Supplementary Information

Modification of Graphene Oxide by a Facile Coprecipitation Method and Click Chemistry for Drug Carrier

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Ⅰ Preparation and characterization of PDMAEMA-N_3

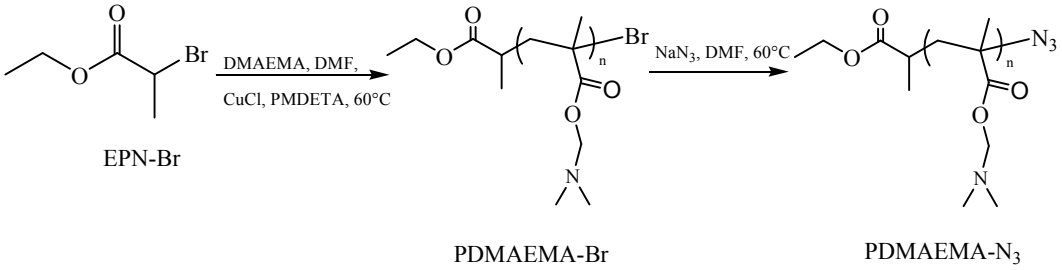

Figure S1. Schematic illustration for the synthesis of PDMAEMA-N_3

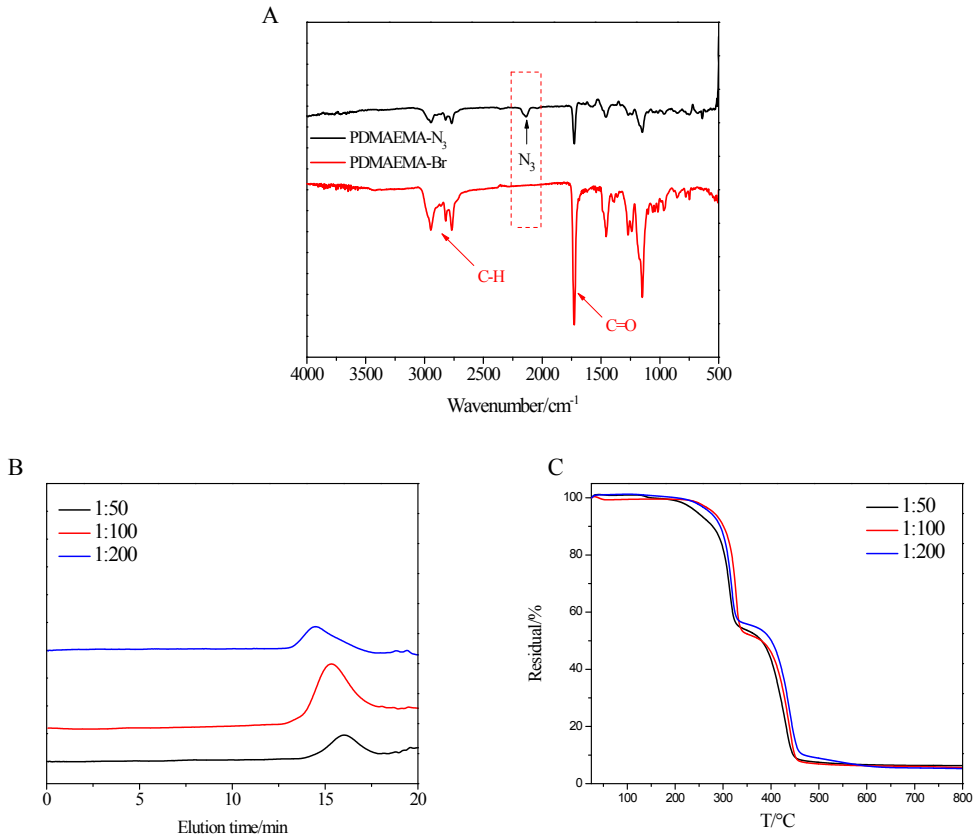

Figure S2. (A) FTIR spectra of PDMAEMA-Br and PDMAEMA-N_3, (B) GPC curves of as-prepared PDMAEMA-N_3, (C) TGA curves of as-prepared PDMAEMA-N_3 at a heating rate of 10 °C·min^{-1}

