Electronic Supplementary Material (ESI) for RSC Advances. This journal is © The Royal Society of Chemistry 2017

1	<b>Electronic Supplementary Information</b>					
2	Determination of pentachlorophenol by anodic					
3	electrochemiluminescence of Ru(bpy) <sub>3</sub> <sup>2+</sup> based on nitrogen doped					
4	graphene quantum dots as co-reactant					
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Fig. S1. (A) XPS survey spectrum of the as-prepared NGQDs; (B-D) high-resolution
survey spectra of C<sub>1s</sub>, N<sub>1s</sub> and O<sub>1s</sub> of NGQDs.

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14 XPS measurements were further carried out to inspect the chemical composition of 15 the as-synthesized NGQDs. Fig. S1A illustrates three apparent peaks at 284.6, 401.4 and 532.2 eV, corresponding to the C<sub>1s</sub>, N<sub>1s</sub> and O<sub>1s</sub>, respectively. Fig. S1B shows the 16 expanded XPS spectrum of the  $C_{1s}$  peaks at 284.3, 285, 285.7, 286.6 and 288.6 eV, 17 which are associated with C=C, C-N, C-O, C=O and O-C=O bonds, respectively.<sup>1,2</sup> 18 N<sub>1s</sub> spectrum (Fig. S1C) of NGQDs can be divided into three components located at 19 399.5, 400.3 and 401.5 eV, which are assigned to C-N-C, N-(C)<sub>3</sub> and N-H, 20 21 respectively.<sup>3</sup> The O<sub>1s</sub> core level spectrum (Fig. S1D) can be deduced at 532.2 and 533.3 eV, corresponding to C=O and C-O-C/C-OH bonds. Comprehensively, XPS 22

23 observations agree well with FT-IR results, which further demonstrate that various
24 oxygen-containing functional groups distribute on the surface of NGQDs, leading to
25 excellent solubility of NGQDs in water.





27 Fig. S2. Optimization of experimental parameters: (A) scan rate and (B) applied28 voltage.

Finally, Fig. S2A shows influence of scan rate from 25 to 500 mV s<sup>-1</sup> on I<sub>ECL</sub>. The ECL intensity increases sharply and reaches the highest value at the scan rate of 100 mV s<sup>-1</sup>, and then decreases when the scanning rate exceeding 100 mV s<sup>-1</sup>. So the optimum scan rate is chosen as 100 mV s<sup>-1</sup>. The effect of voltage applied on I<sub>ECL</sub> (Fig. S2B) suggests that the larger voltage, the higher ECL signal. However, when the high voltage exceeds 700 V, the phenomenon occurs beyond the maximum range. Finally, 700 V is ultimately applied.



Fig. S3. (A) FL and (B) UV-Vis absorption spectra of NGQDs (a), PCP (b) and their
mixture (c).

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In order to confirm that there is no interaction between NGQDs and PCP, FL and UV-Vis spectroscopy are conducted. The FL spectra (Fig. S3A) exhibit that the emission of individual NGQDs features at 392 nm (line a), and the emission wavelength of alone PCP is located at 380 nm (line b). It can be seen from line c that the emission wavelength of the mixture of NGQDs and PCP is 385 nm, from which the interaction between NGQDs and PCP is very difficult to judge. Thus, UV-Vis properties of NGQDs, PCP and their mixture were investigated.

As can be seen from Fig. S3B, NGQDs display one characteristic band at 334 nm (line a), while individual PCP (line b) exhibits two adsorption peaks at 218 and 251 nm, which are ascribed to the E-bands and B-bands, respectively.<sup>4</sup> While for their mixture system (line c), the adsorption bands are exactly the merging of their individuals, demonstrating no interaction occurs directly between NGQDs and PCP.

Sample	Added (pg mL <sup>-1</sup> )	Found (pg mL <sup>-1</sup> )	Recovery (%)	RSD (%) (n=5)
River water	0	$11.22 \pm 0.21$	—	1.92
	5	$16.66 \pm 0.49$	102.7	4.57
	10	$20.42 \pm 0.57$	96.2	5.39
	20	$30.90 \pm 0.48$	99.0	4.56
Tap water	0	Not detected	_	_
	5	5.13±0.15	102.6	1.35
	10	$9.77 \pm 0.37$	97.7	3.38
	20	$20.42 \pm 0.11$	102.1	1.04

**Table S1.** Recovery studies of PCP in tap and river water samples (n=5).

## 55 References:

- 56 1 Z. Yang, M. H. Xu, Y. Liu, F. J. He, F. G. Gao, Y. J. Su, H. Wei and Y. F. Zhang,
- 57 Nanoscale, 2014, **6**, 1890-1895.
- 58 2 Q. H. Liang, W. J. Ma, Y. Shi, Z. Li and X. M. Yang, Carbon, 2013, 60, 421-428.
- 59 3 S. Liu, J. Q. Tian, L. Wang, Y. W. Zhang, X. Y. Qin, Y. L. Luo, A. M. Asiri and
- 60 X. P. Sun, Adv. Mater., 2012, 24, 2037-2041.
- 61 4 M. Figueiredo-González, B. Cancho-Grande and J. Simal-Gándara, Food Chem.,
- 62 2013, **140**, 217-224.