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Ligand replacement induced chemiluminescence for selective detection of an organophosphorus pesticide using bifunctional Au–Fe_3O_4 dumbbell-like nanoparticles†

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A facile ligand replacement induced chemiluminescence method is developed for selective detection of the organophosphorus pesticide parathion-methyl based on the use of bifunctional Au–Fe_3O_4 dumbbell-like nanoparticles to overcome the interference from coexisting substances in a real sample.

As a facile, sensitive, and cost-effective analytical technique, chemiluminescence (CL) has widely been investigated for chemical analyses, biological assays, clinical diagnoses, and environmental detection due to its absence of an unwanted excitation light source, low noise signals, and wide linear dynamic range.[1–3] However, classical CL systems have very low efficiency for converting chemical energy into light, it is very urgent to improve their CL efficiency in order to give an intense emission intensity for accurate quantitative detection.[4] With the increasing availability of nanomaterials, various nanocatalysts such as noble metal nanoparticles, metal oxide nanostructures and carbon-based nanomaterials have been introduced into CL systems for the enhancement of the CL signals by several to tens of times.[5–7] Although, these conventional single-component catalysts could be used for enhancement of the CL efficiency, the operating procedures are also tedious and time-consuming for in-field real sample detection, thus hampering the further application of nanomaterials in CL systems. In comparison, the discovery of bifunctional Au–Fe_3O_4 dumbbell-like nanoparticles (DBNPs), which contain both a magnetic (Fe_3O_4) and a CL catalyst active (Au) unit, has driven a growing interest in low-temperature catalysis and magnetic separation,[8] not only to keep the high catalytic activity for enhancement of the CL efficiency but also to take advantage of superparamagnetic properties to overcome interference from environmental pollutants in real sample detection.[9]

Organophosphorus compounds are the most widely used pesticides in the agricultural field due to their high effectiveness for insect and disease eradication, but they also cause widespread residues in food products and contamination of the environment.[10–12] Most of the organophosphorus compounds cannot be detected by the traditional luminol–H_2O_2 CL system because there are no redox groups in these molecules, such as –NH_2, –OH and –SH groups.[5a,13,14] In this paper, we report a surface ligand replacement induced CL switch-on mechanism for detection of the organophosphorus pesticide parathion-methyl (PM) with high sensitivity and selectivity, based on bifunctional Au–Fe_3O_4 DBNPs. The Au–Fe_3O_4 DBNPs have been prepared by thermal decomposition of an iron–oleate complex in the presence of 12 nm Au NPs. The DBNPs significantly enhanced the CL signals by catalyzing the decomposition of H_2O_2 into superoxide anions and hydroxyl radicals at their surface. As illustrated in Fig. 1, the CL signals could be quenched after modification of the surface of the Au–Fe_3O_4 DBNPs with methionine. However, the quenching effect can be effectively inhibited by replacement of the methionine through a specific binding reaction of the hydrolyzate of parathion-methyl on the surface of Au–Fe_3O_4 DBNPs and a magnetic separation–redispersion process. On the basis of this new finding, a CL switch-on chemosensor was facilely established and would have

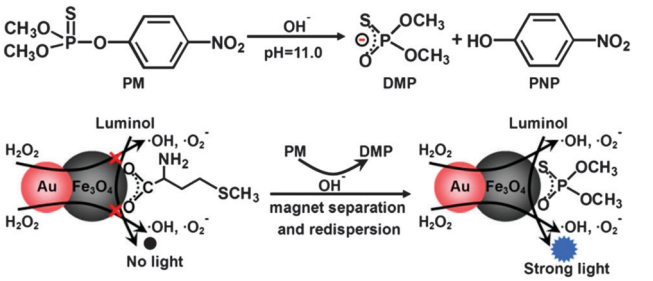

Fig. 1 Illustration of the CL switch-on mechanism for selective detection of PM molecules. The CL of the luminol–H_2O_2–DBNPs system is first quenched by the coordination of methionine to the surface of the Au–Fe_3O_4 DBNPs and subsequently switched on by the replacement of the methionine with dimethylphosphorothioate (DMP) and combining with a magnetic separation–redispersion process in a basic system.

