

Synthesis and Physical Property of Multi-Functional Siloxane Protective Coating Materials Applicable for Electronic Components

Cheol Hyun Kim,^{†,‡} Hyeon Mo Cho,^{§,*} and Myong Euy Lee^{†,*}

[†]Department of Chemistry, Yonsei University, Wonju 220-710, Korea. *E-mail: melgg@yonsei.ac.kr

[‡]Research & Development Division, CALS Corp., Asan 336-748, Korea

[§]University College, Yonsei University, Incheon 406-840, Korea. *E-mail: hyeonmo@yonsei.ac.kr

Received October 15, 2013, Accepted February 10, 2014

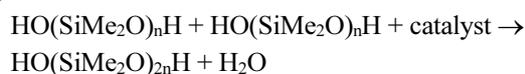
Four multialkoxy-functionalized siloxane base-polymers (**BP-1~4**) were synthesized through either hydrosilylation or condensation reactions in order to prepare multi-networked siloxane polymers having appropriate physical properties for protective coating in fabrications of electronics. Formulations of 4 base-polymers gave coating materials **A** and **B**. Product **A** showed well-controlled flowing and leveling properties, and product **A-2** was successfully applied to protective insulating coating for junction areas of connectors and chips in PDP controller. Tack free time, extrusion rate, dielectric breakdown voltage, hardness, thermal stability, water resistance and flame resistance of products **A** and **B** were examined.

Key Words : Self-leveling, Flowing, Thixotropy, Multi-crosslinking, Siloxane coating

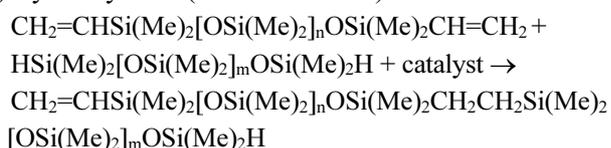
Introduction

Based on the evolution of semiconductors and integrated circuits, electronics' sizes have been shrunk and their complexity has increased, which results in requiring development of new materials. For materials to coat highly integrated connections of PCB (printed circuit board) assembly like ultra slim pattern, nano-scale pattern and ultra small gap, many specific properties, such as flow and leveling rates, curing rate, dielectric strength, weather resistance, thermal stability, flame resistivity, and robotic dispensable extrusion rate, are required.¹⁻³ Silicone material is one of suitable coating materials to meet the requirements and has been widely used in the industrial fields. Siloxane materials have several good properties compared to organic polymer materials.⁴ Firstly, stronger bond energy of Si-O than that of main chain of organic polymers⁵ gives excellent thermal stability. Secondly, easy free rotation caused by higher bond angle of Si-O-Si chain renders flexibility at a wide temperature range from -60 to 250 °C.⁶ Thirdly, siloxane polymers show quite low surface tension (21-22 mN/m) compared to organic polymers, which furnishes good property of spreading out on the substrates and becomes suitable for coating process.⁷ The siloxanes have been generally prepared by condensation and hydrosilylation as followings;⁸

1) Condensation reaction



2) Hydrosilylation (addition reaction)⁹



After alkoxy- and silanol-functional polysiloxanes were commercially developed in the 1950s, numerous protective silicone materials associated with organic groups and inorganic composites have been studied.¹⁰⁻¹³ For instance, quite recently silicon polymers with glycidoxo group for anti-corrosion^{14,15} and for protection of Al^{16,17} and Cu¹⁸ were investigated. We have been interested in a protection of wires in connectors and chips. The primary objective of this work is to control flow and leveling properties during the process of protective coating on wires. Flow and leveling properties are key factors for protective coatings among the several requested physical properties mentioned above. In general unbalance of flow and leveling properties incurs dielectric failures as drawn in Figure 1.¹⁹ Although linear siloxanes are usually used in the coating process,²⁰ it is hard to control their flowing and leveling characters due to low tensile strength, low elongation and low surface tension.²¹

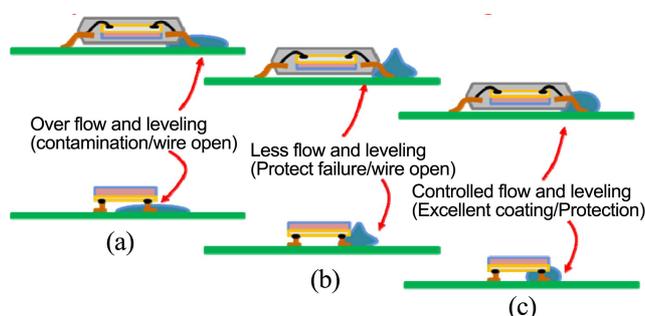


Figure 1. Common phenomena of coating processes in integrated circuits, (a) if flow and leveling rates of coating materials are high, the materials contaminate unwanted areas and upper parts of wires are open. (b) if flow and leveling rates are low, coatings of lower parts of wires are insufficient. (c) if flow and leveling rates are proper, the wires are protected from oxygen, moisture and other contaminators.