Table S1. Number average molecular weight and PDI of different PDMAEMA-N_3 by GPC measurements

Name	Molar ratio of initiator to monomer	$M_{n,(GPC)}$	PDI
$PDMAEMA_{50}$-N_3	1:50	5710	1.38
$PDMAEMA_{100}$-N_3	1:100	8040	1.42

$PDMAEMA_{200}$-N_3	1:200	17130	1.29

Ⅱ Preparation and characterization of Fe_3O_4/Alkynyl-GO

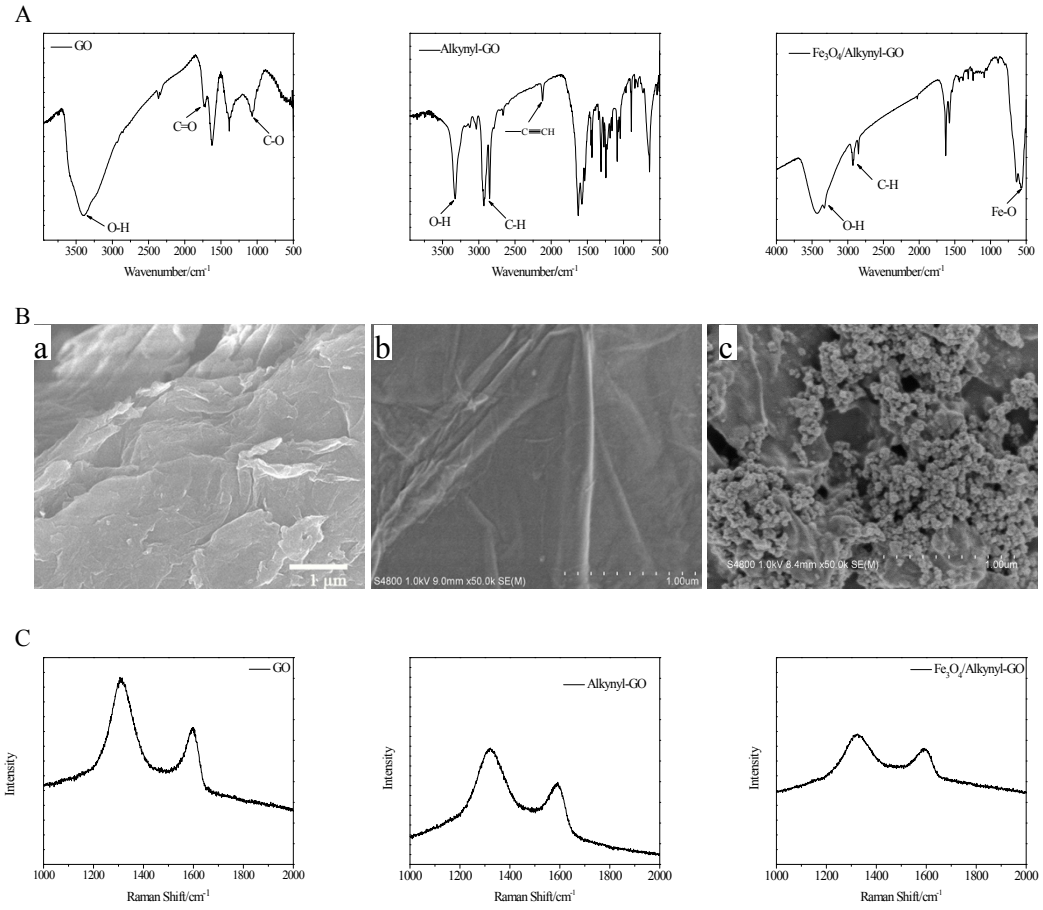

Figure S3. (A) FTIR spectra of graphene oxide (GO) and Alkynyl-GO and Fe_3O_4/Alkynyl-GO, (B) SEM images of (a)GO, (b) Alkynyl-GO and (c) Fe_3O_4/Alkynyl-GO, and (C) Raman spectra of GO, Alkynyl-GO and Fe_3O_4/Alkynyl-GO at a laser excitation wavelength of 532 nm

