SUPPLEMENTARY of PAPER

Phosphorescence and excitation-wavelength dependent fluorescence kinetics of large-scale graphene oxide nanosheets

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1. Reagents

Graphite powder (95%, 325 mesh), concentrated sulfuric acid (H_2SO_4), potassium permanganate (KMnO_4), sulfoxide chloride (SOCl_2), dimethyl formamide (DMF), tetrahydrofuran (THF), triphenylamine, copper nitrate, glacial acetic acid were all purchased from Sinopharm chemical reagent Co.,Ltd (China).

2. Synthesis of graphene oxide and GO-CONH-TPA

2.1. Synthesis of graphene oxide (GO) nanosheets

GO nanosheets were synthesized from natural graphite using a modified Hummer’s method as Liu reported previously. The resulting mixture was washed, using 5% HCl solution and DI water for dozens of times. Finally, GO solid material was obtained after freeze-drying.

2.2. Synthesis of 4-nitrotriphenylamine

5g (20 mmol) triphenylamine, 3.23g (13mmol) copper nitrate and 50ml glacial acetic acid were mixed in a flask and left still at room temperature for 12 h. After that, a large amount of water was poured into the mixture. Then a suction filter was employed to get the yellow solid (solidnamely4-nitrotriphenylamine) from the solution. Finally, the pure 4-nitrotriphenylamine was acquired after ethanol recrystallization.

2.3. Synthesis of 4-aminotriphenylamine

5g (17 mmol) 4-nitrotriphenylamine 0.68g homemade FeO(OH)/C catalyst, 60ml ethyl alcohol and 6.9 ml hydrazine hydrate were slowly dropped. The mixture was refluxed at 90 °C for 5 h, before filtered using suction filtration. Then the filtrate was poured into plenty amount of DI water, white precipitate was got after a segregation process,
this precipitate was recrystallized using methanol and dried after the vacuum
desiccation, then the final white solid produce was named 4-aminotriphenylamine.

2.4. Synthesis of GO-CONH-TPA

Graphene oxide (30 mg) was dispersed in DMF (5 ml) and was refluxed in SOCl₂ (30 ml)
at 80°C for 24 h. The supernatant was removed after centrifugation. The residual solid
was washed twice using anhydrous tetrahydrofuran (THF) to remove the excess SOCl₂.
GO-COCl reacted with TPA-NH₂ in the presence of DMF (6 ml) at 130 °C for 72 h.
After the solution was cooled to room temperature, the mixture was dispersed in
overdose of DI and the reaction was ended. The excess TPA-NH₂, graphene oxide (GO)
and DMF was removed by purification and segregation: including filtration on a Nylon
membrane (0.22 mm), centrifugation at 8000 rpm for 5 min and removing the solvent
by reduced pressure distillation.

Fig. S1. TEM image of the GO and GO-CONH-TPA nanosheets.

The Fig.S1 depicts the typical TEM image of GO and GO-CONH-TPA nanosheets. GO
has good surface topography and structure integrity. In this work, GO covalently functionalized with Triphenylamine named GO-CONH-TPA was synthesized, part of the surface topography was destroyed, but the structure integrity of GO still retains. Intramolecular aggregation causes the dark shadow area in the TEM image.

Fig. S2 (a) The correlation between the excitation wavelength and the emission wavelength. (a) GO-CONH-TPA in EtOH solution and (b) in PMMA film matrix.

Fig. S3 The correlation relationship between dark-noise signal and detection time.

4. Reference