However, multi-dimensional networked siloxane polymers can exhibit controllable thixotropic, flowing and leveling properties by adjusting their crosslinking density.²²⁻²⁴ We hoped to demonstrate an example of how to control flowing and leveling properties with crosslinking degree of siloxane polymers.

Herein, we report synthesis of various multialkoxy-functionalized siloxane polymers through either condensation or hydrosilylation process, and their formulation and curing. Various physical properties including flowing and leveling of products and its successful application to coat PC Board connection are also described.

Experimental

Synthesis of base-polymers was carried out in multi-purpose 3.5 L reactor with triple shaft under argon or vacuum. ¹H, ¹³C and ²⁹Si NMR spectra were recorded on a Bruker Avance II⁺ BBO 400 MHz S1 spectrometer. The chemical shifts were referenced to internal CDCl₃ (¹H and ¹³C NMR) or external tetramethylsilane (²⁹Si NMR).

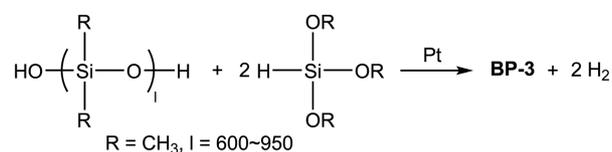
Synthesis of BP-1. Branched multialkoxy-functionalized siloxane base-polymer, **BP-1** was prepared from hydrosilylation of H-terminated poly(dimethylhydridomethyl)siloxane (764.0 g, 30 cSt, KF-99, Shin-Etsu Chemical, Japan) with trimethoxyvinylsilane (373.7 g, ca. 3 equiv) under 10 ppm (wt) of Pt catalyst in the absence of solvent (Scheme 1). After 3 h reaction at 85 °C **BP-1** with about 50 cSt was obtained. Pt catalyst (Karstedt's catalyst) was prepared from the reaction of 1,3-divinyl-1,1,3,3-tetramethyldisiloxane with H₂PtCl₆·6H₂O (PM Research Co.).²⁵⁻²⁸

Synthesis of BP-2. Terminal-functionalized ethylene-bridged siloxane base-polymer (**BP-2**) was prepared from the reac-

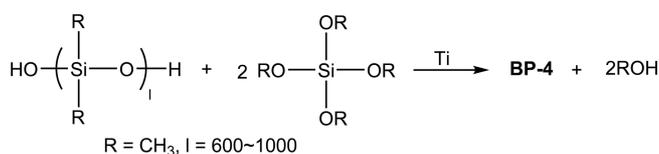
tion of α,ω -divinylpolydimethylsiloxane (805.2 g, 200 cSt, V-200, Tairen, Taiwan) with hydridotrimethoxysilane (24.6 g, 0.99 equiv based on vinyl group) under 10 ppm of Pt catalyst (Scheme 2). After 3 h reaction at 85 °C **BP-2** with 1,000 cSt was obtained.

Synthesis of BP-3. Trimethoxysilyl-terminated siloxane base-polymer (**BP-3**) was prepared from the reaction of α,ω -hydroxypolydimethylsiloxane (839.2 g, 5000 cSt, RF-5000, Shin-Etsu Chemical, Japan) with hydridotrimethoxysilane (4.93 g, 0.99 equiv based on hydroxy group) under 10 ppm of Pt catalyst (Scheme 3). After 3 h reaction at 85 °C **BP-3** with 5,000 cSt was obtained. The generated hydrogen gas during the reaction was completely removed by vacuum.

