



A facile hydrothermal synthesis of novel hollow triple-shell CuNiFe₂O₄ nanospheres with robust catalytic performance in the Suzuki–Miyaura coupling reaction

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ABSTRACT

Triple-shell hollow spheres of crystalline copper–nickel ferrite have been synthesized in a simple one-pot procedure using carbon spheres as templates via a hydrothermal approach. Ferric nitrate, copper nitrate, and nickel nitrate were dissolved in water together with glucose, and the mixture was heated to 180 °C in an autoclave. Finally, the carbon core was removed by calcination at 550 °C. The triple-shell hollow spheres of CuNiFe₂O₄ were characterized by XRD, TEM, FE-SEM, and EDS. High catalytic activity for the Suzuki reaction was obtained for this new triple-shell hollow sphere of CuNiFe₂O₄. This also reveals obvious advantages such as the recyclability of the catalyst, simple experimental operation, and excellent yields.

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1. Introduction

The essential driving force in the critical field of heterogeneous catalysis is the design and synthesis of new catalysts, which are the basis of energy conversion [1]. Transition metal ferrites (MFe₂O₄, M = Ni, Cd, Zn, etc.) possessing the spinel structure have been investigated in detail due to their thermal, mechanical, and chemical stability [2] and for their structural, electrical, and magnetic properties [3,4]. Ferrites are appealing in a wide array of applications in electronics [5], ferrofluids [6], magnetic resonance imaging (MRI) [7], drug delivery systems [8], pigments [9], catalysts [10], and sensors [11]. In particular, ferrites have been used effectively in catalysis [12,13] and photocatalysis [14] for a number of organic reactions, such as C–C and C–X coupling [12], alkylation [15], and oxidation of some species such as alcohols [16], CO [17], styrene [18,19], and toluene [20,21]. The most commonly explored synthesis procedures for these spinel ferrite nanoparticles are sol–gel [22], radiofrequency plasma treatment [23], reverse micelles [24], host templates [25], co-precipitation [26], hydrothermal treatment [27], and polyol-assisted synthesis [28].

Hollow nanostructures, as a class of materials with a particular morphology, have attracted attention in the past decades due to

their special physical and chemical properties, which are different from those of conventional solid nanoparticles [29]. These special properties of hollow nanostructures are owing to their well-defined morphology, uniform size, low density, larger specific surface area, and wide range of potential applications [30–35]. Recently, the preparation of hollow spheres with multiple shells has been attracting attention because of their better performance and their widespread applications in drug delivery, heterogeneous catalysis, sensors, lithium ion batteries, photocatalysis [36–40], and environmental engineering [41–44]. Similarly to single-shell or double-shell micro/nanostructured materials, there are three distinct methods for generating multishell hollow structures with controllable shapes: hard templating, soft templating, and template-free methods [44–46].

C–C bond formation reaction is one of the most useful methods for production of biaryl compounds, which constitute a wide range of natural products and pharmaceuticals [47a]. A large number of protocols have been developed for the Suzuki reaction with the use of iron [48,49], manganese [50], cobalt [51,52], ruthenium [53], copper [54,55], gold [56], nickel [57], rhodium [58], palladium [59], and other complexes [60–62] as catalysts. However, these methods have several major drawbacks: expensive reagents, difficulty in workup, environmental hazards, and difficulty in recycling the catalyst. Therefore, design and synthesis of new heterogeneous catalysts with easy separation and recyclability for C–C cross-coupling reactions have been the subject of much interest [47].

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There are few reports of synthesis of hollow spheres of ternary transition metal ferrites, because formation of a uniform coating of ternary ferrites on the surface of a template is difficult [63]. To the best of our knowledge, hollow nanospheres of CuNiFe₂O₄ as a mixed ternary transition metal ferrite have not been introduced yet as a candidate for catalyzing the Suzuki reaction. Therefore, it could be profitable to investigate the performance of hollow spheres of copper nickel ferrite in the catalysis of the Suzuki reaction, as an important organic reaction.

Here, following our previous work [64], we report a facile one-step hydrothermal method for the synthesis of hollow nanostructured copper nickel ferrite using ferric nitrate, copper nitrate, and nickel nitrate as the reactants and glucose as a chelating agent. In addition, the catalysis performance in the Suzuki cross-coupling reaction has been studied.

