Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Selective Oxidation of Veratryl Alcohol with Au and Graphene Quantum Dots Composites as Catalysts

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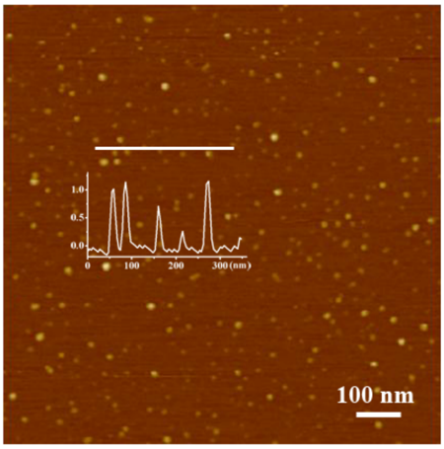

Figure S1. AFM image of grapheme quantum dots.

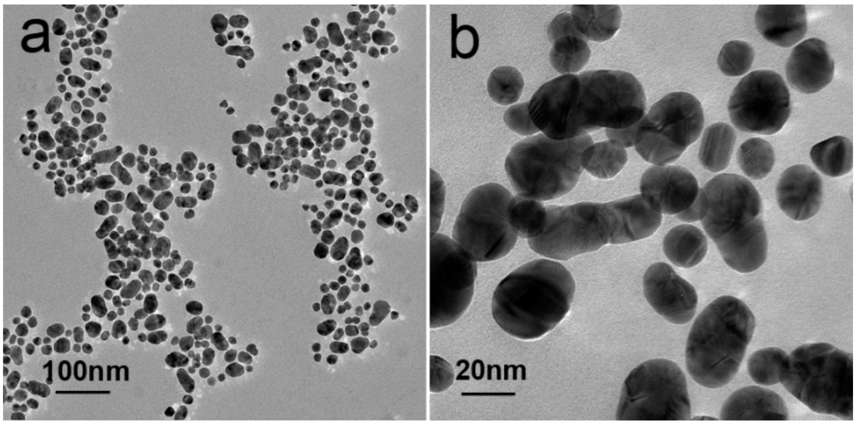

Figure S2. TEM images of Au nanoparticles.

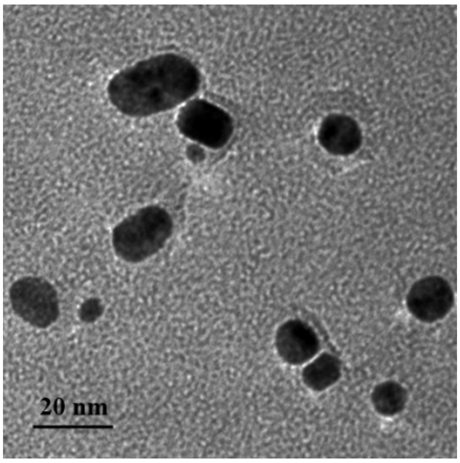

Figure S3. HRTEM image of the Au/GQDs composites.

