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Supporting information

Fabrication of a Novel Nanocomposite Ag/Graphene@SiO_2-$NaLuF_4$: Yb, Gd, Er for Large Enhancing Upconversion Luminescence

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Experimental Section:

Synthesis of small sized GO nanosheets:

In a typical experiment, graphite powder (4 g) was added to a mixture of concentrated H_2SO_4 (24 mL), $K_2S_2O_8$ (6 g), and P_2O_5 (6 g). After stirring for 5 h at 80°C, the resultant dark blue mixture was slowly cooled to room temperature. Then the cooled mixture was diluted to 500 mL with water and filtered through a 0.22 μm membrane. The filtrate of preoxidized graphite powder was dried at 60 °C overnight. Then 3g of the preoxidized graphite powderwas added to 150 mL of cold H_2SO_4 (0°C) and followed by adding 25 g of $KMnO_4$ gradually with stirring in an ice bath. After stirring for 15 min, the mixture was diverted to an oil bath with further stirring for 8 h at 40°C, and then water (750 mL) and H_2O_2 (30 wt %, 30 mL) were gradually added to terminate the reaction. After standing still overnight, the obtained precipitation was washed by diluted hydrochloride acid (1:10 in volume) and water. After centrifuging at 6000 rpm for 10 min, the obtained precipitations were dispersed in water and dialyzed for three days. After being sonicated for 2−3 h at 500 W in an ice bath (lower than 15°C), the obtained brown colloid was normal random distributed sized GO nanosheets (namely GO-1 in the following). For the second oxidization, 2 g of the precipitation (obtained after 6000 rpm centrifugation) of GO-1 was added to 150 mL of cold H_2SO_4 at 0°C, and 25 g of $KMnO_4$ was added gradually with stirring in an ice bath. After stirring for 15min, the mixture was diverted to an oil bath with further stirring 8 h at 40°C, and then 750 mL of distilled water and 30 mL of H_2O_2 (30 wt%) were added gradually to terminate the reaction. After standing overnight, the obtained precipitation was washed with diluted hydrochloride acid (1:10 in volume) and water, and the precipitations were dispersed and dialyzed in water for three days and sonicated for 2−3 h at 500 W in an ice bath (<15°C), the

obtained yellow colloid was the GO nanosheets (namely GO-2 in the following). To obtain the small sized GO nanosheets, further oxidization was employed as follows: 1.5 g of the precipitation (obtained after 8000 rpm centrifugation) of GO-2 was added to 150 mL of cold H_2SO_4 (0°C), and 25 g of $KMnO_4$ was added gradually with stirring in an ice bath. After stirring for 15 min, the mixture was diverted to an oil bath with further stirring for 8 h at 40°C, and then water (250mL) and H_2O_2 (30 wt %, 30 mL) was added gradually to terminate the reaction. After standing still overnight, the obtained precipitation was washed with diluted hydrochloride acid (1:10 in volume) and water. Then the solution was dialyzed for three days and sonicated for 2−3 h at 500 W in an ice bath (<15°C). Finally, the obtained light yellow colloid was the small sized GO nanosheets.

Synthesis of Ag/GN composite:

Briefly, 2.5 mg of small sized GO was dispersed in 10 mL of water by sonication for 2 h, forming stable GN oxide colloid. Then 400 μL of 0.01 mol/L $AgNO_3$ was added to the solution with magnetic stirring for 10 min, then 20 mL of ethylene glycol was added with stirring for another 30min. Subsequently, the mixture was put in an oil bath and heated at 100°C for 6h with magnetic stirring. The formed Ag/GN composite was separated from the ethylene glycol solution by centrifugation and then washed with water for three times. The resulting products were vacuum dried at 60°C overnight.

Synthesis of Ag/GN@SiO_2 nanocomposite:

Ag/GN@SiO_2 nanocomposite was prepared by a modified stöber method.[42] Typically, 5ml 20mg/ml of the Ag/GN aqueous solution was added into 20 mL of ethanol solution, followed by

addition of 1 mL of $NH_3 \cdot H_2O$. After stirring at room temperature for 10 min, 40μL of TEOS was added into the mixture. After that, the mixture was sonicated for more than 9 h and kept overnight at room temperature. Then, 30μL of APTES was added to the above solution, followed by the addition of 0.6 mL of $NH_3 \cdot H_2O$. The resulting mixture was stirred for more than 12 h. Finally, the product was centrifuged, washed with ethanol and water three times, and dried at room temperature, respectively.

Synthesis of $NaLuF_4$：Yb，Gd，Er Upconversion Nanocrystals:

$NaLuF_4$：Yb，Gd，Er upconversion nanocrystals were prepared by a typically thermal decomposition method.[4] In detail, 2 mmol CF_3COONa and 1mmol $RE(CF_3COO)_3$ (54%mol Lu, 24%mol Yb, 20%mol Gd, 2%mol Er) were added to a three-necked flask containing 20 mL of oleylamine (OM). The resulting mixture was heated to 115 °C with constant stirring for 30 min under vacuum to remove water and oxygen. Then the solution was heated to 335 °C and the temperature was maintained for 3.5 hour under N_2 atmosphere. When the reaction was completed, an excess amount of ethanol was poured into the solution at 80°C. The resultant mixture was centrifugally separated, and the products were collected, washed several times with ethanol, and dried in vacuum overnight.

The above prepared UCNs in OM are hydrophobic. In this study, a ligand exchange method was used to make these UCNs becoming hydrophilic.[43] The procedure is as follow: 20mg of $NaLuF_4$：Yb，Gd，Er UCNCs dissolved in 6 mL of ethanol and 2mmol of sodium citrate dissolved in 10 mL water were mixed and stirred for 12 h. The resultant mixture was centrifugally separated, and the products of citrated-coated $NaLuF_4$: Yb, Gd, Er UCNCs were

collected and washed several times with ethanol.

Measurement of upconversion absolute quantum yield:

Fluorescence spectroscopy (Edinburgh FLS-920) was modified by using Ocean Optics UV-VIS-NIR CCD (QE65000) as a detector for detection the excitation light from continuous-wave 980nm laser and upconversion emission. An integrating sphere was also used to measure the efficiency data. The response of the detection systems in photon flux was determined using a calibrated VIS-NIR lamp (Ocean Optics LS-1-CAL). The quantum yield of upconversion luminescence of the nanocrystals was calculated using the following equation.

$$QY = \frac{\text{Photons emitted}}{\text{Photons absorbed}} = \frac{L_{sample}}{E_{blank} - E_{sample}}$$