Effects of graphene oxide on dispersion stability of Titanium dioxide nanoparticles

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Abstract. In this work, we investigated the effects of GO on dispersion stability of the two types of TiO_2 NPs under different pHs. At pH 4, heteroaggregation may occur between GO and the two types of TiO_2 NPs (TiO_2 Nanotube and TiO_2 Nanowire), enhancing the sedimentation of TiO_2 NPs. However, at pH 7 and 10, GO enhanced the suspension of the two types of TiO_2 NPs. Electrostatic interaction could be a major mechanism for TiO_2 NPs-GO interaction.

Introduction

Titanium dioxide nanoparticles (TiO_2 NPs) are widely used in commercial applications such as photocatalysts, ceramic membranes, and cosmetic pigment additives [1]. Graphene Oxide (GO) is a promising material for wide applications such as dispersing agent, adsorbent and catalytic material [2, 3]. With the rapid increases in production and application, TiO_2 NPs and GO will be released into aquatic environment. Upon exposure, they will exhibit adverse impacts on organisms. Hund-Rinke and Simon (2006) reported that TiO_2 NPs can inhibit the growth of algae and the immobilization of daphnia [4]. Once TiO_2 NPs are released into the aquatic environment, their fate and transport will affect their phototoxicity and ecotoxicity [5, 6]. Tong et al. revealed that the presence of both nano-ZnO and dissolved zinc eliminated the damaging effect of nano-TiO_2 on bacterial cell membranes, which was explained by a reduced extent of bacteria/nano-TiO_2 contact [7]. GO can disperse in water to form stable colloidal suspensions [8], and GO may interact with TiO_2 NPs, altering the potential exposure pathways and biovailability of TiO_2 NPs. Therefore, it is important to investigate the effects of GO on the fate and transport of TiO_2 NPs.

The main objective of this study was to investigate the effects of GO on dispersion stability of TiO_2 NPs under different pHs.

Materials and Method

Suspension and Sedimentation Experiment. The two types of TiO_2 NPs (TiO_2 Nanotube and TiO_2 Nanowire) were purchased from Nanjing XFNANO (China). GO was produced by the modified Hummers method [9]. TiO_2 NPs stock solution (200 mg/L) was prepared by sonicating for 10 min (20 kHz, FB 120, Fisher Scientific, USA). GO stock solution (250 mg/L) was prepared by sonicating for 60 min (20 kHz, FB 120, Fisher Scientific, USA).The pH of the suspension was adjusted by adding negligible amounts of NaOH or HCl. 10 mL TiO_2 NPs stock solution and 10 mL DI water were mixed to get 100 mg/L TiO_2 NPs. 10 mL TiO_2 NPs stock solution, 6 mL DI water , and 4 mL GO stock solution were mixed to get the mixture of 100 mg/L TiO_2 NPs and 50 mg/L GO. The mixtures were shaken (150 rpm in dark) at 25 °C for 36 h and then settled for 5 h. The dispersion stability of TiO_2 NPs was measured by UV-Vis spectrophotometer (SHIMADZU 2550, Japan). Briefly, the supernatants (3 mL) were carefully moved to quartz cuvette and examined at 800 nm to get the absorbance A. Before sedimentation, the suspensions (3 mL) were also examined at 800 nm to get the absorbance A_0. The absorbance of GO at 800 nm could be negative (data were not shown), so the sedimentation rate of TiO_2 NPs is calculated by the equation as follows:

$$\text{Sedimentation Rate (\%)} = (A_0-A)/ A_0*100\% \quad (1)$$

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Statistical Analysis. Data was analyzed using a one-way analysis of variance (ANOVA) and compared with LSD test. All data included three replicates and standard error was statistically analyzed ($p<0.05$).

Results and discussion

Characterization of TiO_2 NPs and GO. Characterization of TiO_2 NPs and GO was analyzed by transmission electron microscopy (TEM, H-7650, Hitachi, Japan). The TEM images showed that the length of TiO_2 Nanotube was 100-200 nm and the width was ~10 nm (Fig. 1A). The length of TiO_2 Nanowire was 50-300 nm and the width was ~ 10 nm (Fig. 1B). The lateral size of GO sheets was at the micrometer level, and the GO sheets were flexible and could be folded (Fig. 1C).

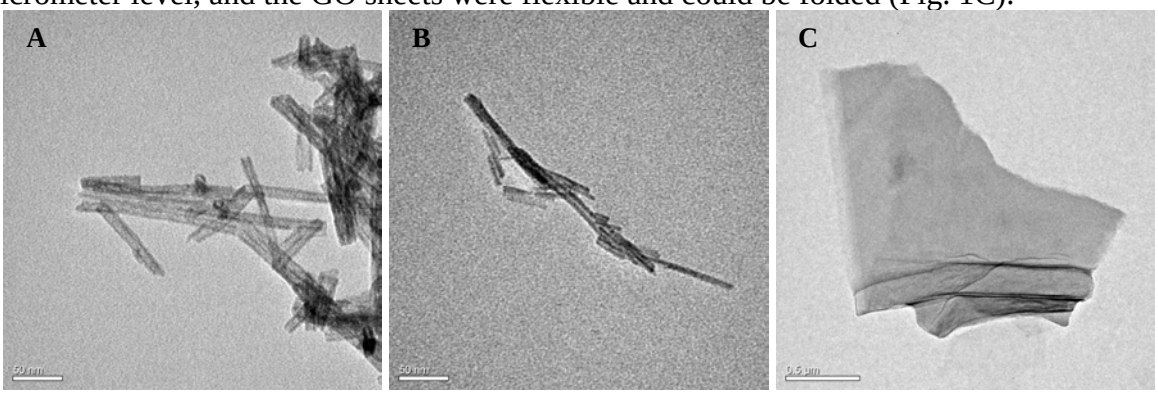

Fig. 1 TEM images of TiO_2 NPs and GO. (A) TiO_2 Nanotube; (B) TiO_2 Nanowire; (C) GO.