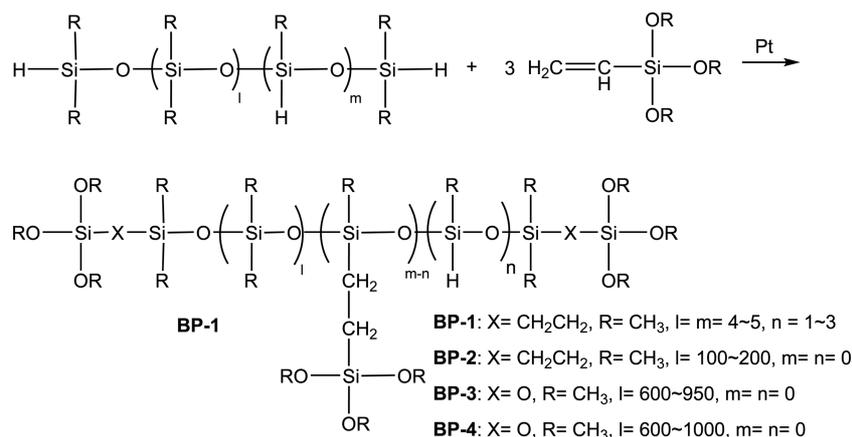
Synthesis of BP-4. High viscous terminal-functionalized siloxane base-polymer (**BP-4**) was prepared from the reaction of α,ω -hydroxypolydimethylsiloxane (1151.4 g, 10000 cSt, RF-10000, Shin-Etsu Chemical, Japan) with tetrameth-



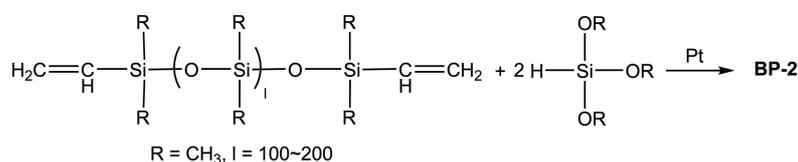
Scheme 3. Preparation of trimethoxysilyl-terminated siloxane base-polymer, **BP-3**.



Scheme 4. Preparation of high viscous terminal-functionalized siloxane base-polymer, **BP-4**.



Scheme 1. Preparation of branched siloxane base-polymer, **BP-1**.²⁹



Scheme 2. Preparation of terminal-functionalized ethylene-bridged siloxane base-polymer, **BP-2**.

Table 1. Formulation of Base-Polymers and Additives (phr: parts per hundred resin)

Composition ^a	A-1	A-2	A-3	B-1	B-2	B-3
BP-1 (wt %)	10	20	30	10	20	30
BP-2 (wt %)	30	20	10	30	20	10
BP-3 (wt %)				30		
BP-4 (wt %)				30		
Catalyst ^b (phr)				2		
Filler ^c (phr)	10	10	10	85	85	85

^aTotal weight is around 2.5 kg. ^bTitanium catalyst. ^cFumed silica for A and calcium carbonate for B.

oxysilane (6.1 g, 0.99 equiv based on hydroxy group) under 100 ppm of tetra-n-butyl titanate catalyst (Scheme 4). After 4 h reaction at 80 °C BP-4 with about 12,000 cSt was obtained. The generated methanol was removed by vacuum.³⁰

Preparation of Coating Products, A and B. Coating materials were prepared from mixing of base-polymers, catalyst for condensation and additives. All formulations were carried out in 3-shaft 3.5 L multi-purpose mixer under N₂ or vacuum at room temperature for 4 h. The same amount of ingredients except BP-1 and -2 was formulated for each coating products (Table 1) and total weights of formulation products were around 2.5 kg. The coating products were divided into two kinds of types A and B; fumed silica (common additive for a hardness enhancement, BET 120 m²/g, TS-720, Cabot) was used as a filler for A and calcium carbonate filler treated with fatty acid (particle size 15 μm, Okyumhwa TCR grade, Dongho Calcium) was used for B. Titanium complex (titanium bis(ethylacetoacetato)diisopropoxide) purchased from DuPont was used.

Measurements

Tack free time, (T.F.T), the period from the start of cure to a point when the material is sufficiently robust to resist to damage by touch or handling, was measured (25 ± 2 °C and 50 ± 5% of relative humidity) according to ASTM C 679-03. Viscosities were determined by Brookfield HAT viscometer using suitable spindles for samples at 1-30 rpm at room temperature under N₂. Dielectric breakdown voltage (DBV) was measured by AUTO mode of 75 KV Puncture tester (Daeyang Elecom) with 1 mm thickness of sample (ASTM D 149a-09). Extrusion rate was determined using syringe with 2 mm diameter nozzle under 1-3 kgf/cm² air pressure (ASTM C 1183-04). Hardness was measured by Shore A durometer.