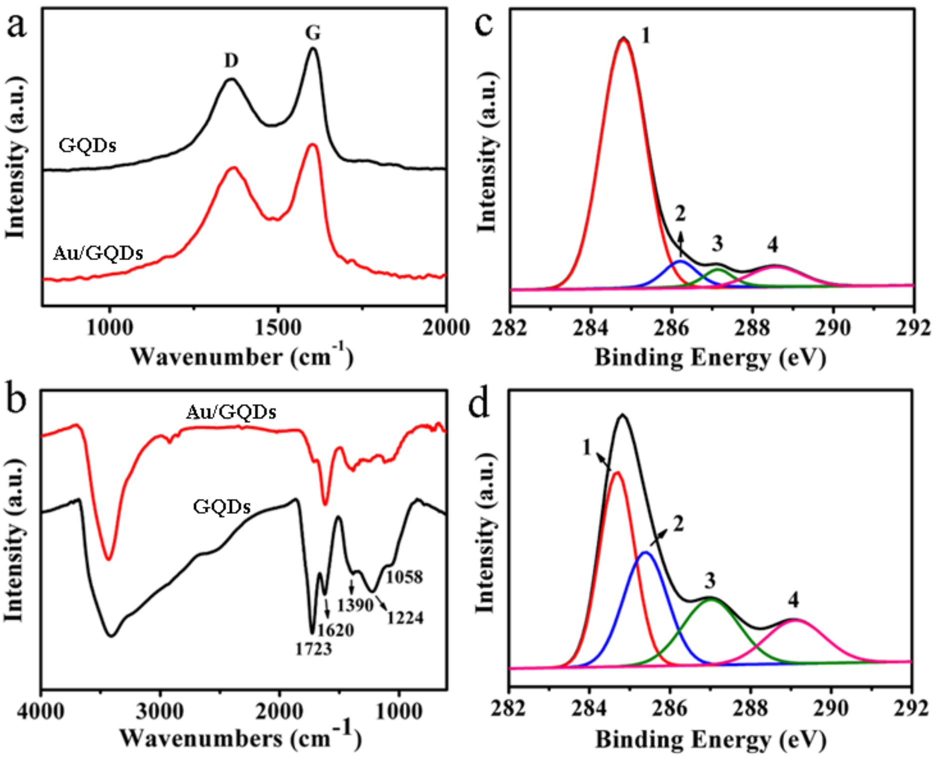

Figure S4. (a) Raman and (b) FTIR spectra of the GQDs and the Au/GQDs composites; (c) and (d) are C 1s XPS spectra of Au/GQDs composites and GQDs, respectively. The peaks 1, 2, 3, and 4 in (c) and (d) correspond to C=C/C-C in aromatic rings, C-O (epoxy and alkoxy), C=O and COOH groups, respectively.

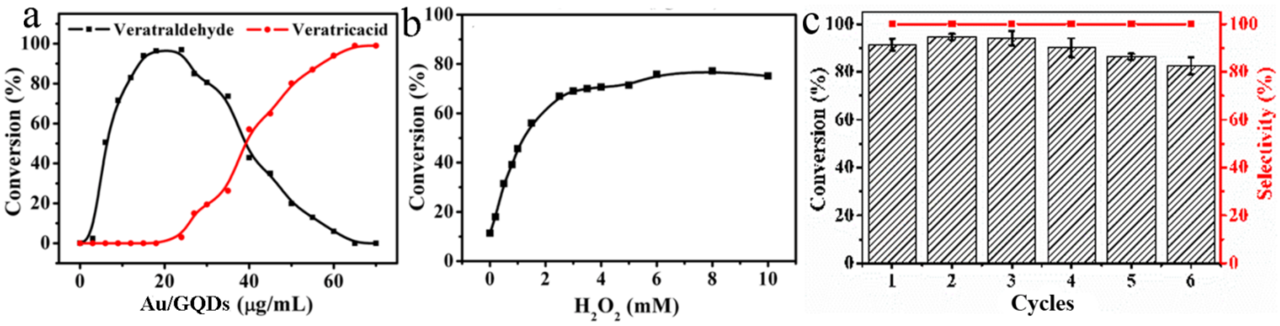

Figure S5. (a) Conversion rates of VA (0.3 mM) catalyzed by the Au/GQDs at pH 8.5 at 50 °C for 2 h with different amount of Au/GQDs or (b) different amount of H_2O_2, reaction time, 1 h; (c) Conversion/selectivity to veratraldehyde on recycling Au/GQDs composites.

