

'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.

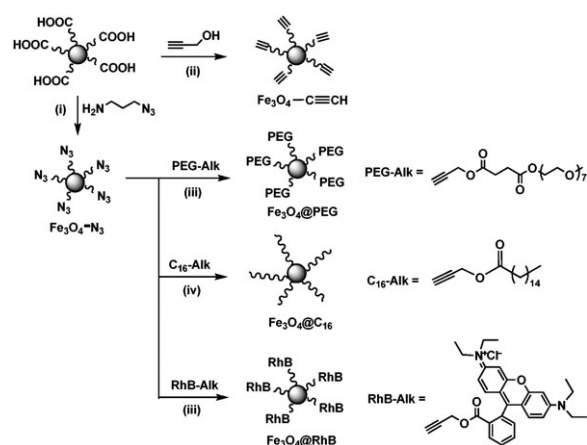
Since their discovery in 1991, carbon nanotubes (CNTs) have sparked extensive research in a broad range of both scientific studies and technological applications.¹ Decorating CNTs with magnetic nanoparticles (MNPs), especially iron oxide nanoparticles, has attracted increasing attention within recent 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 synthesis approach owing to its remarkable virtues such as high specificity, quantitative yields, compatibility with water and moderate reaction conditions.⁶ 'Click' reactions have been used for the further functionalization of block copolymers,⁷ biofunctionalization of MNPs,⁸ immobilization of catalyst,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 functionalizations 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-azidopropan-1-amine 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 2092 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) EDC-HCl, NHS, DMAP, H₂O, r.t., 24 h; (iii) CuSO₄·5H₂O, (+)-sodium L-ascorbate, H₂O, r.t., 24 h; (iv) CuBr/PMDTA, CH₂Cl₂, r.t., 24 h.

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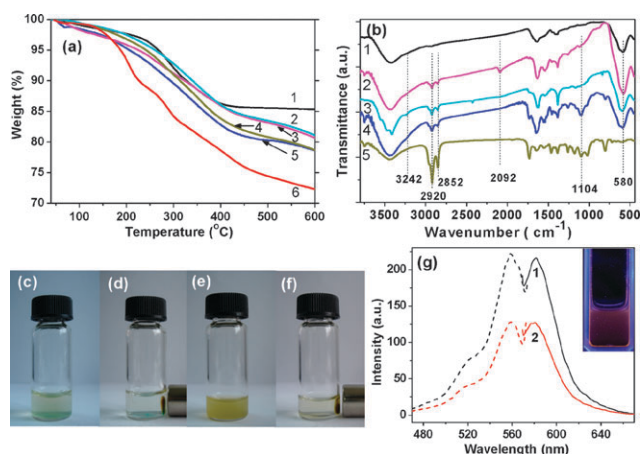


Fig. 1 (a) TGA curves of (1) $\text{Fe}_3\text{O}_4\text{-COOH}$, (2) $\text{Fe}_3\text{O}_4\text{-C}\equiv\text{CH}$, (3) $\text{Fe}_3\text{O}_4\text{-N}_3$, (4) $\text{Fe}_3\text{O}_4\text{@C}_{16}$, (5) $\text{Fe}_3\text{O}_4\text{@PEG}$ and (6) $\text{Fe}_3\text{O}_4\text{@RhB}$. (b) FTIR spectra of (1) $\text{Fe}_3\text{O}_4\text{-COOH}$, (2) $\text{Fe}_3\text{O}_4\text{-N}_3$, (3) $\text{Fe}_3\text{O}_4\text{-C}\equiv\text{CH}$, (4) $\text{Fe}_3\text{O}_4\text{@PEG}$ and (5) $\text{Fe}_3\text{O}_4\text{@C}_{16}$. Photos of $\text{Fe}_3\text{O}_4\text{@PEG}$ in water without (c) and with (d) magnetic field. Photos of $\text{Fe}_3\text{O}_4\text{@C}_{16}$ in *n*-hexane without (e) and with (f) magnetic field. (g) Emission (solid line) and excitation (dashed line) fluorescence spectra of (1) alkyne-modified rhodamine B (*ca.* 0.02 mg mL^{-1} THF solution) and (2) $\text{Fe}_3\text{O}_4\text{@RhB}$ (0.5 mg mL^{-1} THF solution). The inset in (g) shows the photo of $\text{Fe}_3\text{O}_4\text{@RhB}$ in THF under UV light.