Flow distance for the quantification of the fluid movement of sample was measured by a specially designed tool by CALS Corp (Figures S1 and S2).^{31,32} The tool was laid horizontally and a sample was filled up in a hole of 10 mm diameter and 10 mm depth. The sample was pushed out by push-pull button and the tool was immediately set on end. Then, flow distance was measured after 1 h. Self leveling property was determined by how long a sample horizontally spread out on the surface of the tool for 1 h. A sample was

filled up in a hole of 20 mm diameter and 10 mm depth, pushed out by push-pull button, and spread out.

Thermal stability was tested with PDSC (pressure differential scanning calorimeter) analytical equipment according to ASTM E537-07, and water resistance and proof was tested under water immersion at 85 °C (ASTM D870-09). Report of flame resistance test was given from Underwriters Laboratory with 94 V-0 level.

Results and Discussion

Synthesis of Base-polymers. Four multialkoxy-functionalized siloxane base-polymers (BP-1~4) were successfully synthesized. The hydrosilylation of vinylsilane with hydrido-siloxane in the presence of Pt catalyst gave branched siloxane base-polymer BP-1 (Scheme 1), in which the reaction process was monitored by ¹H NMR; The ¹H NMR due to vinyl (5.8-6.2 ppm) in trimethoxyvinylsilane was disappeared and the intensity of ¹H NMR derived from Si-H (4.7 ppm) group was decreased (Figure S6) after the reaction. In similar manner, terminal functionalized siloxane BP-2 was obtained (Scheme 2) and the reaction was also monitored by ¹H NMR; vinyl and hydrogen (Si-H) resonances of ¹H NMR were disappeared (Figure S12) after the reaction. The dehydrogenation of hydroxysilane and hydridotrimethoxysilane with Pt catalyst afforded BP-3 (Scheme 3), and the condensation of hydroxysilane and tetramethoxysilane in the presence of Ti catalyst yielded BP-4 (Scheme 4), which were confirmed by ¹H, ¹³C, and ²⁹Si NMRs (Figures S18-S29).

Physical Properties of A and B.³³ Physical properties of A including flow and leveling properties are summarized in Table 2 which shows that all properties of A are suitable for the protective coating process. Flow distances and diameters of spreading out (leveling) were growing as increasing of portions of trimethoxysilyl-branched siloxane BP-1 having the lowest viscosity among 4 base-polymers. Flow distances and diameters of spreading out of A were tightly correlated with %-composition of BP-1 and were in the range suitable for industrial coating. This result implies that one can precisely control flow and leveling properties by change of formulation ratio according to the requests of industries. In order to compare the flow and leveling properties of the multi-dimensional networked siloxane with those of linear siloxanes, we prepared two linear siloxane polymers (C)³⁴ having similar viscosities to those of product A. The same amounts of fumed silica and catalyst as those in product A were used and their flow distances were examined. Though the products C had similar viscosities (56000 and 33000 cSt) to those of product A, their flow distances (43 and 66 mm) were very long, which were not suitable for industrial coating. It shows that one can control flowing and leveling properties with multi-dimensional networked siloxane polymers more easily than with linear siloxanes. Even though one can speculate that the flow distance would decrease as the degree of multi-networking of siloxane increases, there is no publication regarding the relationship between flow

Table 2. Physical Properties of Coating Product A

Product	Flow (mm)	Leveling ^d (mm)	Viscosity ^b (cSt)	Viscosity ^c (cSt)	Viscosity ^d (cSt)	T.F.T. (min.)	Extrusion (g/min)	DBV (KV/mm)	Durometer ^e (Shore A)
A-1	15	3	48,000	2,452	2,397	8	290	23	36
A-2	18	7	43,200	1,814	1,776	8	300	21	43
A-3	21	13	40,800	1,380	1,316	9	320	17	52

^aLeveling property was evaluated from a diameter of spreading out. ^bViscosity of coating product. ^cViscosity of mixture of only BP-1~4. ^dCalculated viscosity of mixture of only BP-1~4; $\ln M = x \ln H + (1-x) \ln L$, M: mixed viscosity, H: high viscosity, L: low viscosity. ^eHardness of moisture-cured product.

property and network degree of siloxane polymer. Thus the finding that the adding of trimethoxysilyl-branched siloxane BP-1 for making high networked bonds caused proportional diminution of flow and leveling distances is an interesting example.

