‘Clicked’ magnetic nanohybrids with a soft polymer interlayer†

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We have developed a facile and efficient methodology to prepare magnetic nanohybrids from ‘clickable’ magnetic nanoparticles and polymer-coated nanomaterials by Cu(i)-catalyzed azide–alkyne cycloaddition ‘click’ chemistry.

Since their discovery in 1991, carbon nanotubes (CNTs) have sparked extensive research in a broad range of both scientific studies and technological applications.1 Decorating CNTs with magnetic nanoparticles (MNPs), especially iron oxide nanoparticles, has attracted increasing attention within recent years due to their potential applications in heterogeneous catalysis,2 alignment of CNTs,3 biochemical separations and drug delivery.4 To date, various synthesis methods to prepare magnetic nanotubes have been reported,5 but these methods suffer from certain drawbacks. For example, in situ generation of magnetic nanoparticles lacks proper control of particle size or requires rigorous reaction conditions, covalent or noncovalent attachment of magnetic nanoparticles involves low efficiency or tedious processes. Accordingly, it is worthwhile to explore a novel method for the preparation of magnetic nanohybrids, which is supposed to be featured as convenient, efficient and compatible for different nanoparticles.

In the past few years, ‘click’ chemistry, specifically the Cu(i)-catalyzed 1,3-dipolar cycloaddition reaction of an azide and an alkyne, has emerged as a striking and promising strategy for the surface functionalizations of the nanoparticles.5,6 ‘Click’ reactions have been further extended to the functionalization of block copolymers,7 bioconjugation of nanoparticles,8 immobilization of catalysts,9 decoration of gold nanoparticles on carbon nanotubes and artificial DNA templates.10 In this respect, we investigated the ‘click’ chemistry as a novel strategy for the preparation of magnetic nanohybrids.

Here we report the first synthesis of ‘clicked’ nanohybrids from ‘clickable’ Fe3O4 nanoparticles and polymer-coated CNTs/silica spheres. Based on the ‘click’ chemistry, our synthesis protocol possesses the following merits: (1) the reaction proceeds under sufficiently mild conditions (room temperature, insensitive to water and other solvents); (2) covalent linkages between nanoparticles and nanomaterials are formed in a simple manner with high efficiency; (3) because monodisperse nanoparticles of desired size can be first synthesized and then linked to other nanomaterials, it is easy to control the particle size in the first synthesis step, and the surface functionalities of the nanoparticles can be specifically designed as well.

In order to fabricate hybrid nanomaterials by ‘click’ chemistry, the precursors of nanoparticles with ‘clickable’ functional groups should be synthesized, respectively in advance. At first, we prepared water-soluble poly(acrylic acid)-capped Fe3O4 nanoparticles (Fe3O4–COOH) following the procedure reported by Ge et al.11 Subsequently, the Fe3O4–COOH possessing abundant carboxyl groups on their surfaces were coupled with 3-azidopropyl-1-amino or propargyl alcohol, affording azide-functionalized Fe3O4 nanoparticles (Fe3O4–N3) and alkyne-functionalized Fe3O4 nanoparticles (Fe3O4–C≡CH), respectively (Scheme 1). The presence of surface functionalized groups can be confirmed from FTIR spectra (Fig. 1(b)). The peak at 580 cm−1 was assigned to the vibration of the Fe–O bond, and the characteristic peaks of alkyne and azide groups were clearly visible at 3242 cm−1 (≡C–H stretching) and 2902 cm−1 (asymmetric azide stretching), respectively. To examine the relative quantity of organic compounds grafted to the Fe3O4 nanoparticles, thermal gravimetric analysis (TGA) measurements were performed and the results are shown in Fig. 1(a). The Fe3O4–COOH showed a weight loss of 14.45% below 500 °C, which corresponded to ca. 2.01 mmol carboxyl groups per gram of Fe3O4–COOH. The Fe3O4–N3 and

Scheme 1 ‘Click’ modification of the surfaces of magnetic nanoparticles. Reagents and conditions: (i) EDC·HCl, NHS, H2O, r.t., 18 h; (ii) HCl, NHS, H2O, r.t., 24 h; (iii) CuSO4·5H2O, (+)-sodium L-ascorbate, H2O, r.t., 24 h; (iv) CuBr/PMDETA, CH2Cl2, r.t., 24 h.
Fe₃O₄–C had 2.39 and 2.06% more weight loss than Fe₃O₄–COOH at 500°C, and thus the densities of azide and alkyne groups were calculated to be ca. 0.34 and 0.63 mmol g⁻¹, respectively (corresponding to 17.5 and 32.3% conversion for the amidation and esterification, respectively). The X-ray diffraction (XRD) pattern of Fe₃O₄–N₃ (Fig. 3(d)) displayed good crystalline quality, and the peak position and relative intensity fit well with the standard XRD data for magnetite (JCPDS card, file No. 19-0629). As seen in the typical TEM image of Fe₃O₄–N₃ in Fig. 2(a), the average diameter of Fe₃O₄–N₃ was ca. 6 nm, which was very close to the value of 5.7 nm calculated using the Debye–Scherrer formula from the XRD data.