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two unique advantages in CL detection: (1) the selectivity is determined by the coordination capacity of the organophosphorus pesticide molecules on the surface of Au–Fe_3O_4 DBNPs, therefore, the novel sensing concept can be used to sensitively detect nonredox targets without the need for costly antibodies or enzymes, or any additional techniques; (2) the superparamagnetic properties of the Au–Fe_3O_4 DBNPs provide a simple magnetic separation approach to attain interference-free measurements for real sample detection.

Water-soluble Au–Fe_3O_4 DBNPs were synthesized using Wu's method with minor modifications for achieving the high CL catalytic activity. Fig. 2A presents representative transmission electron microscopy (TEM) images of the as-prepared Au–Fe_3O_4 DBNPs consisting of 12 nm Au NPs and 18 nm Fe_3O_4 NPs. The Au NPs appear black and the Fe_3O_4 NPs are a light colour in the image because Au NPs have a higher electron density and allow fewer electrons to transmit.[15] The crystallinity of the Au–Fe_3O_4 DBNPs was characterized by XRD (Fig. 2B). The position and relative intensity of all the diffraction peaks match well with standard inverse spinel structured Fe_3O_4 (Joint Committee on Powder Diffraction Standards (JCPDS) card no. 03-0863) and face-centered cubic (fcc) Au (JCPDS card no. 01-1174), and the results indicate that the products have good crystallinity. Like Fe_3O_4 NPs, the hysteresis loop measurements show that Au–Fe_3O_4 DBNPs with a saturation moment reaching 26 emu g^{-1} are superparamagnetic at room temperature (Fig. 2C). Thus, the Au–Fe_3O_4 DBNPs could be quickly separated from a suspension under an external magnetic field, providing a rapid method to overcome the interference of coexisting substances in a real sample. When adding the Au–Fe_3O_4 DBNPs into the luminol–H_2O_2 solution, the CL signal intensity could be amplified by at least 5 times (see Fig. S2, ESI†). Meanwhile, the maximum emission wavelength of the CL spectrum was ~425 nm, which clearly indicated that the luminophor was still the excited state 3-aminophthalate anions. Therefore, the use of Au–Fe_3O_4 DBNPs did not lead to the generation of a new luminophor for this CL system. The enhanced CL signals were thus ascribed to the catalysis by the Au–Fe_3O_4 DBNPs. In order to investigate the effect of Au–Fe_3O_4 DBNPs on the improvement of the CL intensity, a series of experiments was performed (Fig. 2D). Under the same conditions, the catalytic CL activity of Fe_3O_4 and Au nanoparticles was 35.4% and 41.9% of that of the Au–Fe_3O_4 DBNPs, respectively. Similarly, when a mixture of Fe_3O_4 and Au NPs with the same content as the Au–Fe_3O_4 DBNPs was used as the catalyst, its catalytic activity was only 48.9% of that for the DBNPs nanostructure. From the above analyses, the CL-enhancing phenomena of the luminol–H_2O_2 system by Au–Fe_3O_4 DBNPs might result from the special electron structure in the composites. It has been reported that coupling Pt NPs with Fe_3O_4 NPs in dumbbell-like Pt–Fe_3O_4 NPs increased the catalytic activity of Pt NPs towards the redox reaction and the catalytic enhancement was proposed to arise from partial electron transfer from Fe_3O_4 to Pt at the nanoscale interface, improving O_2 adsorption and activation on the Pt surface adjacent to Fe_3O_4.[16–18] In the present system, Au–Fe_3O_4 DBNPs changed the electronic structure at the interface which may accelerate electron transfer, facilitate H_2O_2 adsorption and catalyze the decomposition of H_2O_2 into oxygen-related radicals such as the superoxide radical anion $^{\bullet}O_2^-$ and the hydroxyl radical $^{\bullet}OH$. The resultant oxygen-related radicals further oxidize luminol in basic media to produce a strong CL emission (see Fig. S6, ESI†). Thus, these characteristics will provide Au–Fe_3O_4 DBNPs with versatility and power as a CL enhancer, sensing probe, and separation tool.[9b]

