Electronic Supplementary Material (ESI) for New Journal of Chemistry.

(Supporting Information)

Highly sensitive detection of human papillomavirus E6 protein by DNA-protected silver nanoclusters and the intrinsic mechanism

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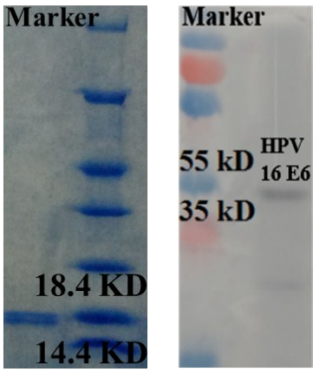

Fig. S1 SDS-PAGE (left) of HPV E6 and Western-blot (right) of GST-E6 after purification.

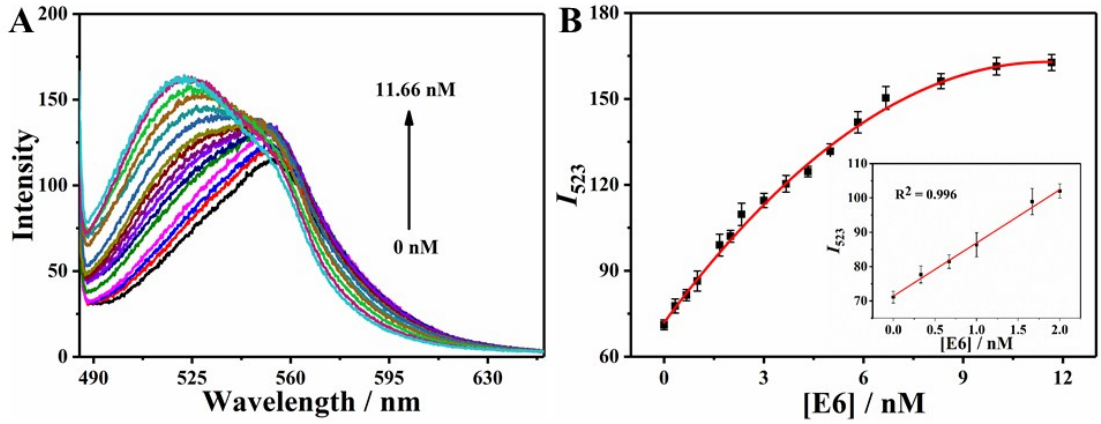

Fig. S2 (A) Fluorescence spectra of AgNCs-dsDNA (0.33 μM) in the absence and presence of E6 at the concentration from 0.33 to 11.6 nM; (B) The plot of corresponding intensity at 523 nm of (A) *versus* the concentration of E6.

In the low region of concentration (≤ 2.0 nM), the additions of E6 into solution lead a linear emission increase of AgNCs-dsDNA but almost no band-shift; while in the high concentrational region (2.0 - 11.66 nM) the increase rate of AgNCs-dsDNA emission

is slowed down but the band-shift is larger ($\Delta\lambda$ = -22 nm). Furthermore, a formula of y = 25.8166x + 71.4144 is achieved by linear fitting on the plot for low concentration region (≤ 1.3 nM; insert in Fig. S2B) and a limit of detection (LOD) of 0.886 nM is achieved through LOD = 3*σ/r.

To verify the potential utility of this assay in clinical diagnosis, we detect E6 protein in fetal bovine serum by using AgNCs-dsDNA as a fluorescence probe. AgNCs-dsDNA is added firstly to 1% bovine serum (diluted with PBS, pH = 7.4) to instead of the previous buffer, then different amount of E6 protein is gradually titrated to the solution. The fluorescence spectra of AgNCs-dsDNA in responding to each concentration of E6 protein are shown in Fig. S3A, where a gradual enhancement and blue-shift are illustrated at the same time. The corresponding plot of intensity in Fig. S3B reveals a good linear response of AgNCs-dsDNA emission to E6 in the low concentration region (1.0 - 15 nM), indicating that this method has great potential in future for the clinical application.