In order to verify the 'clickable' capability of the as-prepared Fe₃O₄–N₃, we performed various click reactions to modify its surface with alkyne-terminated poly(ethylene glycol) (PEG-Alk), propargyl alcohol-esterified palmitic acid (C₁₆-Alk), and alkyne-functionalized rhodamine B (RhB-Alk), affording hydrophilic, hydrophobic and fluorescent magnetic nanoparticles, respectively (Scheme 1). As seen in Fig. 1(c)–(f), Fe₃O₄@PEG and Fe₃O₄@C₁₆ dissolved well in water and n-hexane, respectively, and they could be separated quickly by applying an external magnetic field. The weight losses of Fe₃O₄@PEG, Fe₃O₄@C₁₆ and Fe₃O₄@RhB increased significantly compared with that of Fe₃O₄–N₃, proving the presence of a large amount of newly added organic moiety (Fig. 1(a)). FT-IR spectroscopy (Fig. 1(b)) showed the characteristic absorption peak of the azide group near 2092 cm⁻¹ essentially vanished, revealing the high degree of surface functionalization. Meanwhile, the intensity of symmetrical and asymmetrical stretching of the C–H bond (at 2928 and 2862 cm⁻¹, respectively) was greatly augmented in Fe₃O₄@C₁₆, and a distinct band appeared at 1104 cm⁻¹ in the FTIR spectrum of Fe₃O₄@PEG, which was ascribed to the C–O–C of PEG chain. In the fluorescence spectrum of RhB-Alk (Fig. 1(g)), the maximum emission wavelength was 582 nm if excited at its maximum excitation wavelength of 560 nm; Fe₃O₄@RhB showed a similar fluorescence pattern and the maximum emission and excitation wavelengths did not change.

We initially attempted to prepare nanohybrids directly from MWNT-C≡CH and Fe₃O₄–N₃. However, nanohybrids were hardly observed in the TEM images of the as-prepared samples (Fig. S3, ESI), demonstrating that this direct click coupling was not feasible despite the high density of surface functional groups. This is likely due to the huge steric hindrance of ‘hard’ matter and low touching frequency between reactive groups resulting from the low motion rate of the solid particles as compared with the organic molecules. We thus modified MWNT-C≡CH with a polymer containing an abundant level of azide groups (affording MWNT-pAz),
The nanocomposites were also characterized by TGA and Raman spectroscopy (Fig. S4, S5, ESI†). Control experiments in the absence of CuBr were also carried out, but nearly no nanohybrids were found by TEM (Fig. S3, ESI†), thus excluding the possibility that the nanohybrids were formed by noncovalent adsorption. In addition, the ‘clicked’ nanohybrids were quite stable even under ultrasonication, and can be well-dispersed in water and in common organic solvents such as DMF and THF. Given the aforementioned evidence, the efficient realization of click reactions can be tentatively ascribed to the ‘soft’ polymer interlayer that made the relatively ‘hard’ surfaces of nanotubes more accessible for magnetic nanoparticles.

In order to examine whether this click methodology can be extended to other nanomaterials, we replaced CNTs with silica spheres. Similarly, azide modified SiO$_2$ spheres without polymer coating cannot be evenly and effectively decorated with Fe$_3$O$_4$–C≡CH as confirmed by TEM (Fig. S3, ESI†), while alkyl polymer-grafted SiO$_2$ spheres can react with Fe$_3$O$_4$–N$_3$ efficiently to produce uniformly anchored SiO$_2$/Fe$_3$O$_4$ hybrids (Fig. 2(f)), which still retain good crystalline structure as characterized by its XRD pattern (Fig. 3(c)) and superparamagnetic property (Fig. 4(c)). These results manifest the remarkable universality of the click strategy and the crucial importance of the soft polymer interlayer which can adhere two kinds of particles together covalently.

In summary, we have developed a novel methodology to effectively prepare ‘clicked’ magnetic nanohybrids using polymer-coated nanomaterial precursors. Moreover, we demonstrated that the soft polymer interlayer was indispensable for the surface click reactions between hard nanoparticles. This strategy offers notable versatility, opening the avenue for the facile fabrication of multifunctional hybrid compounds with tailor-made structures and properties from the huge resource of individual nanosubstances.

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Notes and references