In case of product B, flow distances increased as increasing of portions of BP-1, however, the flow distances (40-45 mm) were too long to apply to coat electronics (Table S1), which was attributed to the filler, calcium carbonate.

Tack free times of A and B in the air at room temperature (25 ± 2 °C and $50 \pm 5\%$ of relative humidity) were measured (Tables 2 and S1). Their surface curing times (8-9 min) were almost same and were compatible with industrial coating process. Extrusion rates showed 280-320 g/min which values are applicable for semiconductor or LCD automatic assembly process. The lower viscous product, the larger ratio of BP-1, gave the higher extrusion rate as expected. DBVs of A and B were obtained in the range between 17 and 23 KV/mm that are enough values to apply to electronic insulating application. The smaller ratio of trimethoxysilyl-branched BP-1 was, the higher DBV was. It seems that trimethoxysilyl-branched BP-1 might increase free volumes in the materials to lower DBV.

Hardness, thermal stability, water resistance and flame resistance of moisture-cured A and B were measured; products A and B were cured by moisture in the atmosphere at room temperature (25 ± 2 °C and $50 \pm 5\%$ of relative humidity) over 72 h through the condensation of silanol and/or methoxysilane in the presence of Ti catalyst where the silanol was formed from the hydrolysis of alkoxysilane. Hardness of cured A and B increased when the ratio of BP-1 increased, possibly due to higher degree of crosslinking of branched siloxane polymer BP-1 than those of the other base-polymers. Cured A and B were stable to 330 °C and 366 °C, respectively, which were examined by PDSC. Water immersion tests of cured A and B at 85 °C for 144 h with the coating thickness of 0.3 to 2.0 mm on a packaged LED chip showed strong waterproof. Flame resistances of cured A and B were certified as 94 V-0 level by Underwriter Laboratory. Hardness, thermal stability, water resistance and flame resistance of cured A and B indicated that the cured materials could be applied to electronics coating.

Finally the product A-2 was applied to protective insulating coatings for wires of connectors and chips in PDP controller. As shown in Figure 2, coatings with width of 4 mm and thickness of 2.5 mm successfully protected junction

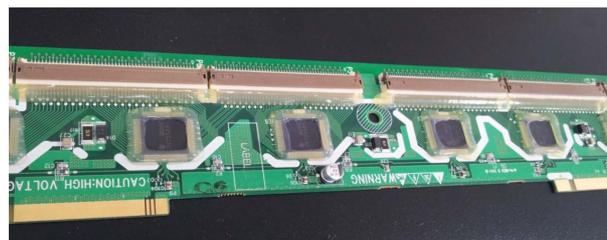


Figure 2. Coatings with product A-2 for 4 connectors and 4 chips in PDP controller.

areas using product A-2 showing well-controlled flowing and self-leveling properties.

Conclusion

Various multialkoxy-functionalized siloxane polymers as base-polymers were synthesized through either hydrosilylations or condensations. Trimethoxysilyl-branched siloxane (BP-1) and trimethoxysilyl-terminated ethylene-bridged siloxane (BP-2) were synthesized in the presence of Pt catalyst through hydrosilylations. Trimethoxysilyl-terminated siloxane (BP-3) and high viscous terminal-functionalized siloxane (BP-4) were synthesized from hydroxy-terminated siloxane through condensation reactions. The formulations of 4 base-polymers with catalyst and fillers gave coating products A and B. Trimethoxysilyl-branched siloxane (BP-1) effectively affected leveling and flow properties of product A. Physical properties, such as controllable leveling and flow properties, tack free time, extrusion rate, dielectric breakdown voltage, hardness, thermal stability, water resistance and flame resistance of products A and B, or moisture-cured A and B were suitable for protective insulating coatings. Finally, product A-2 was successfully applied to protective insulating coating for junction areas of connectors and chips in PDP controller.

Acknowledgments. This work was supported by Industrial Strategic Technology Development Program (#10031935) funded by the Ministry of Trade, Industry & Energy (MI, Korea). The authors wish to thank Sung Jin Park for NMR measurement and Jun Hyun Song for the preparation of Pt catalyst.

References

- Mathew, R. J.; Mekdhanasarn, B. US Patent 6,357,763, 2002.