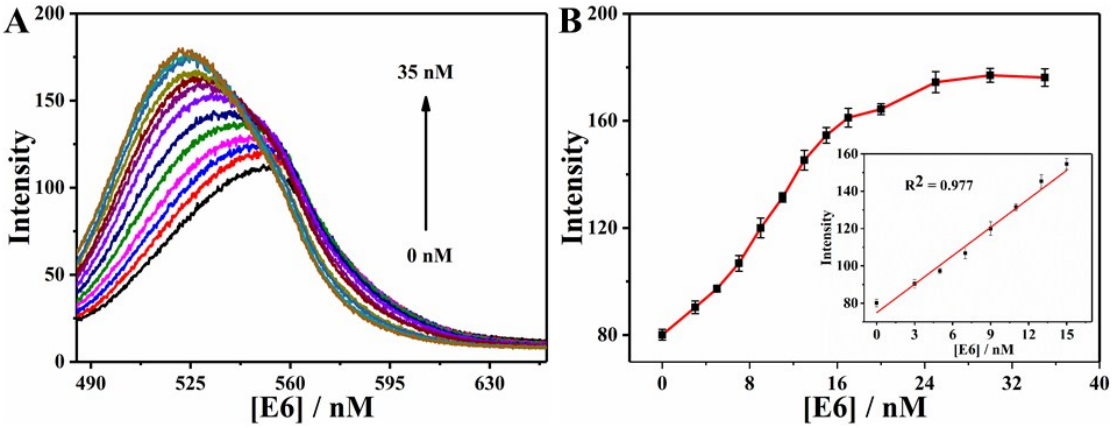

Fig. S3 (A) Fluorescence spectra of AgNCs-dsDNA (1.0 μM) in the absence and presence of E6 protein from 3.0 to 35 nM in the diluted fetal calf serum (1% in PBS, pH = 7.4); (B) The plot of corresponding intensity at 523 nm of (A) *versus* the concentration of E6.

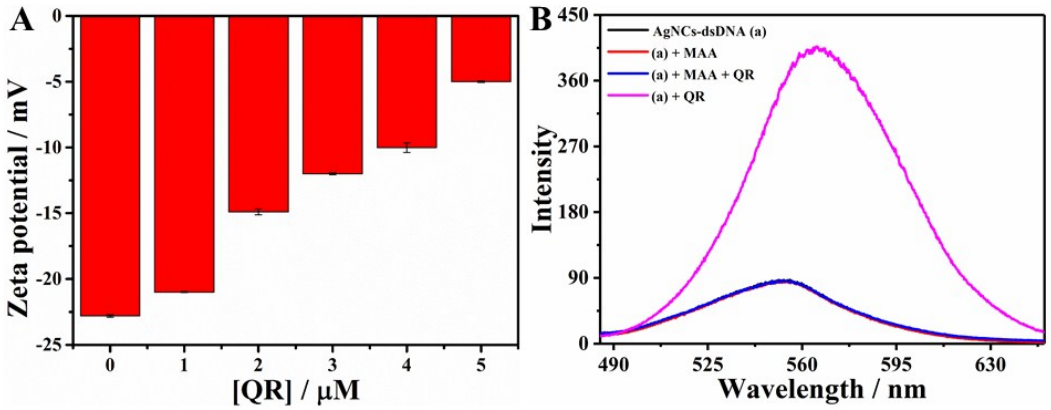

Fig. S4 (A) Zeta potential changes of AgNCs-dsDNA (1.0 μM) in titrating with different amount of QR peptide; (B) fluorescence spectrum of AgNCs-dsDNA (1 μM), and that of it in presence of 20 equiv. MAA, 20 equiv. MAA and 2 μM QR, and 2 μM QR in PBS (pH =7.4), respectively.

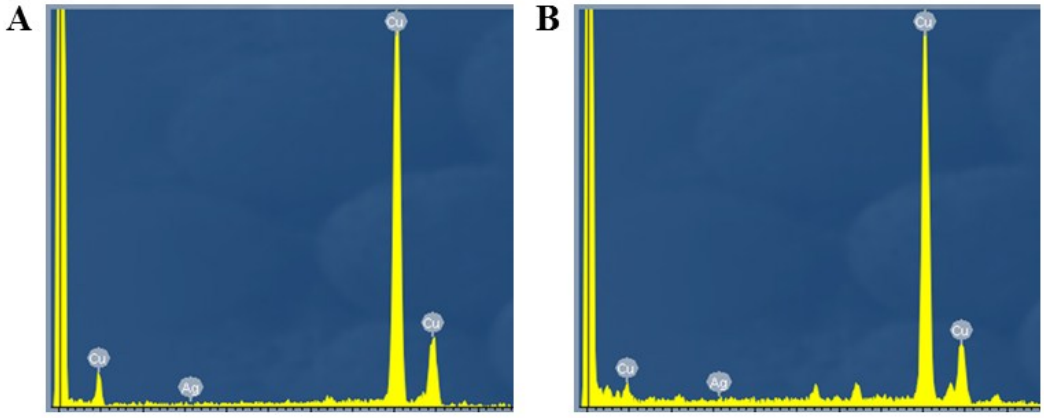

Fig. S5 EDX spectrum of the representative particle (A) in Fig 3(C) for QR-AgNCs-dsDNA assembly; and (B) in Fig 3(D) for GC-AgNCs-dsDNA assembly, respectively.