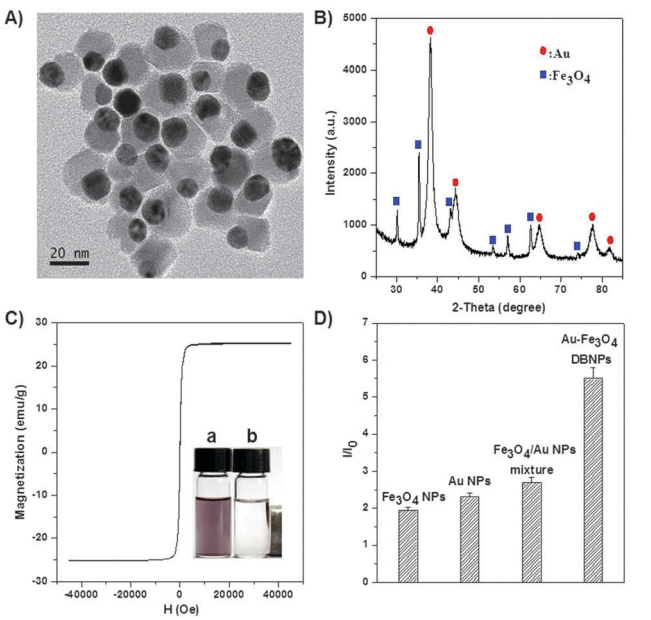

Fig. 2 (A) Typical TEM image of Au–Fe_3O_4 DBNPs in water. (B) XRD of the Au–Fe_3O_4 DBNPs. (C) Room-temperature magnetization curve for the Au–Fe_3O_4 DBNPs. (Inset: photos of Au–Fe_3O_4 DBNPs in water (a) and with a magnet (b).) (D) The enhancement effectiveness of various nanoparticles on luminol–H_2O_2 CL system.

When the Au–Fe_3O_4 DBNPs were mixed with methionine solution, the methionine was thus bound onto the surface of the Au–Fe_3O_4 DBNPs through the COO^- bond coordination effect. Meanwhile, the CL of the luminol–H_2O_2–DBNPs was quenched due to the reducing groups $-NH_2$ and $-SCH_3$ of methionine.[19] Fig. 3A shows the CL quenching behaviour due to the modification of methionine onto the surface of Au–Fe_3O_4 DBNPs. The CL intensity decreased gradually upon the addition of methionine, and the CL was nearly completely quenched at a concentration of 50 μM. The quenching process follows a nonlinear behaviour and shows a saturation concentration of methionine. Methionine is well-known as a radical scavenger and consequently quenches the CL signals from the luminol–H_2O_2–DBNPs system due to the loss of oxygen-related radicals. On the other hand, methionine may cooperate with Au–Fe_3O_4 DBNPs to reduce the active surface area, interrupting the formation of luminol radicals and hydroxyl radicals taking place on the surface of nanoparticles. The TEM images of the new DBNPs, the maximum emission CL wavelength and the shape of the emission spectra are still retained, which implies that the methionine ligand cannot alter the size and size distribution of the DBNPs but can only reduce the CL intensity. Therefore, a methionine–Au–Fe_3O_4 dumbbell-like nanoparticle (me–Au–Fe_3O_4 DBNP) probe can be constructed by the modification

