

Surface Modification of Carbon Black Using Polymer Resin Synthesized by a Phenyl Radical Reaction

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Carbon black (CB) has a variety of industrial uses due to its high strength and electrical conductivity.^{1,2} It has been used in industry for almost 100 years, and over this period, new manufacturing methods and products have been developed, leading to a constantly changing market for CB.³ Currently, CB is widely used in semiconductors, tires, rubber, ink, paint, and toner resin.⁴

The particle size and surface area of CB are important properties that affect the product performance. In general, CB for use in composites is composed of particles approximately 1,000–5,000 nm in size with a surface area of 20–100 m²/g; however, some CB grades, such as acetylene black, have surface areas of approximately 600 m²/g while maintaining particle sizes in this range.^{5,6}

In particular, CB ('plasma black') particles produced using plasma have a relatively small particle size, and the CB particles typically range from 10 to 50 nm; correspondingly, plasma black has a relatively high surface area. Nowadays, plasma black has emerged as a core material in nanotechnology and is of significant interest in various fields. In this study, we report the development of CB dispersions with improved thermal stability for use in a variety of applications, such as toner resins, nano inks, and the manufacture of composites.⁷

In many fields, it is important that the CB is uniformly dispersed in the bulk material, i.e., bulk rubber or polymer. A uniform dispersion affects the final product properties, and thus, control over the dispersion is vital to produce a product with outstanding and distinctive properties.⁸ However, because CB particles are small, they often aggregate together due to strong interparticle cohesion. Because the surface area and interparticle interaction increase with decreasing particle size, it becomes difficult to uniformly disperse very small CB particles within a polymer matrix.⁹ Consequently, it is necessary to develop a method to control the dispersion precisely.¹⁰

In last few years, many studies have been conducted to develop a dispersion method for CB aggregates.¹¹ In general, these methods improve the degree of particle dispersion by reducing particle interactions through the addition of a dispersing agent or by surface modification of the particles, allowing dispersion of the CB particles in the matrix.¹² For example, a surfactant or a mixture of surfactants is commonly used to achieve a stable dispersion. To modify the particle surfaces, the attractive interactions between particles are reduced by grafting an amphiphilic polymer resin, which can be dispersed in aqueous solution, onto the particle surface (Fig. 1).¹³ In general, adding surfactant is easy, allowing applications in various industrial fields due to the low viscosity of the resultant dispersions. However, there are disadvantages; for example, adjustment to balance the surface charges is difficult and the stability of the dispersion can decrease due to environmental effects, such as temperature and pressure. In contrast, although surface modification by grafting an amphiphilic polymer resin onto the particle surface increases the viscosity, the process reduces environmental effects because strong chemical bonds are formed between the CB particles and the grafted polymer, and these are not affected by heat and pressure in the same way as surfactants adsorbed to the particle surface.

Various methods have been studied to modify the particle surface, such as thermal, chemical, electrochemical, plasma treatment, and encapsulation methods, e.g., surface coating with organic/inorganic materials.¹⁰ Chemical surface modification improves the dispersion stability of particles by grafting polymer resin chains onto the CB particle surface.^{11,14} The polymers that can be used for this method include polystyrene derivatives,¹² polyethylene oxide,¹³ polyamide amine,¹⁵ polyethyl amine,¹⁶ and polyacrylate.¹⁷

The objective of this study was to develop a modification of the surface of CB particles to obtain CB dispersions

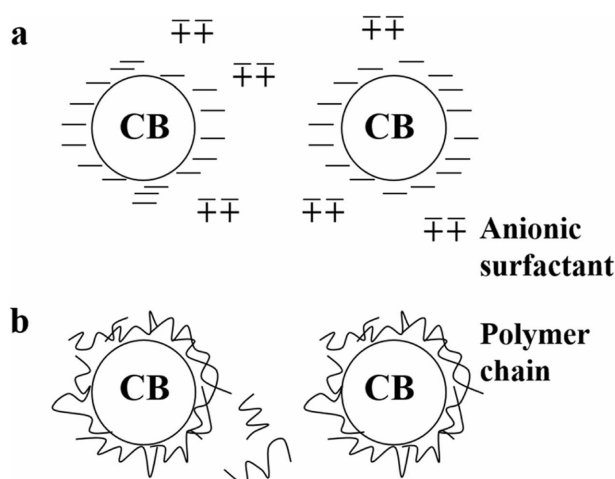


Figure 1. Particle dispersion achieved by adding a dispersing agent (surfactant) (a) or by surface modification (b).

with a high thermal stability for applications in industries requiring the thermal processing of CB dispersions. First, the polymer ('PR-polymer') was synthesized by means of a phenyl radical reaction (PR), and the CB particle surface was modified by grafting the synthesized PR-polymer onto the CB particle surface.