$\text{Fe}_3\text{O}_4\text{-C}\equiv\text{CH}$ had 2.39 and 2.06% more weight loss than $\text{Fe}_3\text{O}_4\text{-COOH}$ at $500\text{ }^\circ\text{C}$, 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 $\text{Fe}_3\text{O}_4\text{-N}_3$ (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 $\text{Fe}_3\text{O}_4\text{-N}_3$ in Fig. 2(a), the average diameter of $\text{Fe}_3\text{O}_4\text{-N}_3$ 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 $\text{Fe}_3\text{O}_4\text{-N}_3$, we performed various click reactions to modify its surface with alkyne-terminated poly(ethylene glycol) (PEG-Alk), propargyl alcohol-esterified palmitic acid ($\text{C}_{16}\text{-Alk}$), and alkyne-functionalized rhodamine B (RhB-Alk), affording hydrophilic, hydrophobic and fluorescent magnetic

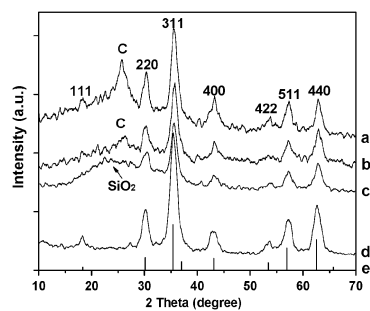


Fig. 3 X-Ray powder diffraction patterns for (a) $\text{MWNT-pAlk}@Fe_3O_4$, (b) $\text{MWNT-pAz}@Fe_3O_4$, (c) $\text{SiO}_2@Fe_3O_4$, (d) $\text{Fe}_3\text{O}_4\text{-N}_3$ and (e) standard XRD peaks for magnetite (JCPDS card, file No. 19-0629).

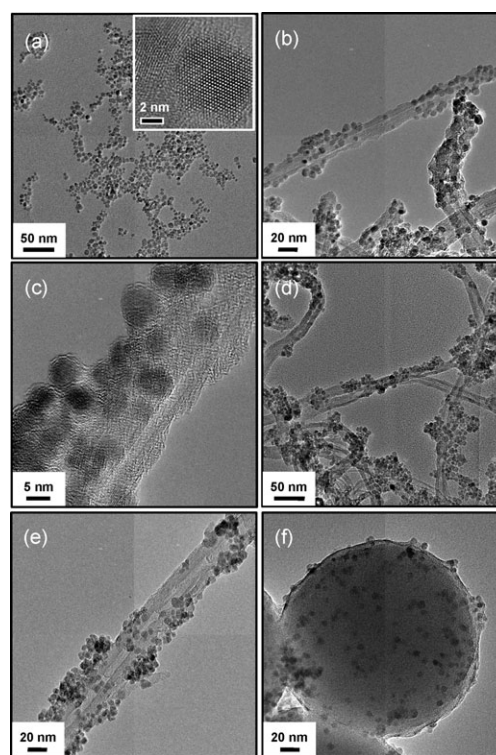
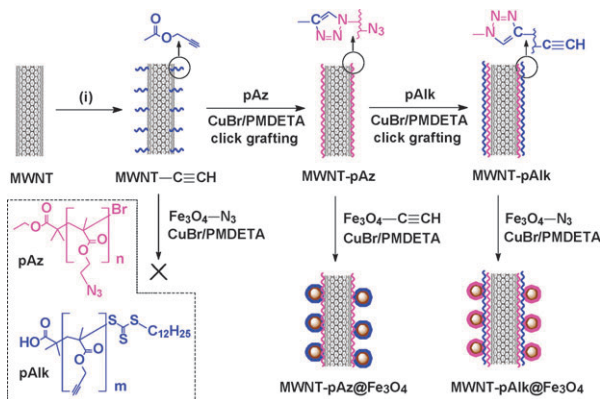


Fig. 2 TEM images of (a) $\text{Fe}_3\text{O}_4\text{-N}_3$, (b, c) $\text{MWNT-pAlk}@Fe_3O_4$, (d, e) $\text{MWNT-pAz}@Fe_3O_4$ and (f) $\text{SiO}_2@Fe_3O_4$.

nanoparticles, respectively (Scheme 1). As seen in Fig. 1(c)–(f), $\text{Fe}_3\text{O}_4\text{@PEG}$ and $\text{Fe}_3\text{O}_4\text{@C}_{16}$ dissolved well in water and *n*-hexane, respectively, and they could be separated quickly by applying an external magnetic field. The weight losses of $\text{Fe}_3\text{O}_4\text{@PEG}$, $\text{Fe}_3\text{O}_4\text{@C}_{16}$ and $\text{Fe}_3\text{O}_4\text{@RhB}$ increased significantly compared with that of $\text{Fe}_3\text{O}_4\text{-N}_3$, 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 $\text{Fe}_3\text{O}_4\text{@C}_{16}$, and a distinct band appeared at 1104 cm^{-1} in the FTIR spectrum of $\text{Fe}_3\text{O}_4\text{@PEG}$, 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; $\text{Fe}_3\text{O}_4\text{@RhB}$ showed a similar fluorescence pattern and the maximum emission and excitation wavelengths did not change.