Figure S3 A displays that characteristic absorption peaks of modified GO that represent alkynyl group and stretching vibration of Fe-O bond are shown at 2100 cm^{-1} (alkynyl group) and 582 cm^{-1} (Fe-O) in FTIR spectra of Alkynyl-GO and Fe_3O_4/Alkynyl-GO.

Figure S3 B presents SEM images of GO and modified GO. The image of GO reveals a crumpled and rippled structure as a result of deformation upon the exfoliation and restacking process. The skeleton of GO sheets and anchored Fe_3O_4 nanoparticles are clearly shown in SEM images. A large quantity of Fe_3O_4 nanoparticles are deposited on surface of the GO sheets and distributed randomly without aggregation. Without the presence of GO sheets, bare Fe_3O_4 nanoparticles can easily aggregate to large particles or clusters (Figure S5).

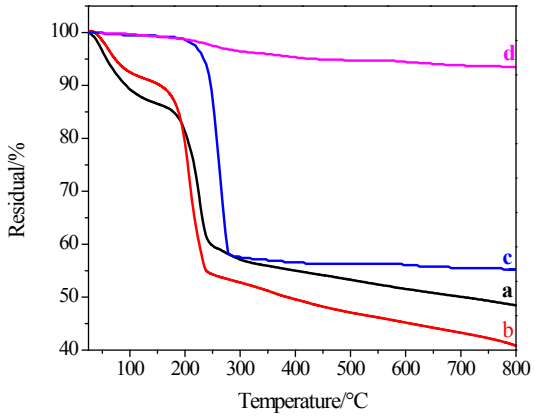

Figure S4. TGA curves of (a) GO, (b) Alkynyl-GO, (c) Fe_3O_4/Alkynyl-GO and (d) Fe_3O_4 at a heating rate of 10 °C·min^{-1} in nitrogen

Table S2. Weight ratio and grafting density determined by TGA

Sample	Weight ratio(%)		Alkynyl groups per 10000 carbons[(a)]
	GO basal plane	Alkynyl	
GO	100	0	0
Alkynyl-GO	93.4	6.2	144
	Alkynyl-GO	Fe_3O_4	
Fe_3O_4/Alkynyl-GO	86.1	13.9	144

[(a)] Calculated from Eq. S1

$$D_A = 10^4 M_C W_A / M_A W_C \qquad \text{Eq. S1}^1$$

Where D_A is the grafting density (alkynyl groups per 10000 carbons), M_C is the relative molar mass of carbon (M_C = 12 g/mol), M_A is the molecular weight of alkynyl groups (M_A =55 g/mol), W_C and W_A are the weight fractions of the GO backbone and the alkynyl groups. W_C and W_A can be obtained from the TGA curves.

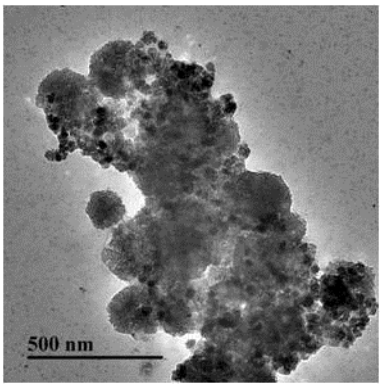

Figure S5. TEM image of bare Fe_3O_4 nanoparticles

Ⅲ Preparation and characterization of Fe_3O_4/PDMAEMA-GO

Table S3. Preparation of various Fe_3O_4/PDMAEMA-GO composites by click reaction

Sample \ Ingredients		PDMAEMA		Fe_3O_4/Alkynyl-GO
		$M_{n,(GPC)}$	Feed	Feed
S_1	Fe_3O_4/PDMAEMA-GO	5710	0.51 g	0.1 g
S_2	Fe_3O_4/PDMAEMA-GO	5710	0.425 g	0.1 g
S_3	Fe_3O_4/PDMAEMA-GO	5710	0.34 g	0.1 g
S_4	Fe_3O_4/PDMAEMA-GO	8040	0.48 g	0.1 g
S_5	Fe_3O_4/PDMAEMA-GO	17130	1.02 g	0.1 g