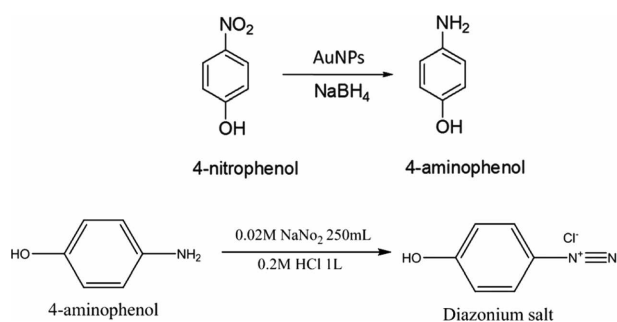
Lipophilic aromatic rings and hydrophilic hydroxyl groups (OH) are both present on the surface-modified CB particles ('aromatic ring-CB-OH'). The OH groups facilitate the dispersion of the CB particles in aqueous solution,¹⁸ whereas the aromatic rings improve the thermal stability of the particles.¹⁹ In this study, the effect of the composition of the lipophilic aromatic rings and hydrophilic OH groups in the PR-polymer on CB dispersion was investigated.

The surface modification method developed in this study prevented aggregation of CB particles and improved the thermal stability. Therefore, this study provides useful information for various industrial fields, especially industries involving thermal processing of CB. In particular, a novel synthetic method of a new polymer/CB composite material is presented.

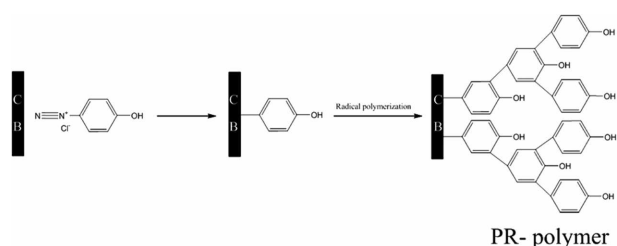
EXPERIMENTAL

Synthesis of PR-polymer

1 L of 0.2 M HCl (DUKSAN PURE CHEMICALS, Korea) was placed into a 2-L beaker in an ice bath, and 27.428 g of 4-aminophenol (SAMCHUN CHEMICALS, Korea) was added while stirring at 300 rpm. After slowly adding 0.02 M NaNO₂ (250 mL) using a peristaltic pump,²⁰ the solution stirred at 300 rpm for 2 h.²¹ The obtained PR-polymer was formed as a diazonium salt with a pH of about 10 (Scheme 1). More-



Scheme 1. Formation of the diazonium salt.



Scheme 2. Polymerization of the diazonium salt on the CB surface.

over, the diazonium salt formed a PR-polymer on the surface of the CB particles by radical polymerization (Scheme 2).

CB powder samples

In this study, three kinds of commercial CB were used. Because the pH of the synthesized PR-polymer was close to 10, CBs with acidic surface pH values were selected for a steady acid-base reaction on the CB particle surface. The CBs used in this study were MA-100 (MITSUBISHI, Japan), Nipex 160IQ (ORION ENGINEERED CARBONS, Kingwood, USA), and Raven 3500 (COLUMBIAN CHEMICALS COMPANY, Marietta, USA) with particle sizes, surface areas, and surface pH values as summarized in Table 1. The commercial CBs have particle sizes decreasing in the order MA-100, Nipex 160IQ, and Raven 3500; the decrease in particle size is concomitant with a gradual increase in surface area.