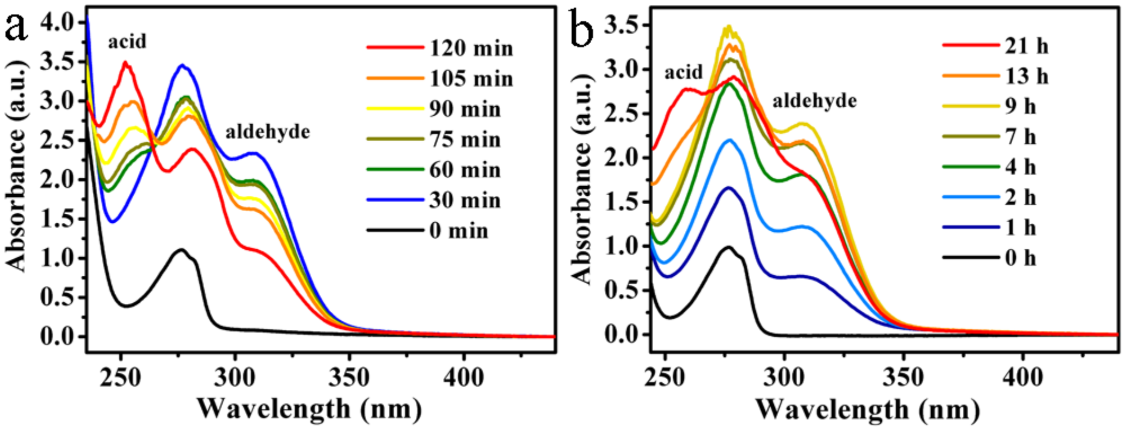

Figure S6. The UV-vis spectra of the VA oxidation products *versus* reaction time at pH 11(a) and 5 (b), the reaction were carried out with 15 µg of Au/GQDs, 3 mM of H_2O_2 and 0.3 mM of VA at 50 °C.

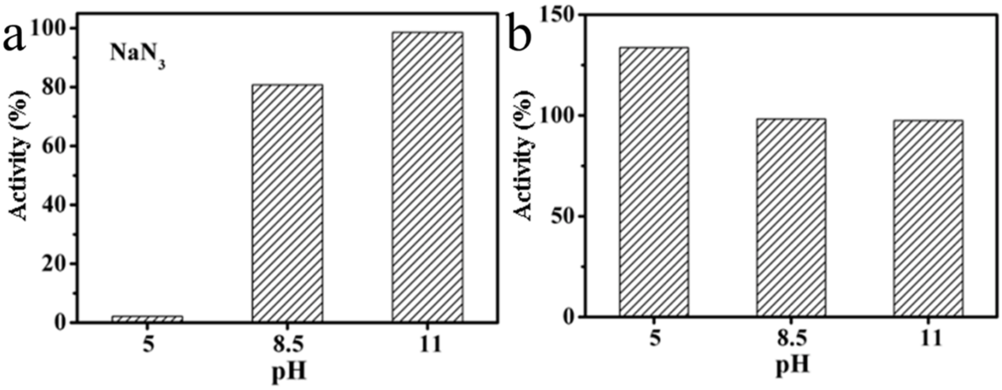

Figure S7. The catalytic activity of the Au/GQDs composites at different pH in the presence of singlet oxygen inhibitor (a) 10 mM of NaN_3. (b) The reaction was carried out in 40 % D_2O without inhibitors. All reactions were carried out with 15 µg of Au/GQDs, 3 mM of H_2O_2, 0.3 mM of VA at 50 °C in solutions with different pH.