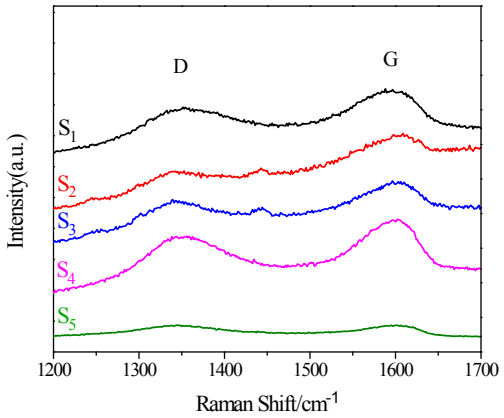

Figure S6. Raman spectra of Fe_3O_4/PDMAEMA-GO at a laser excitation wavelength of 532 nm

Table S4. The I_D/I_G ratio and crystallite size from Raman spectra

Sample	I_D/I_G ratio	La[(a)]
GO	1.39	13.83
Alkynyl-GO	1.29	14.9
Fe_3O_4/Alkynyl-GO	1.12	17.16
S_1	0.87	22.1
S_2	0.84	22.88
S_3	0.77	24.96
S_4	0.86	22.34
S_5	1.00	18.84

[(a)] Calculated from Eq. S2

$$L_a(nm) = (2.4\times10^{-10})\lambda_{laser}{}^4(\frac{I_D}{I_G})^{-1} \quad \text{Eq. S2}^2$$

As shown in Figure S3 C, Figure S6 and Table S4, the variation of I_D/I_G ratio suggests the change of the average size of the sp^2 domains. Decreased I_D/I_G ratio of products indicates the increase in size of the in-plane sp^2 domains[3], possibly due to the partial reduction of GO basal plane caused by the reductant sodium *L*-ascorbate in reaction process[4]. Crystallite size in Raman spectra is used to confirm the formation of covalent links between the GO sheets and grafted polymer chains[2]. The faint increment of the crystallite sizes (La) after click chemistry attributes to the formation of covalent linkages between the alkynyl groups of GO sheets and the azide groups of polymer.

Table S5. Photographs of samples with different grafting densities at selected time

Sample	S_1		S_2		S_3	
Time	1st day	30th day	1st day	30th day	1st day	30th day
Photograph						

Table S6. Photographs of samples with different grafted chain length at selected time

Sample	S_3		S_4		S_5	
Time	1st day	30th day	1st day	30th day	1st day	30th day
Photograph						

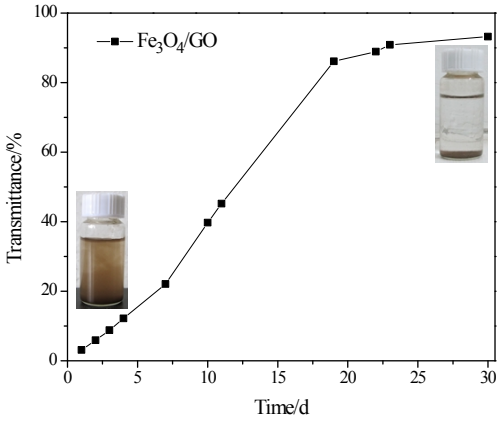

Figure S7. Stability test of Fe_3O_4/GO in PBS (pH=7.2) and photographs on 1st and 30th day

Table S7. Zeta potential (ζ) of Fe_3O_4/PDMAEMA-GO

Sample	ζ(mV)
S_1	34.14
S_2	18.10
S_3	13.62
S_4	31.4
S_5	49.25

References

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