CB dispersion using PR-polymer

The PR-polymer (15 g) and CB (15 g) were mixed in distilled water (70 g) and stirred at 300 rpm for 1 h.²² After

Table 1. CB samples used in this study and their physical characteristics

CB sample	Particle size (nm)	Surface area (m ² /g)	Surface pH
MA-100	24	110	3.5
Nipex 160IQ	21	150	4.0
Raven 3500	13	375	4.0

stirring, each CB dispersion was prepared using a centrifugal UAM-015 zirconia bead mill (Ultra apex mill, Japan). Preparation of the dispersion lasted 3 h under the following bead-mill operating conditions: the drive speed was 6–15 m/s, the grinding chamber volume was 150 mL, the mill pressure was 0.4 MPa, the mill heat was <60 °C, the bead diameter was 0.1 mm, the rotor rotational speed was 3,320 rpm, the media volume was 100 mL, bead filling rate was 70%, and the flow rate was 86 mL/min.²² The resultant dispersions were labeled by CB type; the MA-100 dispersion is referred as ‘CB-1’, the Nipex 160IQ dispersion as ‘CB-2’, and the Raven 3500 dispersion as ‘CB-3’.

Instruments

To confirm the presence of PR-polymer on CB particle surface, a Nicolet iS5 FT-IR spectrometer (Thermo Scientific, Waltham, USA) was used. A Brookfield LVDV-E Viscometer (Brookfield AMETEK, Middleboro, USA) was used to measure the viscosity of the dispersion, and a Jenway 3510 pH meter (Dunmow, England) was used to measure the pH of the dispersions. To measure the size of CB particles, a DynaPro NanoStar Dynamic light scattering device (DLS) (Wyatt Technology, Santa Barbara, USA) was utilized.²³

RESULTS AND DISCUSSION

FT-IR analysis of the PR-polymer

Fig. 2 shows the FT-IR spectrum of the PR-Polymer synthesized in this study. The presence of OH groups is confirmed by a broad peak at 3,343 cm⁻¹, CO, and CH by a peak at 2,870 cm⁻¹, and aromatic rings by peaks between 1,400 and 1,600 cm⁻¹.

Viscosity and pH of CB dispersions

Table 2 shows the viscosities and pH values of disper-

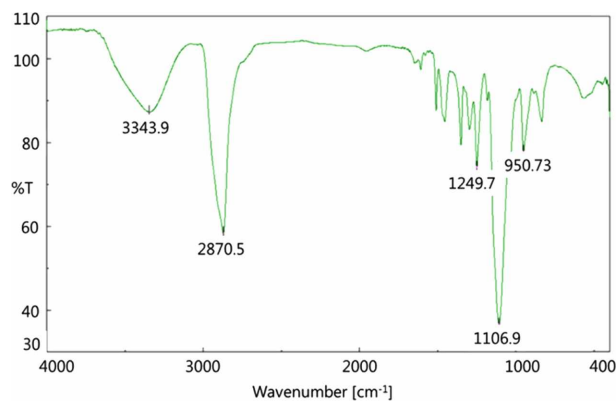


Figure 2. FT-IR spectrum of the PR-polymer synthesized in this study.

Table 2. Viscosity and pH of CB dispersions

CB dispersion	Viscosity (cps)	pH
CB-1	6.4	8.05
CB-2	8.2	8.37
CB-3	8.5	8.74

sions obtained by reacting three types of CB with the PR-polymer, based on a previously described method, followed by bead milling for 3 h.

As shown in Table 2, the initial viscosity and pH were gradually increased with decreasing CB particle size. This increase is due to a gradual increase in particle aggregation because the supply of PR-polymer for particle grafting was not steady as particle size decreased. When particle aggregation increased, the fluidity of the dispersion decreased, resulting in higher viscosity. Meanwhile, an increase in pH was also observed due to increase in the basic PR-polymer.

Bead-milling results of CB dispersions

Table 3 shows the sizes of CB particles in the dispersions and the volume percentage of particles having sizes greater than 0.200 μm listed against bead-milling processing time after surface modification of CB samples using the PR-polymer. In the case of CB-1, the particle size decreased from 0.179 μm before bead milling to 0.101 μm after 3 h treatment, while the volume percentage of particles larger than 0.200 μm decreased from 37.4 to 9.2%. However, the volume percentage increased to 17.5% after storing the CB-1 dispersion at 50 °C for 24 h, indicating the low thermal stability of CB-1.

In the case of CB-2, particle size decreased from 0.165 to 0.079 μm after 3 h dispersion, while particles larger than 0.200 μm were almost non-existent (volume percentage is 0.1%). Moreover, the volume percentage was maintained at 0.1% even after storing at 50 °C for 24 h, demonstrating the outstanding thermal stability of CB-2.