2. Liao, B. J. US Patent 7,268,850, 2007.
 3. Hsu, F. Y. US Patent 7,787,094, 2010.
 4. Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; John Wiley & Sons, Inc.: New York, USA, 2000; p 257.
 5. Burger, C.; Kreuzer, F. H. *Silicon in Polymer Synthesis*; Kricheldorf, H. R., Ed.; Springer: New York, USA, 1996; p 113.
 6. Dvornic, P. R.; Lenz, R. W. *High Temperature Siloxane Elastomers*; Hüthig & Wepf: New York, USA, 1990; p 44.
 7. Kricheldorf, H. R.; Hertler, W. R.; Vurger, C.; Kochs, P.; Kreuzer, F. H. *Silicon in Polymer Synthesis*; Springer: New York, USA, 1996; p 113.
 8. Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; John Wiley & Sons, Inc.: New York, USA, 2000; p 282.
 9. Patai, S.; Rappoport, Z. *The Chemistry of Organic Silicon Compounds Part 1*; John Wiley & Sons, Inc.: New York, USA, 1989; p 658.
 10. Simionescu, B.; Olaru, M.; Aflori, M.; Doroftei, F. *High Perform. Polym.* **2011**, 326.
 11. Zielecka, M.; Bujnowska, E. *Prog. Org. Coat.* **2006**, 55, 160.
 12. Seifzadeh, D.; Golmoghani-Ebrahimi, E. *Surf. Coat. Tech.* **2012**, 210, 103.
 13. Han, Y.-H.; Taylor, A.; Knowles, K. M. *Surf. Coat. Tech.* **2009**, 203, 2871.
 14. Khelifa, F.; Druart, M.-E.; Habibi, Y.; Benard, F.; Leclere, P.; Olivier, M.; Dubois, P. *Prog. Org. Coat.* **2013**, 76, 900.
 15. Rauter, A.; Slemenick Perse, L.; Orel, B.; Bengu, B.; Sunetci, O.; Surca Vuk, A. *J. Electroanal. Chem.* **2013**, 703, 97.
 16. Wang, Y.; Li, Y.; Wang, F. *E-J. Chem.* **2012**, 9, 435.
 17. Nderi, R.; Fedel, M.; Urios, T.; Poelman, M.; Olivier, M.-G.; Deflorian, F. *Suf. Interfance Anal.* **2013**, 45, 1457.
 18. Peng, S.; Zhao, W.; Li, H.; Zeng, Z.; Xue, Q.; Wu, X. *Appl. Surf. Sci.* **2013**, 276, 284.
 19. Song, M. K.; Hong, S. M.; Park, J. M. *Polymer Science and Technology* **2001**, 12, 689.
 20. Kim, C. H.; Kim, G. Y. KR Patent 10-0982161, 2010.
 21. Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; John Wiley & Sons, Inc.: New York, USA, 2000; p 309.
 22. Al-Malaika, S.; Golovoy, A.; Wilkie, C. A. *Chemistry and Technology of Polymer Additives*; Blackwell Science: Oxford, U. K., 1999; p 62.
 23. Simpson, T. R. E.; Parbhoo, B.; Keddie, J. L. *Polymer* **2003**, 44, 4829.
 24. Baney, R. H.; Itoh, M.; Sakakibara, A.; Suzuki, T. *Chem. Rev.* **1995**, 95, 1409.
 25. Marciniec, B. *Hydrosilylation: A Comprehensive Review on Recent Advances*; Springer: New York, USA, 2009; p 3.
 26. Chandra, G.; Lo, P. Y. *Organometallics* **1987**, 6, 191.
 27. Lewis, L. N.; Stein, J.; Gao, Y.; Colborn, R. E.; Hutchins, G. *Platinum Metals Rev.* **1997**, 41, 66.
 28. Green, M. L. H.; Griffith, W. P. *Platinum Metals Rev.* **1998**, 42, 168.
 29. Kim, C. H.; Lee, M. E. KR Patent 10-1128735, 2012.
 30. Kim, C. H.; Kim, G. Y. KR Patent 10-0972565, 2011.
 31. Kim, C. H.; Lee, M. E. KR Patent 10-1222876, 2013.
 32. Kim, C. H.; Cho, H. M.; Lee, M. E. *Analytical Science & Technology* **2012**, 25, 127.
 33. Kim, C. H.; Lee, M. E. KR Patent 10-1262125, 2013.
 34. Products C are the similar materials to existing products except additive ratios. See table S1.
-