and consequently HCrO₄⁻ is more favorably adsorbed than CrO₄²⁻ at the same concentration [21]. Thus, the removal quantities of Cr(VI) at lower pH value is larger than that of at higher pH value.

4. Conclusions

In summary, we have prepared C/TiO₂ nanocomposites by a facile and rapid electrostatic self-assembly method. By adjusting the pH value, pre-synthesized TiO₂ nanoparticles can be efficiently assembled on the surface of carbon spheres. The as-prepared C/TiO₂ hybrid microspheres exhibit a superior adsorption capacity for Cr(VI) that is 3.6 times greater than that of Degussa P25 TiO₂ nanoparticles. The effect of pH values on the adsorption capacity of the as-prepared products has also been investigated. The result demonstrates that these hybrid microspheres can be used as a reusable adsorbent for fast, convenient, and high-efficiency removal of Cr(VI) from contaminated water.

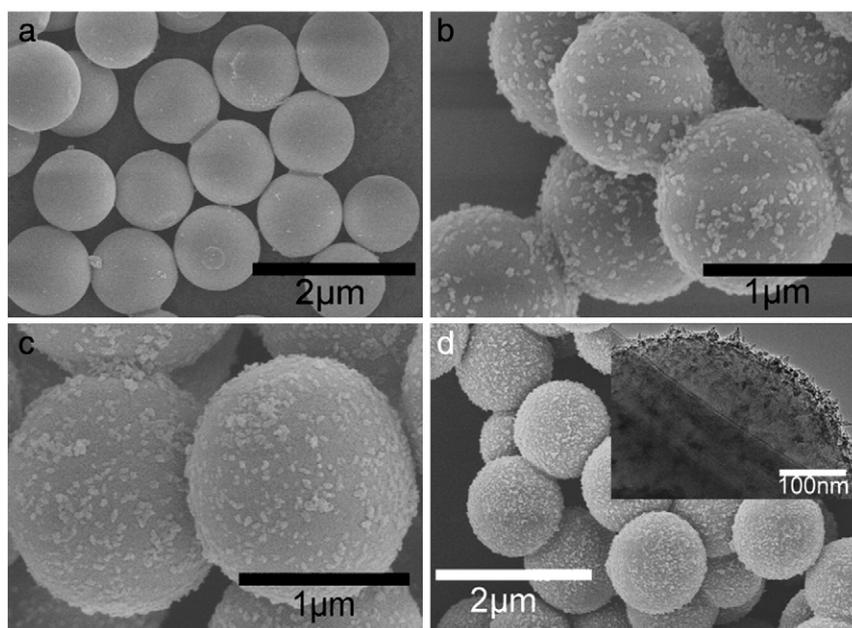


Fig. 2. SEM images of (a) the as-prepared carbon spheres, and C/TiO₂ hybrid spheres obtained by mixing TiO₂ nanoparticles suspension at pH 4.0 and carbon spheres dispersed in ultrapure water by simple mechanical stirring for (b) 2 min, (c) 5 min, and (d) 10 min. The inset in (d) is a transmission electron microscopy (TEM) image of the corresponding sample.

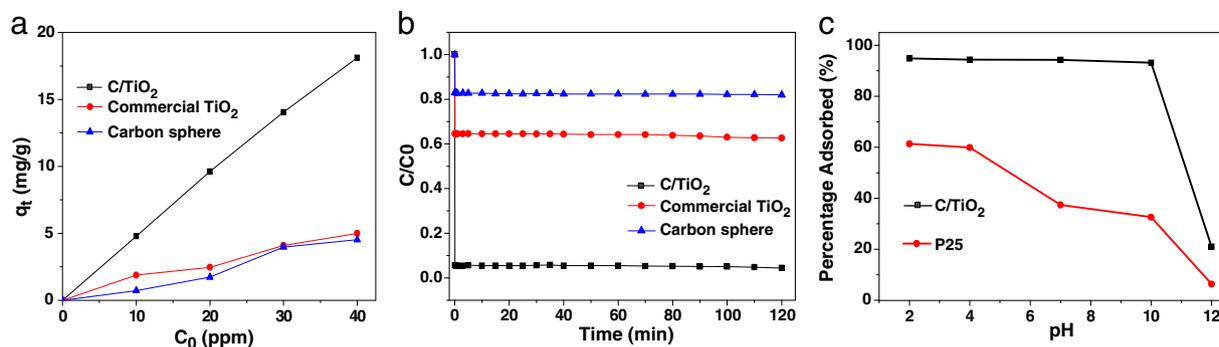


Fig. 3. a) Adsorption isotherms of Cr(VI) using different adsorbents, b) adsorption rate of Cr(VI) on different adsorbents, and c) Cr(VI) adsorption onto different adsorbents at various pH values.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.matlet.2011.10.054.

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