In the case of CB-3, the particle size decreased from 0.189 to 0.136 μm after 3 h dispersion, while the volume per-

Table 3. Results of bead mill dispersion for CB particles

CB dispersion	Particle diameter (μm)			
	(Particles with diameters greater than 0.2 μm)			
	0 h	1 h	2 h	3 h
CB-1	0.179 (37.4%)	0.115 (14.8%)	0.110 (9.6%)	0.101 (9.2%)
CB-2	0.165 (37.4%)	0.102 (0.6%)	0.090 (0.5%)	0.079 (0.1%)
CB-3	0.189 (42.5%)	0.144 (11.3%)	0.137 (6.9%)	0.136 (7.9%)

centage of particle larger than 0.200 μm decreased from 42.5 to 7.9%. However, the CB-3 dispersion was found to have a relatively low thermal stability, similar to that of CB-1, because the volume percentage increased to 11.4% after storage at 50 °C for 24 h. These results show that there is a high possibility that the CB particles in CB-1 and 3 re-aggregate, unlike CB-2. This re-aggregation may be due to the loss of grafted PR-polymer from the CB particle surfaces in CB-1 and 3 on exposure to heat. In contrast, this did not occur in the CB-2 dispersion.

Based on the results shown in Table 3, the percentage of PR-Polymer grafted onto the CB particle surface varied according to the difference in CB particle size and surface area. Accordingly, different dispersion states were obtained.

Effect of PR-polymer content

Another method to confirm the differences between dispersions is to determine the degree of reaction as a function of the amount of PR-polymer relative to that of CB particles.

To investigate the reaction of CB particles and PR-polymer, the dispersion state of CB-2 was compared by varying the amount of PR-polymer. As shown in Table 4, the mass composition of the CB sample (Nipex 160IQ) was fixed at 15%, and the amount of PR-polymer was varied to be 5.0, 10.0, 15.0, and 25.0%. A total of four CB dispersions were obtained by adjusting to the total volume with water.

The viscosities and pH values of the four CB dispersions are listed in Table 5. When the pH was reduced from 8.37 to 8.01, the CB-2-1 dispersion formed a gel; the gel was obtained when the amount of PR-polymer was reduced to 5%. This gelation may be due to CB particles aggregation because insufficient PR-polymer was grafted onto the CB particle surface.

In the case of the CB-2-3 dispersion, which was obtained by increasing PR-polymer amount to 25%, the viscosity and

Table 4. CB dispersions obtained at various PR-polymer percentages

CB dispersions	Nipex 160IQ (%)	PR-Polymer (%)	Water (%)
CB-2	15.0	15.0	70.0
CB-2-1	15.0	5.0	80.0
CB-2-2	15.0	10.0	75.0
CB-2-3	15.0	25.0	60.0

Table 5. Viscosity and pH of the CB dispersions

CB dispersions	Viscosity (cps)	pH
CB-2	8.2	8.37
CB-2-1	Gel state	8.01
CB-2-2	6.3	8.68
CB-2-3	25.1	8.78

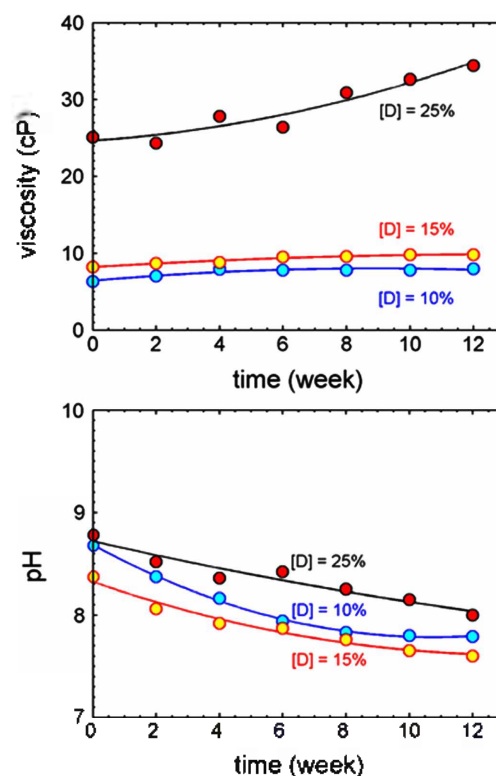


Figure 3. Viscosity and pH stability of CB-2, CB-2-2, and CB-2-3 dispersions stored at 50 °C.

pH increased due to an increase in the amount of PR-polymer. Moreover, the percentage of particles larger than 0.200 μm also increased. These observations may originate from the presence of excess PR-polymer not bonded to the surface of CB particles.

