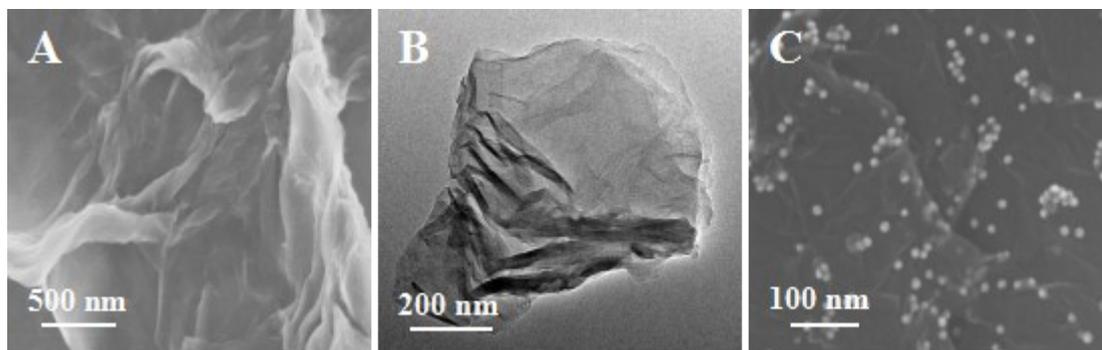
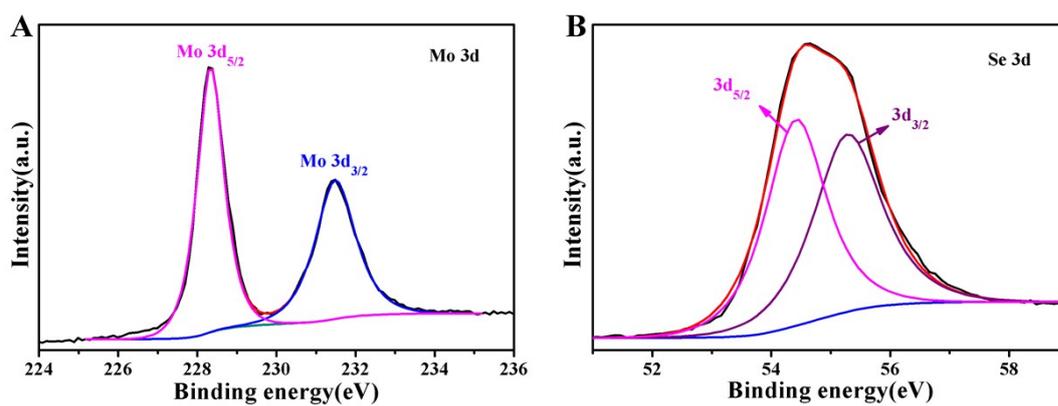