We initially attempted to prepare nanohybrids directly from $\text{MWNT-C}\equiv\text{CH}$ and $\text{Fe}_3\text{O}_4\text{-N}_3$. 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 $\text{MWNT-C}\equiv\text{CH}$ with a polymer containing an abundant level of azide groups (affording MWNT-pAz),



Scheme 2 The synthesis procedures of 'clicked' magnetic nanohybrids. *Reagents and conditions:* (i) (1) $\text{H}_2\text{SO}_4/\text{HNO}_3$, 90–133 °C, 100 min; (2) SOCl_2 , 60 °C, 24 h; (3) propargyl alcohol, triethylamine, CHCl_3 , r.t., 24 h.

and subsequently with polymer containing an abundant level of alkyne groups (affording MWNT-pAlk). We hoped that the coated 'soft' polymer layer could not only proliferate surface reactive groups and increase touchable area, but also decrease the solid hindrance and collision energy when two particles touch each other. Interestingly, $\text{Fe}_3\text{O}_4\text{-C}\equiv\text{CH}$ and $\text{Fe}_3\text{O}_4\text{-N}_3$ could successfully 'click' onto the polymer-coated nanotubes to give magnetic nanohybrids of MWNT-pAz@ Fe_3O_4 and MWNT-pAlk@ Fe_3O_4 , respectively (Scheme 2). As seen in the TEM images (Fig. 2(b)–(e)), both MWNT-pAz and MWNT-pAlk were evenly decorated with magnetic nanoparticles. The crystalline structures of the two samples were confirmed by XRD measurements (Fig. 3(a) and (b)). These nanohybrids exhibited superparamagnetic behavior at room temperature with no coercivity or remanence, and the saturation magnetization of nanohybrids were reduced compared with that of pure MNPs, as expected (Fig. 4).¹² 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

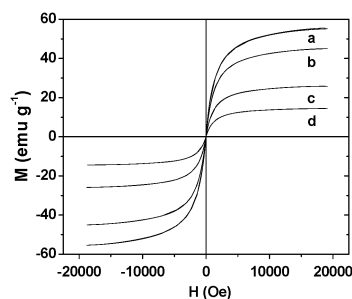


Fig. 4 The curves of magnetic hysteresis loop at 300 K of (a) $\text{Fe}_3\text{O}_4\text{-COOH}$, (b) $\text{Fe}_3\text{O}_4\text{-N}_3$, (c) $\text{SiO}_2@\text{Fe}_3\text{O}_4$ and (d) MWNT-pAz@ Fe_3O_4 .

'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 $\text{Fe}_3\text{O}_4\text{-C}\equiv\text{CH}$ as confirmed by TEM (Fig. S3, ESI†), while alkyne polymer-grafted SiO_2 spheres can react with $\text{Fe}_3\text{O}_4\text{-N}_3$ efficiently to produce uniformly anchored $\text{SiO}_2@\text{Fe}_3\text{O}_4$ 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

- S. Iijima, *Nature*, 1991, **354**, 56–58.
- S. C. Tsang, V. Caps, I. Paraskevas, D. Chadwick and D. Thompsett, *Angew. Chem., Int. Ed.*, 2004, **43**, 5645–5649.
- M. A. Correa-Duarte, M. Grzelczak, V. Salgueirino-Maceira, M. Giersig, L. M. Liz-Marzan, M. Farle, K. Sieradzki and R. Diaz, *J. Phys. Chem. B*, 2005, **109**, 19060–19063.
- S. J. Son, J. Reichel, B. He, M. Schuchman and S. B. Lee, *J. Am. Chem. Soc.*, 2005, **127**, 7316–7317.
- (a) V. Georgakilas, V. Tzitzios, D. Gournis and D. Petridis, *Chem. Mater.*, 2005, **17**, 1613–1617; (b) J. Q. Wan, W. Cai, J. T. Feng, X. X. Meng and E. Z. Liu, *J. Mater. Chem.*, 2007, **17**, 1188–1192; (c) L. R. Kong, X. F. Lu and W. J. Zhang, *J. Solid State Chem.*, 2008, **181**, 628–636.
- (a) H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2001, **40**, 2004–2021; (b) H. Binder and R. Sachsenhofer, *Macromol. Rapid Commun.*, 2007, **28**, 15–54.
- J. A. Opsteen, R. P. Brinkhuis, R. L. M. Teeuwen, D. Lowik and J. C. M. van Hest, *Chem. Commun.*, 2007, 3136–3138.
- L. Polito, D. Monti, E. Caneva, E. Delnevo, G. Russo and D. Prosperi, *Chem. Commun.*, 2008, 621–623.
- G. H. Lv, W. P. Mai, R. Jin and L. X. Gao, *Synlett*, 2008, 1418–1422.
- (a) Y. Zhou, S. X. Wang, K. Zhang and X. Y. Jiang, *Angew. Chem., Int. Ed.*, 2008, **47**, 7454–7456; (b) R. Voggu, P. Suguna, S. Chandrasekaran and C. N. R. Rao, *Chem. Phys. Lett.*, 2007, **443**, 118–121; (c) M. Fischler, A. Sologubenko, J. Mayer, G. Clever, G. Burley, J. Gierlich, T. Carell and U. Simon, *Chem. Commun.*, 2008, 169–171.
- J. P. Ge, Y. X. Hu, M. Biasini, C. L. Dong, J. H. Guo, W. P. Beyermann and Y. D. Yin, *Chem.–Eur. J.*, 2007, **13**, 7153–7161.
- W. W. Li, C. Gao, H. F. Qian, J. C. Ren and D. Y. Yan, *J. Mater. Chem.*, 2006, **16**, 1852–1859.