The viscosity of the CB2-2 dispersion, which contains 10% PR-polymer amount, was reduced, whereas the pH was slightly higher compared to 15% in CB-2. These results show that, for the Nipex 160IQ sample, a relatively stable CB dispersion could be prepared when the amount of PR-polymer was in the range of 10–15%.

Fig. 3 shows the variation of viscosity and pH of CB-2, CB-2-2, and CB-2-3 dispersions stored at 50 °C as a function of time. As expected, a relatively high thermal stability was observed when the amount of PR-polymer was in the range of 10–15%.

Bead mill dispersion results of carbon black suspensions

Table 6 shows the CB particle size and volume percentage of particles larger than 0.200 μm of the four CB dispersions based on bead-milling processing times.

In the case of CB-2-1 (PR-polymer 5%), the particle sizes

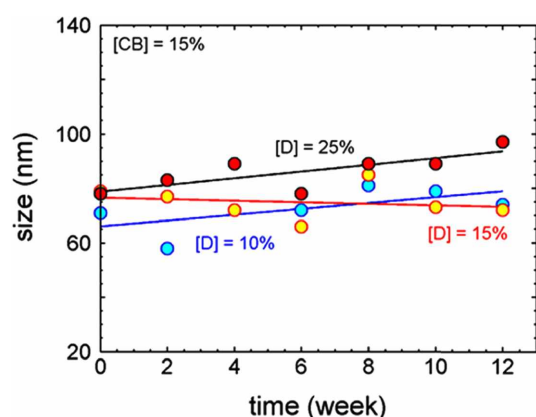
Table 6. Results of bead mill dispersion of CB suspensions

CB dispersions	Particle diameter (μm) (Particles with diameters greater than 0.2 μm)			
	0 h	1 h	2 h	3 h
CB-2	0.165 (37.4%)	0.102 (0.6%)	0.090 (0.5%)	0.079 (0.1%)
CB-2-1	0.172 (29.6%)	0.083 (2.6%)	0.082 (3.3%)	0.077 (1.6%)
CB-2-2	0.168 (39.2%)	0.078 (2.6%)	0.074 (0.2%)	0.071 (0.1%)
CB-2-3	0.224 (33.5%)	0.093 (6.8%)	0.091 (1.6%)	0.078 (0.8%)

rapidly decreased from 0.172 to 0.077 μm after bead milling for 3 h. Meanwhile, the volume percentage of particles larger than 0.200 μm was 1.6%. After storing at 50 $^{\circ}\text{C}$ for one day, a gel formed. The formation of a gel indicates that 5% PR-polymer was insufficient to modify the CB particle surfaces adequately.

The particle sizes of the CB-2-2 (PR-polymer 10%) rapidly decreased from 0.168 to 0.071 μm after 3 h bead milling. The volume percentage of particles larger than 0.200 μm was found to be 0.1%. After storing at 50 $^{\circ}\text{C}$ for one day, the volume percentage was 0%, confirming the excellent thermal stability of the CB-2-2 dispersion. We found that dispersion stability and thermal stability of CB dispersion increased at the correct ratio of CB particle and PR-polymer.

In the case of CB-2-3 (PR-polymer 25%), the particle size decreased from 0.224 to 0.078 μm after bead-milling, while the volume percentage of particles larger than 0.200 μm was 0.8%. The volume percentage of 0.7% was maintained even after storing at 50 $^{\circ}\text{C}$ for one day, confirming its outstanding thermal stability. However, both viscosity and pH increased with increasing quantity of PR-Polymer because

**Figure 4.** Storage stability of CB-2, CB-2-2, and CB-2-3 at 50 $^{\circ}\text{C}$ plotted as a function of size vs time.

of the presence of an excess of PR-polymer that was not bonded to the surface of the CB particles.

Fig. 4 shows the variation in CB particle size of the CB-2, CB-2-2, and CB-2-3 dispersions stored at 50 $^{\circ}\text{C}$ as a function of time.

From the obtained results, we concluded that both the dispersion stability and thermal stability of the CB dispersions were determined by CB particle size, surface area, pH, and the amount of added PR-polymer.