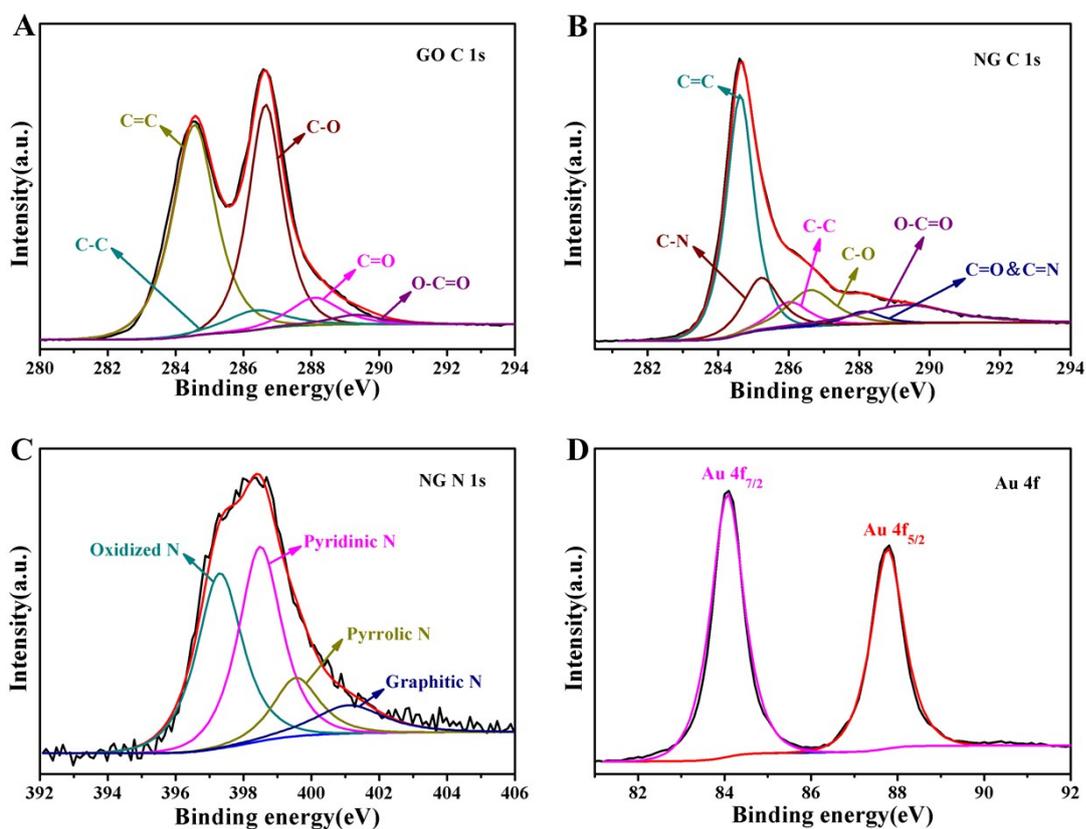
## Supporting Information



**Figure S1.** (A) SEM, (B) TEM images of the original GO. (C) SEM image of NG-AuNPs.



**Figure S2.** (A) Mo 3d and (B) Se 3d spectra of MoSe<sub>2</sub>.



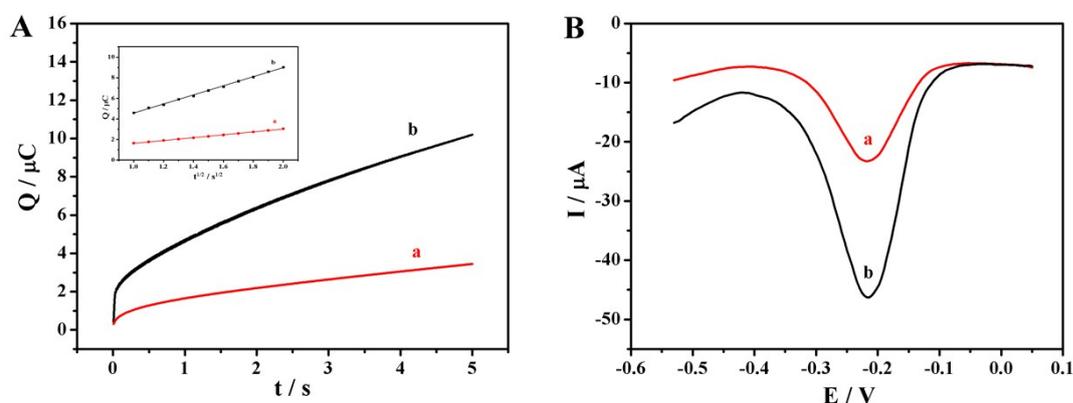
**Figure S3.** (A) C 1s spectra of GO, (B) C 1s and (C) N 1s spectra of NG, (D) Au 4f spectra of NG-AuNPs.

In order to calculate the effective surface areas, the chronocoulometry (CC) was performed in 0.1 mM  $[\text{Fe}(\text{CN})_6]^{3-}$  and 1.0 M KCl solution.<sup>1</sup> According to the equation as follows:

$$Q = 2nFAcD^{1/2}t^{1/2}/\pi^{1/2} + Q_{dl} + Q_{ads} \quad (1)$$

where  $Q$  (C),  $n$ ,  $F$  ( $\text{C mol}^{-1}$ ),  $A$  ( $\text{cm}^2$ ),  $c$  ( $\text{mol cm}^{-3}$ ),  $D$  ( $\text{cm}^2 \text{s}^{-1}$ ),  $t$  (s),  $Q_{dl}$  (C) and  $Q_{ads}$  (C) are charge, charge transfer number, Faraday constant, effective surface areas, substrate concentration, diffusion coefficient, electrolysis times, double layer charge and adsorption charge, respectively. According to Fig. S4A and B shown that the A calculation values of bare GCE and AuNPs/MoSe<sub>2</sub>/GCE were 0.015 cm<sup>2</sup> and 0.047 cm<sup>2</sup>, respectively. It was shown that MoSe<sub>2</sub> could apparently increase the effective surface area of electrode and the active sites. Nevertheless, as displayed in Fig. S4C, after MoSe<sub>2</sub> was immobilized onto electrode surface,

the DPV response dramatically increased by 227.4% owing to the signal amplification effect of the material. It was helpful to improve the sensitivity of the sensor.



**Figure S4.** (A) Q-t curve of bare GCE (a) and AuNPs/MoSe<sub>2</sub>/GCE (b) in 0.1 mM [Fe(CN)<sub>6</sub>]<sup>3-</sup> and 1.0 M KCl solution. The inset was the Q-t<sup>1/2</sup> curve. (B) The DPV responses of hemin/assistance DNA/DNA-linked NG-AuNPs hybrids/miRNA/MCH/ capture probe/AuNPs/GCE (a) and hemin/ assistance DNA/DNA-linked NG-AuNPs hybrids /miRNA/MCH/capture probe/AuNPs/MoSe<sub>2</sub>/GCE (b), which were measured in a certain volume of 10 mM PBS buffer (pH 8.0) containing 50 mM NaCl, 10 mM MgCl<sub>2</sub>.

**Table S1.** Different methods for miRNA-21 detection.

DPV: differential pulse voltammetry; ECL: electrochemiluminescence.

Amplification strategy	Methods	LOD	References
Target-guide assembly of AuNPs	ECL	20 fM	2
Polymerase chain reaction amplification	DPV	1.0 pM	3
Gold nanoparticle loaded split-DNAzyme-probe amplification	Fluorescence	10 pM	4
Mismatched catalytic hairpin assembly	DPV	0.6 pM	5
AuNPs-decorated MoS <sub>2</sub> nanosheet amplification	DPV	0.78 fM	6

Duplex-specific nuclease signal amplification	Fluorescence	1 pM	7
Hairpin assembly target recycling amplification	DPV	0.35 fM	8
Hybrid antibody and enzymatic amplification	DPV	0.4 fM	9
NG-AuNPs hybrids and supersandwich amplification	DPV	0.17 fM	This work

**Table S2.** Detection of miRNA-21 in serum samples ( $n=3$ ).

Samples	qRT-PCR <sup>a</sup> (fM)	Proposed biosensor (fM)
1	$32.7 \pm 2.8$	$33.1 \pm 3.8$
2	$35.6 \pm 3.4$	$34.8 \pm 4.1$
3	$36.7 \pm 2.5$	$37.8 \pm 2.4$
4	$38.9 \pm 2.9$	$38.1 \pm 4.2$

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