

Polypyrrole-supported graphite felt electrode for C-C bond formation reaction in solid-phase
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The solid-phase synthesis has attracted much interest in organic synthesis,¹ because it can improve the reaction yield by using an excessive reagent and the used reagent can be removed by the easy operation such as washing. The solid supports for the solid-phase synthesis usually are polymer resins such as polystyrene. On the other hand, the possibility of using electrochemistry in solid-phase synthesis has recently been reported.^{2,3} Pilard *et al.* have demonstrated the solid-phase chemistry with the modified electrode prepared by electrochemical polymerization of substrate precursors containing thiophene side chain.² Pickett and co-workers have developed the polypyrrole-supported solid-phase chemistry on electrode surface.³ However, they used a platinum (Pt) plate electrode as solid support. Here we reported the first efficient, the solid-phase chemistry with a graphite felt (GF) electrode as solid support.

A GF electrode has much larger surface area ($0.7 \text{ m}^2 \text{ g}^{-1}$) in comparison with polystyrene resin and Pt electrode and is commercially available in low price. We were intrigued by the possibility of using electrochemistry to generate polymer film support on GF electrode surface with the substrate site attached to the polymer chain. Thus, we tried to prepare substrate-modified GF electrode by electrochemical polymerization of substrate precursors containing pyrrole side chain and used for palladium (Pd) catalyst reactions which are widely researched using polystyrene resin.⁴

The preparation of substrate-modified GF electrode for Sonogashira reaction⁵ as one of Pd catalyst reactions is as follows. The substrate precursors containing pyrrole side chain were synthesized from 3-(pyrrol-1-yl)propionic acid and 4-iodobenzyl alcohol. This pyrrole-based monomer was modified on GF electrode by electrochemical polymerization at repeated cyclic voltammetric scans between 0 and +1.5 V vs. Ag/AgCl. † The amount of substrate on the GF electrode surface was determined by the amount of recovered 4-iodobenzyl alcohol which was yielded by the treatment of iodobenzene-modified GF electrode with NaOCH_3 . The amount of substrate on GF electrode surface increased with the increasing repeated cyclic voltammetric scanning. The loading of substrate on GF electrode of 20-times scanning was *ca.* $80 \mu\text{mol g}^{-1}$.

Preparative Sonogashira reaction was performed on the iodobenzene-modified GF electrode ($3.0 \times 1.0 \times 0.5 \text{ cm}$) in DMF (10 ml) containing Et_3N (10 mmol), terminal acetylene (5 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.25 mmol) and CuI (0.5 mmol). The result when using 1-octyne as terminal acetylene is as follows. The coupling product yield was 70% when the substrate-modified GF electrode of 5-times scanning (loading $10 \mu\text{mol g}^{-1}$) was used. On the other hand, the homogeneous Sonogashira reaction using pyrrole-based monomer was carried out with lower yield (30%) than the solid-phase system using the substrate-modified GF electrode. We also tried under standard polymerization and reaction conditions on Pt plate electrode instead of GF electrode, however, the generated polymer film was not strongly attached on Pt electrode

surface and could not use the solid-phase synthesis. The coupling product yield decreased with the increasing immobilized substrate on GF electrode surface. This observation suggested that a thick polymer film on GF electrode surface was formed with the increasing repeated cyclic voltammetric scanning and did not infiltrate the terminal acetylene and catalyst into a polymer layer.

The results of Sonogashira reaction of various terminal acetylenes using the iodobenzene-modified GF electrode of 5-times scanning were converted to the corresponding coupling products in adequate yield (59 - 70%). We also attempted the use of pyrrole-based monomer possessing terminal acetylene instead of iodobenzene. It was seen that the same tendency as the using iodobenzene-modified GF electrode for the amount of terminal acetylene on GF electrode surface by repeated cyclic voltammetric scans and the coupling product yield by Sonogashira reaction.

We have described the first efficient, the immobilization of substrate on GF electrode by electrochemical polymerization of substrate precursors containing pyrrole side chain and use for solid-phase synthesis in place of polystyrene resin.

Notes and references

† *General procedure for electrochemical polymerization*
Electrochemical polymerization was performed in a one-compartment cell with graphite felt ($3.0 \times 1.0 \times 0.5 \text{ cm}$) as working electrode and a platinum wire as counter electrode, respectively. A Ag/AgCl electrode was used as reference electrode. All electrochemical polymerization experiments were performed in acetonitrile solution with 0.01 M monomer concentration and 0.1 M tetraethylammonium perchlorate as supporting electrolyte. Repeated cyclic voltammetric scans between 0 and +1.5 V at 50 mV s^{-1} led to the formation of conducting polymer film at the GF electrode.

- 1 S. V. Ley, I. R. Baxendale, R. N. Bream, P. S. Jackson, A. G. Leach, D. A. Longbottom, M. Nesi, J. S. Scott, R. I. Storer and S. J. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 2000, 3815.
- 2 J. F. Pilard, G. Marchand and J. Simonet, *Tetrahedron*, 1998, **54**, 9401; G. Marchand, J. F. Pilard, J. R. Berthelot and J. Simonet, *New J. Chem.*, 1998, **23**, 869; G. Marchand, J. F. Pilard and J. Simonet, *Tetrahedron Lett.*, 2000, **41**, 883.
- 3 M. S. Passos, M. A. Queiros, T. L. Gall, S. K. Ibrahim and C. J. Pickett, *J. Electroanal. Chem.*, 1997, **435**, 189; S. M. Therias, M. S. Passos, S. K. Ibrahim, T. L. Gall, M. A. Queiros and C. J. Pickett, *Chem. Commun.*, 1998, 1175.
- 4 S. Bräse, J. H. Kirchhoff and J. Köbberling, *Tetrahedron*, 2003, **59**, 885.
- 5 K. Sonogashira, *Metal-Catalyzed Cross-Coupling Reaction*, Chap.5, Wiley-VCH, New York, 1998.