CONCLUSION

In conclusion, a thermally stable polymer (PR-polymer) was grafted, by means of a phenyl radical reaction, to the surface of CB particles, leading to dispersions with high thermal stability. This surface-modified CB has applications in industries requiring the thermal processing of CB additives. CB dispersions with high dispersion and thermal stabilities were obtained by preventing aggregation of CB particles as PR-polymer formed strong covalent bonds on CB particle surfaces. The results of this study show that both dispersion and thermal stability of CB are determined by CB particle size, surface area, pH, and PR-polymer amount.

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REFERENCES

1. Auer, E.; Freund, A.; Pietsch, J.; Tacke, T. *Appl. Catal. A. Gen.* **1998**, *173*(2), 259.
2. Medalia, A. I. *Rubber Chem. Technol.* **1986**, *59*(3), 432.
3. Sumita, M.; Sakata, K.; Asai, S.; Miyasaka, K.; Nakagawa, H. *Polym. Bull.* **1991**, *25*(2), 265.
4. Lin, Y.; Smith, T. W.; Alexandridis, P. *Langmuir* **2002**, *18*(16), 6147.
5. Ko, S. Design of Surface-Modified Anode Materials with High Electrical Conductivity for High-Performance Lithium-Ion Batteries. M. S. Thesis, Graduate School of UNIST, Ulsan, 2015.
6. Karasek, L.; Sumita, M. *J. Mater. Sci.* **1996**, *31*(2), 281.
7. Loganathan, K.; Bose, D.; Weinkauff, D. *Int. J. Hydrogen Energy* **2014**, *39*(28), 15766.
8. Vaseghi, M. R.; Southwart, D. W.; Murray, G. W. *J. Polym. Sci. Technol.* **1995**, *4*(2), 146.
9. Donnet, J.-B.; Bansal, R. C.; Wang, M. J. *Carbon Black Science and Technology, 2nd ed.*; Marcel Dekker: New York, 1993.
10. Tiarks, F.; Landfester, K.; Antonietti, M. *Macromol. Chem. Phys.* **2001**, *202*(1), 51.

11. Liu, T.; Jia, S.; Kowalewski, T.; Matyjaszewski, K.; Casado-Portilla, R.; Belmont, J. *Macromolecules* **2006**, *39*(2), 548.
 12. Lee, C.-F.; Yang, C.-C.; Wang, L.-Y.; Chiu, W.-Y. *Polymer* **2005**, *46*(15), 5514.
 13. Xu, H.; Li, B.; Wu, C. *Polym. J.* **2006**, *38*(8), 807.
 14. Nguyen, V. T.; Bellmann, G.; Bousset, F. Low Viscosity Stable Aqueous Dispersion of Graft Carbon Black. WO 1984000372 A1, February 2, 1984.
 15. Tsubokawa, N. *Polym. J.* **2007**, *39*(10), 983.
 16. Tsubokawa, N. Modification of Particle Surfaces by Grafting of Functional Polymers. In *Fundamental and Applied Aspects of Chemically Modified Surfaces*, Little, J. P., Blitz, B. Eds.; Woodhead Publishing: Cambridge, 1999; p 36.
 17. Li, W.; Xie, Z.; Li, Z. *J. Appl. Polym. Sci.* **2001**, *81*(5), 1100.
 18. Kim, J.-H.; Park, Y.-H.; Ha, G.-H. *J. Korean Powder Metall. Inst.* **2011**, *18*(4), 332.
 19. Choi, G.-S.; Chang, B.-K. *Polym. Sci. Technol.* **1991**, *2*(2), 71.
 20. Chung, D.-J.; Oh, S.-H.; Komathi, S.; Gopalan, A. I.; Lee, K.-P.; Choi, S.-H. *Electrochim. Acta* **2012**, *76*, 394.
 21. Matrab, T.; Chehimi, M. M.; Perruchot, C.; Adenier, A.; Guillez, A.; Save, M.; Charleux, B. Cabet-Deliry, E.; Pinson, J. *Langmuir* **2005**, *21*(10), 4686.
 22. Bae, J.; Kim, W.; Rah, K.; Jung, E. C.; Lee, S. *Microchem. J.* **2012**, *104*, 44.
 23. Mévellec, V.; Roussel, S.; Tessier, L.; Chancelon, J.; Mayne-L'Hermite, M.; Deniau, G.; Viel, P.; Palacin, S. *Chem. Mater* **2007**, *19*(25), 6323.
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