Supporting information

Simple Method for O-GlcNAc Sensitive Detection Based on Graphene Quantum Dots

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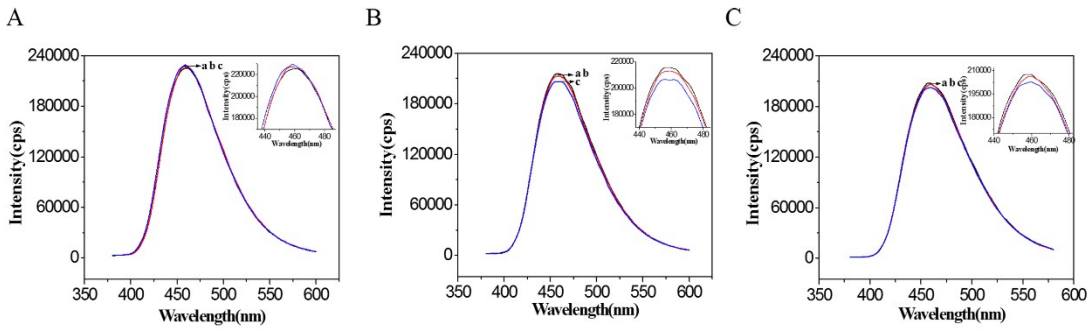

Figure. S1. The fluorescence spectra of GQDs/WGA (a) with different amount of WGA 1 pg/mL (A), 5 (B) and 25 pg/mL (C) at different solution: 1 pg/mL peptide without O-GlcNAc modification (b) and O-GlcNAcylated peptide(c). Insets are the amplification of the fluorescence spectra.

If the concentration of WGA was 0.1 pg/mL, there no fluorescence signal change was observed (b in Fig. 3). Considering at this concentration may be little WGA adsorbed on the surface of GQDs, which may affect the identification of WGA to O-GlcNAc. The other three GQDs/WGA systems (1 pg/mL, 5 pg/mL and 25pg/mL WGA) were used for the sensitive detection of O-GlcNAc. When 1 pg/mL O-GlcNAcylated peptide was added into 1 pg/mL WGA modified GQDs system (Fig. S1A curve c), the fluorescence signal of GQDs/WGA system was not affected. The result demonstrated that less WGA adsorbed on the surface of GQDs, which make little O-GlcNAc adsorbed on the surface of GQDs, which result negligible fluorescence quenching, thus this system is insensitive to the O-GlcNAc detection. While after the same concentration of O-GlcNAcylated peptide was added into 5 or 25 pg/mL WGA modified GQDs system (curve c of Fig. S1B and Fig. S1C), a big fluorescence signal change can be observed. That was due to more O-GlcNAcylated peptide can immobilized onto the surface of GQDs by interact with WGA, and then the fluorescence signal of GQDs was decreased by the O-GlcNAcylated peptide shield effect, as shown in scheme 1. The fluorescence quenching of 5 pg/mL WGA system was more obviously than 25 pg/mL WGA system. Although 25 pg/mL WGA system provide more WGA to recognize O-GlcNAc, due to the effect of stereo-hindrance, not all immobilized WGA could react to O-GlcNAc. On the other hand,

more WGA immobilized onto the surface of GQDs made the fluorescence intensity of GQDs be shield more serious. In this case, even if O-GlcNAc adsorbed on the surface of GQDs, it cannot induce the change of fluorescence signal. This means that though more WGA immobilized on the surface of GQDs in 25 pg/mL WGA system, but this system in insensitive for the O-GlcNAc detection, thus the 5 pg/mL WGA modified GQDs was used to detect O-GlcNAc. In order to verify the fluorescence quenching belonged to the recognition between O-GlcNAc and WGA. The same sequence peptide without O-GlcNAc was used as the control experiment (Fig. S1B curve b), the fluorescence signal of GQDs/WGA have not been affected when 1 pg/mL peptide was added, which further proved the decrease of fluorescence signal should be attributed to recognition between WGA and O-GlcNAc.

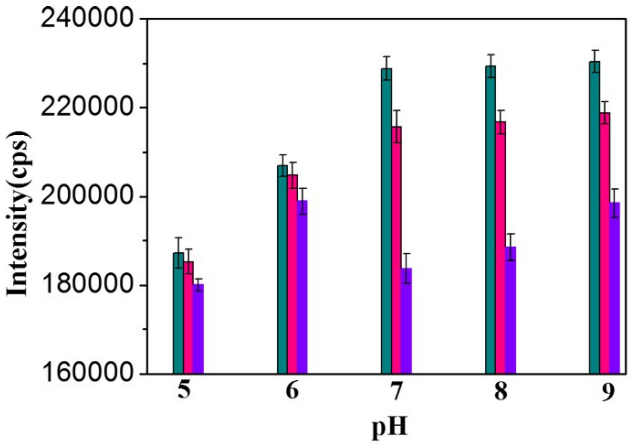

Figure. S2. Fluorescence response of GQDs (green) and GQDs/WGA in the absence (red) and presence of 200pg/mL O-GlcNAcylated peptide (violet) at different pH values

The effect of pH toward this system was studied and the results were shown in Fig. S2. It is could be found that the fluorescence signal of WGA/GQDs system is pH dependent, fluorescence signal of GQDs is relatively low in acidic solutions. Though the addition of O-GlcNAcylate molecular can also result in the decrease of the fluorescence signal, but the change is small, which demonstrated that O-GlcNAcylate molecular detection is not suitable in acid solution. The fluorescence signal of GQDs reaches a maximum and keeps stable over pH 7.0 [1]. As point out above, the pK_a of

carboxylic acid groups is about 4.7, this mean in the acid solution less carboxylic acid groups can dissociate intocarboxylates, thus the negative charge on the surface of GQDs become less, which induced less WGA absorbed on the surface of GQDs by electrostatic interaction. This result in the system is insensitive to the detection of O-GlcNAc. The fluorescence intensity of the GQDs were decreased after WGA added into different pH value GQDs solution, then the fluorescence signal further decreased after the O-GlcNAcylated peptide added into the solution respectively. This phenomenon indicated that the system at different pH value can also be used to detect O-GlcNAc, but in pH 7.4 medium, the signal changes is the biggest after the addition of O-GlcNAcylate molecular. Considering the pH of 7.4 is also close to the physiological situations, thus pH 7.4 medium was selected for the O-GlcNAc detection.

Reference

1. Y. Q. Dong, G. L. Li, N. N. Zhou, R. X. Wang, Y. W. Chi and G. N. Chen, *Anal Chem*, 2012, **84**, 8378-8382.