2. Experimental

2.1. General procedure for preparation of triple-shell hollow spheres

Certain amounts of 1 M glucose solution, Fe(NO₃)₃·9H₂O solution (1 M, 2 eq.), Cu(NO₃)₂·6H₂O solution (1 M, 0.5 eq.), and Ni(NO₃)₂·6H₂O solution (1 M, 0.5 eq.) were dispersed in 10 mL distilled water. After being stirred for about 30 min, the mixture was transferred into a Teflon-lined stainless steel autoclave. The autoclave was maintained at 180 °C for 24 h and then naturally cooled to ambient temperature. The precipitate was filtered, washed with water and ethanol, and dried at 100 °C. Finally, the hollow spheres were obtained after calcination at 550 °C for 3 h.

2.2. General procedure for the cross coupling of arylboronic acids with aryl halides

The quantities 1.2 mmol of phenylboronic acid, 1.0 mmol of aryl halides, 2 mmol K₂CO₃, and 0.01 g CuNiFe₂O₄ hollow spheres as catalysts were added to 5 mL ethanol/water (3:1) under stirring for an appropriate time at 80 °C. After completion of the reaction, the catalyst was separated by an external magnet and the product was extracted with ethyl acetate and purified by column chromatography. The recovered catalyst was washed with ethanol and dried at 80 °C for further use.

2.2.1. Biphenyl (1)

White solid; m.p. 70–71 °C; ¹H NMR (CDCl₃, 300 MHz): δ = 7.37–7.40 (m, 2H), 7.43–7.53 (m, 4H), 7.63–7.68 (m, 4H); ¹³C NMR (CDCl₃, 75 MHz): δ = 122.45, 123.73, 124.03, 136.54.

2.2.2. 4-Methyl-1,1'-biphenyl (2)

White solid; m.p. 43–44 °C; ¹H NMR (CDCl₃, 300 MHz): δ = 2.43 (s, 3H), 7.27–7.63 (m, 9H); ¹³C NMR (CDCl₃, 75 MHz): δ = 21.11, 126.99, 128.72, 129.49, 137.03, 138.38, 141.19.

2.2.3. 4-Methoxy-1,1'-biphenyl (3)

White solid; m.p. 88–89 °C; ¹H NMR (CDCl₃, 300 MHz): δ = 3.88 (s, 3H), 7.01 (d, 2H, J = 8.7 Hz), 7.29–7.36 (m, 1H), 7.46 (d, 2H, J = 8.7 Hz), 7.54–7.60 (m, 4H); ¹³C NMR (CDCl₃, 75 MHz): δ = 55.36, 114.22, 126.66, 126.75, 128.16, 128.72, 133.81, 140.85, 159.16.

2.2.4. 4-Nitro-1,1'-biphenyl (4)

Yellow solid; m.p. 113–114 °C; ¹H NMR (CDCl₃, 300 MHz): δ = 7.39–7.50 (m, 1H), 7.51 (d, 2H, J = 7.8 Hz), 7.68 (d, 2H, J = 7.8 Hz), 7.77 (d, 2H, J = 6.9 Hz), 8.33 (d, 2H, J = 6.9 Hz).

2.2.5. [1,1'-Biphenyl]-2-carboxylic acid (5)

White solid; m.p. 113 °C; ¹H NMR (CDCl₃, 300 MHz): δ = 7.41–7.54 (m, 5H); 7.55–7.63 (m, 1H), 7.71–7.80 (m, 2H), 8.53–8.55 (m, 1H), 13.62 (broad, 1H); ¹³C NMR (CDCl₃, 75 MHz): δ = 120.14, 128.64, 130.53, 132.97, 137.23, 140.99, 168.51.

2.2.6. 3-(Trifluoromethyl)-1,1'-biphenyl (6)

White solid; m.p. 41 °C; ¹H NMR (CDCl₃, 300 MHz): δ = 7.23–7.29 (m, 3H), 7.61–7.64 (m, 2H), 7.90–7.99 (m, 4H); ¹³C NMR (CDCl₃, 75 MHz): δ = 124.52, 124.57, 128.37, 130.40, 131.74, 132.18, 132.61, 133.04, 134.24, 134.29, 140.88, 141.89.