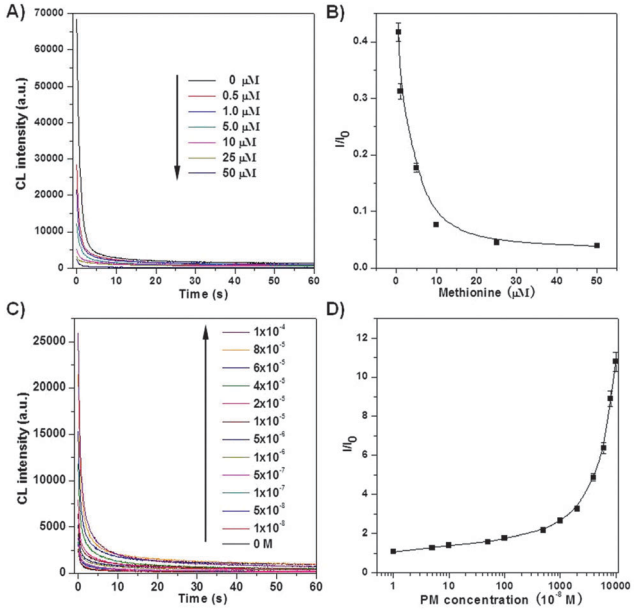

Fig. 3 (A) CL quenching of a luminol–H_2O_2–DBNPs system upon the addition of methionine. (B) The relationship between I/I_0 and methionine concentration (where I_0 and I are the CL intensity in the absence and presence of methionine, respectively). (C) CL enhancement of the me–Au–Fe_3O_4 DBNPs probe in a luminol–H_2O_2 system with the addition of PM. (D) The relationship between I/I_0 and PM concentration (where I_0 and I are the CL intensity before and after methionine on the surface of the Au–Fe_3O_4 DBNPs was replaced with a DMP ligand, respectively).

of methionine onto the surface of DBNPs. This probe shows an extremely weak CL intensity compared with that of the bare Au–Fe_3O_4 DBNPs at the same concentration level in the luminol–H_2O_2 CL system. The weak CL of the probe stays fairly stable over a relatively long time. Thus, the CL of the probe will switch on if the surface methionine ligands are replaced by an appropriate analyte, which is expected for ultrasensitive CL detection.

In a strongly basic system, parathion-methyl (PM) molecules are rapidly hydrolysed to dimethylphosphorothioate (DMP) and *p*-nitrophenol (PNP).[20] The DMP moiety with a P═S bond exhibits a very strong coordinative ability with many metal ions.[21] Accordingly, the methionine ligands at the surface of the DBNPs are rapidly replaced by strongly binding DMP ligands, to form a more stable complex because the P═S bond has a stronger coordinative ability to Au–Fe_3O_4 DBNPs than the COO^- bond.[22] Then, combined with the magnetic separation–redispersion process for overcoming the methionine interference effect, a significant CL enhancement can be clearly observed with an increase in PM concentration. Fig. 3C shows that about a 12-fold CL enhancement was measured when the concentration of PM reached 100 μM. Even at a concentration as low as 10 nM, CL enhancement can be clearly observed, demonstrating an ultrasensitive response to the hydrolyzate DMP of the PM pesticide. In the absence of methionine, however, the direct addition of PM to a pure Au–Fe_3O_4 DBNPs solution with basicity does not result in any CL enhancement and even causes a slight quench of the strong CL. This also reveals that the phosphorothioate analyte and its hydrolyzates do not have any direct effect on pure Au–Fe_3O_4 DBNPs and the luminol–H_2O_2 CL system. To understand the mechanism of CL switching, we studied in detail the interaction between DMP and me–Au–Fe_3O_4 DBNPs through the infrared spectrum, which further confirmed that DMP bonds to the nanocrystal surface in place of methionine. Fig. S8 (ESI†) is the infrared spectrum before and after the surface modification of Au–Fe_3O_4 DBNPs with methionine and replacement with DMP ligand. The absorption bands at 1245 and 1508 cm^{-1} in the infrared spectrum are assigned to C–N bond stretching vibration and deformation of the $-NH_2$ group of the methionine on the surface of the Au–Fe_3O_4 DBNPs, the peak at 1391 cm^{-1} is from the asymmetric deformation vibration mode of the $-CH_3$ groups.[23] After DMP replacement of the methionine on the surface of the Au–Fe_3O_4 DBNPs, the methionine molecule's characteristic absorption bands (1508 cm^{-1}) disappear. Meanwhile, two new bands (1154 and 950 cm^{-1}) appeared, which were attributed to the S═P and P–O–Fe stretching vibrations of the organophosphorus pesticide.[24]