The zeta potentials of TiO_2 NPs and GO were measured by Zetasizer (Nano ZS90, Malvern, UK). The zeta potentials of TiO_2 NPs and GO under different pHs were showed in Table 1. At pH 4, the zeta potential of TiO_2 Nanotube and TiO_2 Nanowire was 5.52 mV and 2.30 mV, respectively. At pH 7, the zeta potential of TiO_2 Nanotube and TiO_2 Nanowire was -32.5 mV and -47.4 mV, respectively. At pH 10, the zeta potential of TiO_2 Nanotube and TiO_2 Nanowire was -41.5 mV and -48.1 mV, respectively. However, GO was highly negatively charged at 4, 7, and 10.

Table 1 The zeta potentials of TiO_2 NPs and GO under different pHs

pH	TiO_2 Nanotube(mV)	TiO_2 Nanowire (mV)	GO (mV)
4	5.52±0.57	2.30±0.3	-40.5±0.9
7	-32.5±1.5	-47.4±4.3	-40.2±2.0
10	-41.5±2.0	-48.1±2.4	-42.1±1.8

Effects of GO on Dispersion Stability of TiO_2 NPs. Fig. 2 showed the effects of GO on dispersion stability of TiO_2 NPs under different pHs. At pH 4, the presence of GO enhanced the sedimentation rate of the two types of TiO_2 NPs in comparison with that in the absence of GO. It showed that GO enhanced the sedimentation of the two types of TiO_2 NPs at pH 4. For the two types of TiO_2 NPs, GO enhanced the sedimentation rate of TiO_2 Nanotube more significantly than that of TiO_2 Nanowire. However, at pH 7 and 10, the presence of GO reduced the sedimentation rate of the two types of TiO_2 NPs in comparison with that in the absence of GO. It showed that GO enhanced the suspension of the two types of TiO_2 NPs at pH 7 and 10. For the two types of TiO_2 NPs, GO reduced the sedimentation rate of TiO_2 Nanowire more significantly than that of TiO_2 Nanotube. In Table 1, TiO_2 NPs and GO were opposite charged at pH 4, heteroaggregation may occur between GO and the two types of TiO_2 NPs. However, TiO_2 NPs and GO were both highly negatively charged at pH 7 and 10. We assumed that electrostatic interaction could be a major mechanism for TiO_2 NPs-GO interaction. The results in our study were consistent of the study on the interaction between GO and goethite [10].

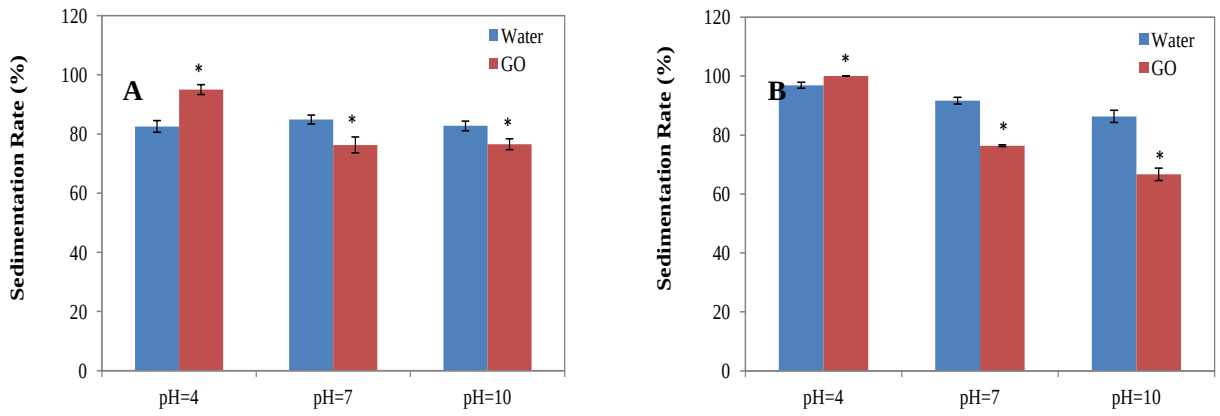

Fig. 2 Effects of GO on dispersion stability of TiO_2 NPs under different pHs. (A) TiO_2 Nanotube; (B) TiO_2 Nanowire. The blue column indicates 100 mg/L TiO_2 NPs in DI water, and the red column indicates 100 mg/L TiO_2 NPs in 50 mg/L GO. Error bars indicate one standard deviation of at least three measurements. "*" indicates significant difference of sedimentation rate in the presence of GO in comparison with that in the absence of GO ($p < 0.05$).

Summary

At pH 4, heteroaggregation may occur between GO and the two types of TiO_2 NPs, enhancing the sedimentation of the two types of TiO_2 NPs. For the two types of TiO_2 NPs, GO enhanced the sedimentation rate of TiO_2 Nanotube more significantly than that of TiO_2 Nanowire. At pH 7 and 10, GO enhanced the suspension of the two types of TiO_2 NPs. For the two types of TiO_2 NPs, GO reduced the sedimentation rate of TiO_2 Nanowire more significantly than that of TiO_2 Nanotube. Electrostatic interaction could be a major mechanism for TiO_2 NPs-GO interaction.

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