2.2.7. 1,1',4',1''-Terphenyl (7)

White solid; m.p. 212–214 °C; ¹H NMR (CDCl₃, 300 MHz): δ = 7.28 (s, 4H), 7.40–7.49 (m, 6H), 7.81–7.91 (m, 4H); ¹³C NMR (CDCl₃, 75 MHz): δ = 127.30, 128.28, 128.96, 133.47, 139.09.

2.2.8. 2,5-Diphenylpyridine (8)

Yellow solid; m.p. 132 °C; ¹H NMR (CDCl₃, 300 MHz): δ = 7.09–7.26 (m, 5H), 7.29–7.49 (m, 4H), 7.61–7.64 (m, 3H), 8.47 (s, 1H); ¹³C NMR (CDCl₃, 75 MHz): δ = 115.21, 121.14, 127.21, 128.18, 128.86, 136.09, 140.34, 151.88.

2.2.9. 4'-Methoxy-3-nitro-1,1'-biphenyl (9)

Yellow solid; m.p. 126 °C; ¹H NMR (CDCl₃, 300 MHz): δ = 3.90 (s, 3H), 7.05 (d, J = 8.7 Hz, 2H), 7.60 (d, 2H, J = 8.7 Hz), 7.61–7.63 (m, 1H), 7.89–7.92 (m, 1H), 8.16–8.19 (m, 1H), 8.43–8.45 (m, 1H).

2.2.10. 3,4'-Dinitro-1,1'-biphenyl (10)

White solid; m.p. 238 °C; ¹H NMR (CDCl₃, 300 MHz): δ = 7.71–8.53 (m, 8H); ¹³C NMR (CDCl₃, 75 MHz): δ = 122.31, 123.57, 124.47, 128.12, 130.27, 133.20, 140.27, 148.87, 150.07.

2.2.11. 4'-Methyl-3-nitro-1,1'-biphenyl (11)

With solid; m.p. 75–76 °C; ¹H NMR (CDCl₃, 300 MHz): δ = 2.28 (s, 3H), 7.18 (d, 2H, J = 8.1 Hz), 7.22 (d, 2H, J = 8.1 Hz), 7.98–8.02 (m, 2H), 8.32–8.35 (m, 1H), 8.53–8.54 (m, 1H); ¹³C NMR (CDCl₃, 75 MHz): δ = 22.70, 122.13, 123.32, 128.33, 129.03, 130.10, 130.30, 133.05, 138.97, 140.37, 148.93.

2.2.12. [1,1'-Biphenyl]-4-carbaldehyde (12)

White solid; m.p. 57–59 °C; ¹H NMR (CDCl₃, 300 MHz): δ = 7.41–7.45 (m, 5H), 7.68 (d, 2H, J = 6.9 Hz), 7.75 (d, 2H, J = 6.9 Hz), 9.98 (s, 1H); ¹³C NMR (CDCl₃, 75 MHz): δ = 129.78, 130.98, 132.44, 135.06, 141.08, 148.06, 191.08.

2.2.13. 1-([1,1'-Biphenyl]-4-yl)ethan-1-one (13)

White solid; m.p. 122–123 °C; ¹H NMR (CDCl₃, 300 MHz): δ = 2.66 (s, 3H), 7.41–7.53 (m, 3H), 7.64–7.67 (m, 2H), 7.71 (d, 2H, J = 8.4 Hz), 8.06 (d, 2H, J = 8.4 Hz); ¹³C NMR (CDCl₃, 75 MHz): δ = 26.71, 127.24, 127.30, 128.28, 128.96, 129.00, 135.86, 139.86, 145.77, 197.77.

3. Results and discussion

A brief procedure for synthesis of triple-shell hollow CuNiFe₂O₄ spheres with carbon spheres as templates is depicted in Scheme 1. At the first step, metal precursors were fabricated in situ on the surfaces of carbon spheres from a mixed solution of glucose, Fe³⁺, Ni²⁺, and Cu²⁺ by a hydrothermal method. The carbon core was eliminated by calcination and the expected hollow spheres were obtained. The nanocatalyst was characterized by field emission scanning electron microscopy (FE-SEM), energy-dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM), and X-ray diffraction (XRD).

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