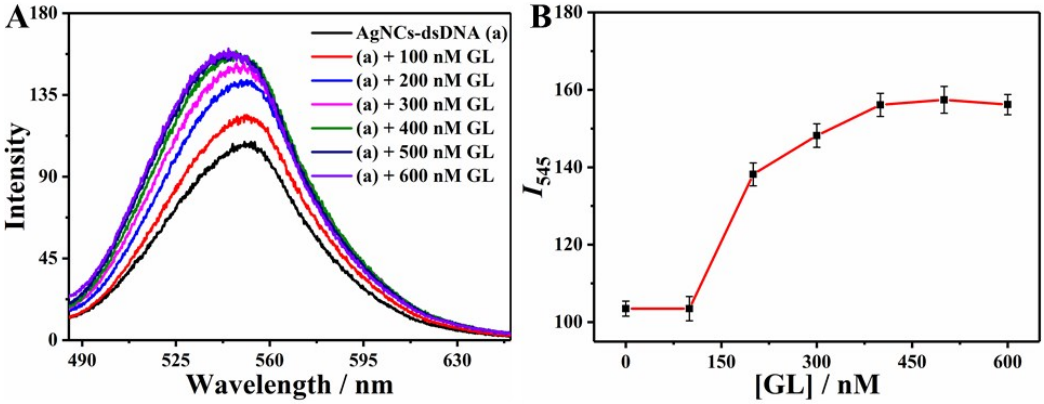

Fig. S6 (A) Fluorescence spectra of AgNCs-dsDNA (1.0 μM) in the absence and presence of different amount of GL peptide (100-600 nM); (B) The plot of the fluorescence intensity at 545 nm in changing with the concentration of GL peptide.

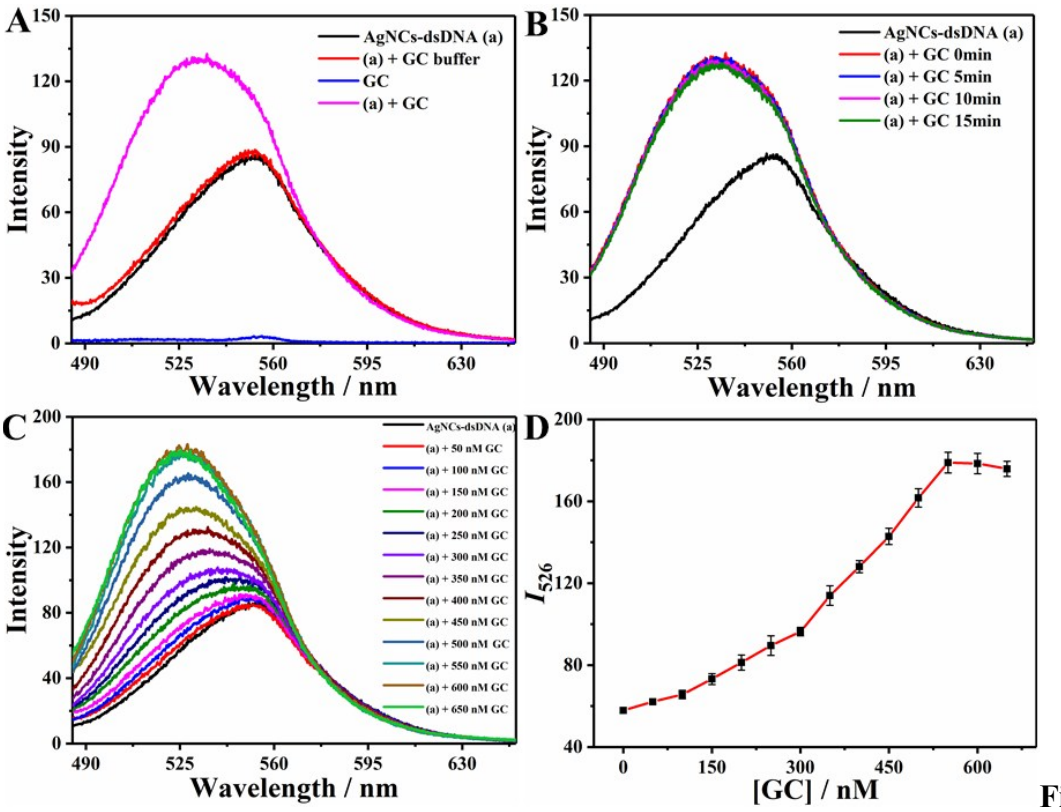

Fig. S7 (A) Fluorescence spectrum of AgNCs-dsDNA (1.0 μM), and that of it in the presence of 400 nM GC, as well as that for GC alone in PBS (pH = 7.4), respectively; (B) Time-dependent fluorescence spectra of AgNCs-dsDNA (1.0 μM) in the presence 400 nM GC; (C) Fluorescence spectra of AgNCs-dsDNA (1.0 μM) in the absence and presence of different amount of GC peptide (50-650 nM); (D) The plot of the fluorescence intensity at 526 nm of (C) in changing with the concentration of GC peptide.