To better understand the mechanism of the CL sensor, the CL switch-on selectivity for various pesticides was determined using four typical pesticide structures. As shown in Fig. 4, only PM, with a phosphorothioate moiety, was able to switch-on the CL of the probe and resulted in a remarkable CL enhancement. Although the other organophosphorus pesticides, methamidophos (MP), profenofos (PF) and ethoprophos (EP), can also be hydrolyzed into organophosphorus moieties with a P═O bond in basic media, these moieties are very weak coordinative ligands that are not able to replace methionine on the surface of the Au–Fe_3O_4 DBNPs. Therefore, the addition of these three pesticides did not cause any change in the CL intensity from that of the blank sample. This indicates that the P═S double bond, but not the P–S single bond, COO^- or P═O double bond, can replace methionine to form a more stable complex at the surface of the Au–Fe_3O_4 DBNPs. Therefore, the me–Au–Fe_3O_4 DBNP probe shows very high specificity for the detection of parathion-methyl pesticides by a CL turn on mechanism through surface ligand replacement.

The utility of the chemosensor is largely dependent upon the direct detection of ultratrace PM residues in a real sample. However, for detection of analytes in a real sample, general CL techniques either show the sample as undetectable or need complicated sample pretreatments, such as solid phase extraction (SPE) and high performance liquid chromatography (HPLC). In this work, we chose

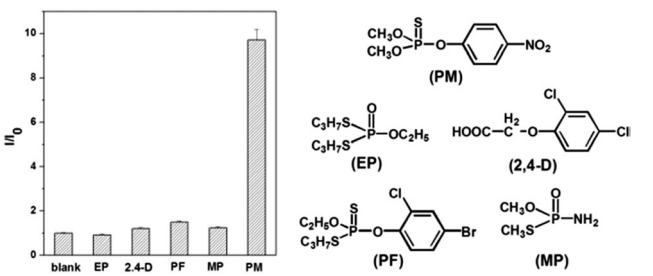

Fig. 4 The CL switch-on selectivity for various OP pesticides (100 μM): parathion-methyl (PM), ethoprophos (EP), 2,4-dichlorophenoxyacetic acid (2,4-D), profenofos (PF), and methamidophos (MP).

green tea as the test sample. As shown in Fig. S9 (ESI†) the me–Au–Fe_3O_4 DBNPs were first dispersed in real samples spiked with PM molecules at three different concentrations (100, 200, 400 nM). Through the ligand replacement reaction, most of the hydrolyzate of the PM molecules will bind on the me–Au–Fe_3O_4 DBNPs in the basic system. When a small magnet was put near the vial, the DBNPs with DMP were drawn to the wall of the vial. After discarding the remaining sample solutions, the reddish brown aggregates were redispersed in a certain amount of water for measuring of the CL signals. The above separation–redispersion procedure was repeated two times, and noninterference detection was achieved. The recovery for an added known amount of PM in the green tea samples was in the range of 95–104% (Fig. S9C, ESI†), which indicated the utility of the methionine modification of Au–Fe_3O_4 DBNP CL nanosensors for the detection of pesticide residues in complex samples.

In summary, this work has proposed a sample selective CL switch-on chemosensor by the modification of the radical scavenger methionine on the surface of Au–Fe_3O_4 DBNPs. The sensing mechanism is based on our new findings that the replacement of methionine ligands by the hydrolyzate of organophosphorothioate pesticides and a magnetic separation–redispersion process for inhibiting the scavenging of surface radicals, leads to the switch-on of the CL. The CL switch-on chemosensor was used to selectively detect the nonredox organophosphorothioate pesticide molecule parathion-methyl and exhibited high anti-interference in real samples after a simple magnetic separation. Moreover, the construction of this CL chemosensor does not involve the use of antibodies or enzymes or require complicated surface modification and thus is very simple and inexpensive. The novel and facile strategy reported here should open a new window of interest in the application of nanomaterials for the assay of organophosphorothioate pesticides in agricultural products and the development of CL chemosensors for the detection of a wide range of organic and biological molecules.

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