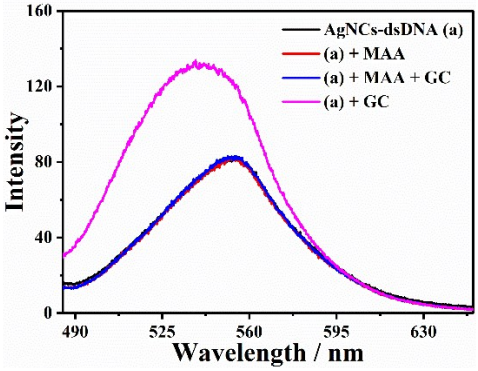

Fig. S8 Fluorescence spectrum of AgNCs-dsDNA, and that of it in the presence of 20 equiv. MAA, 20 equiv. MAA and 400 nM GC, and 400 nM GC in PBS (pH = 7.4), respectively.

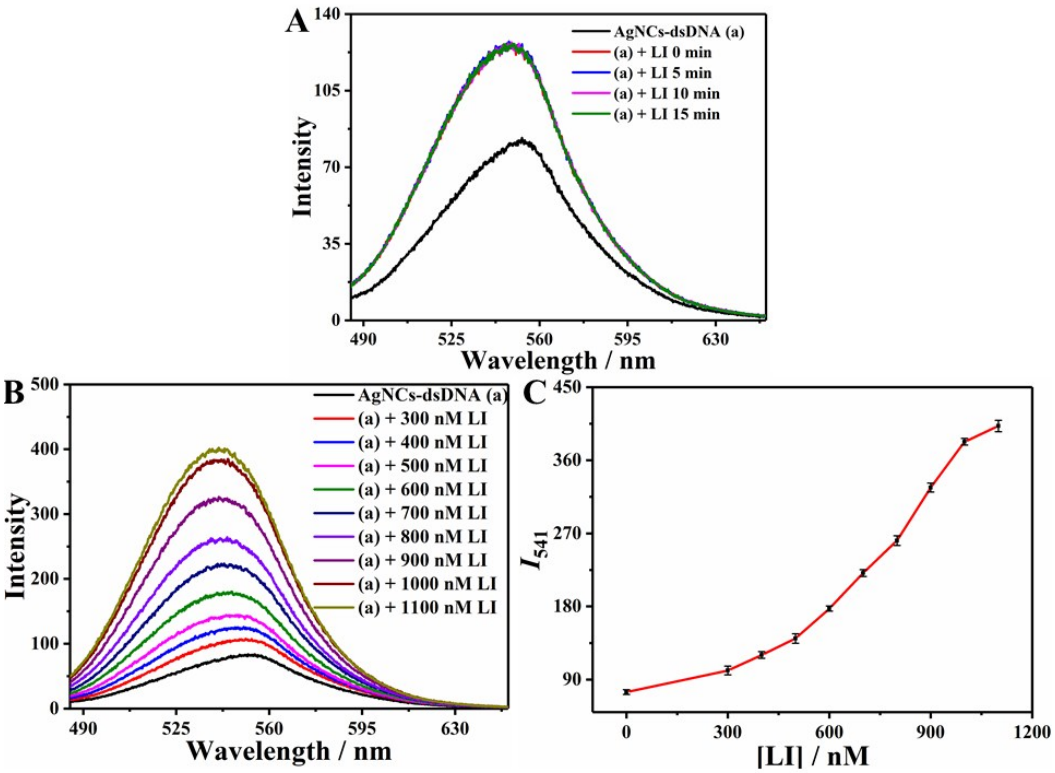

Fig. S9 (A) Time-dependent fluorescence spectra of AgNCs-dsDNA (1.0 μM) in the presence of 400 nM LI; (B) Fluorescence spectra of AgNCs-dsDNA in the absence and presence of different amount of LI peptide (300-1100 nM); (C) The plot of the fluorescence intensity at 541 nm of (B) in changing with the concentration of LI peptide.