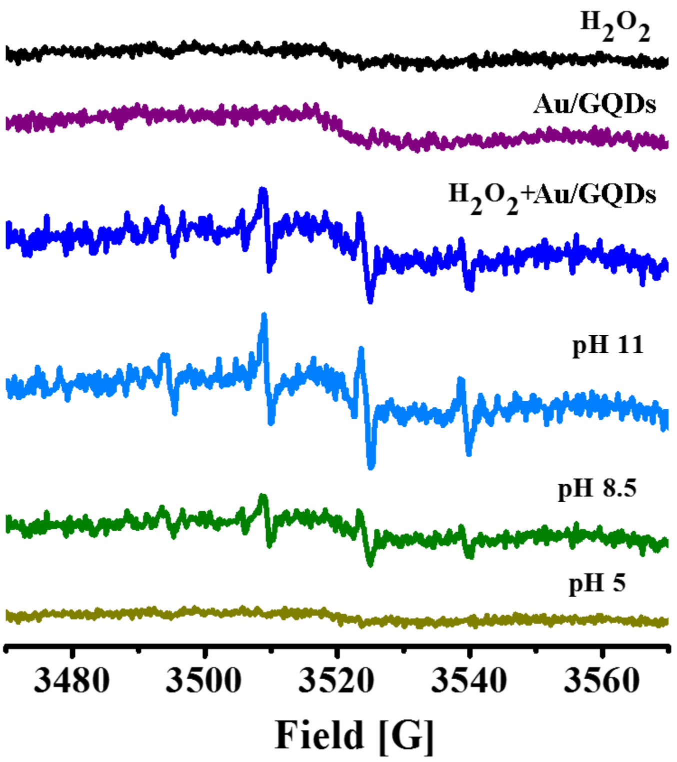

Figure S8. EPR spectra of Au/GQDs (10 μg/mL) with H_2O_2 (20 mM) in the presence of DMPO (80 mM) at pH 11, 8.5, and 5. EPR spectra of H_2O_2 (20 mM), Au/GQDs (5 μg/mL), and Au/GQDs (5 μg/mL) with H_2O_2 (20 mM) in the presence of DMPO (80 mM) at pH 11 are controls.

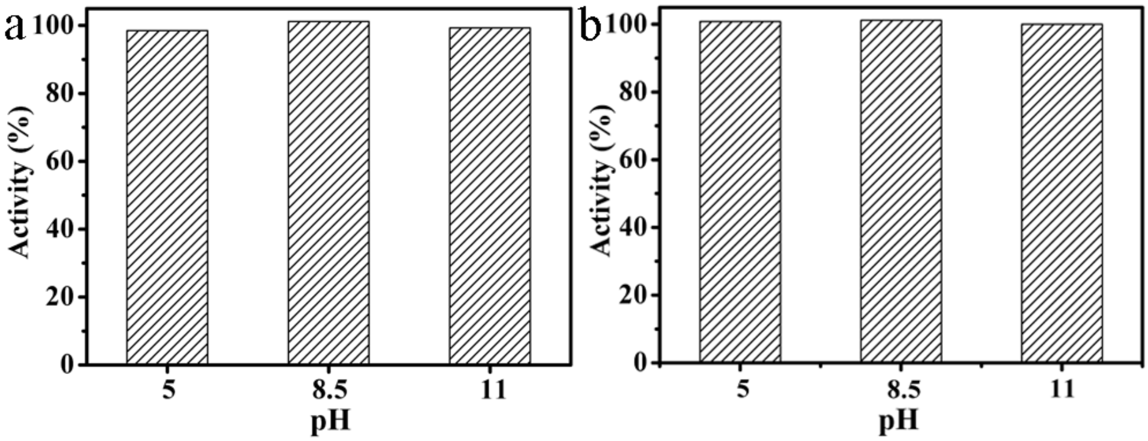

Figure S9. The catalytic activity of the Au/GQDs composites at different pH in the presence of hydroxyl radical inhibitors. (a) 10 mM of isopropanol; (b) 10 mM of tert-Butanol. The experiments were carried out with 15 μg of Au/GQDs, 3 mM of H_2O_2, 0.3 mM of VA at 50 °C in solution with different pH.

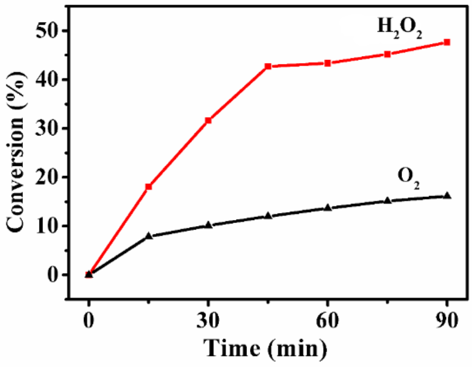

Figure S10. The oxidation of VA catalyzed by the Au/GQDs composites with/without H_2O_2 against time. The experiments were carried out in H_2O (pH = 8.5) with 15 μg of Au/GQDs, 3 mM of H_2O_2, and 0.3 mM of VA at 40 ℃.

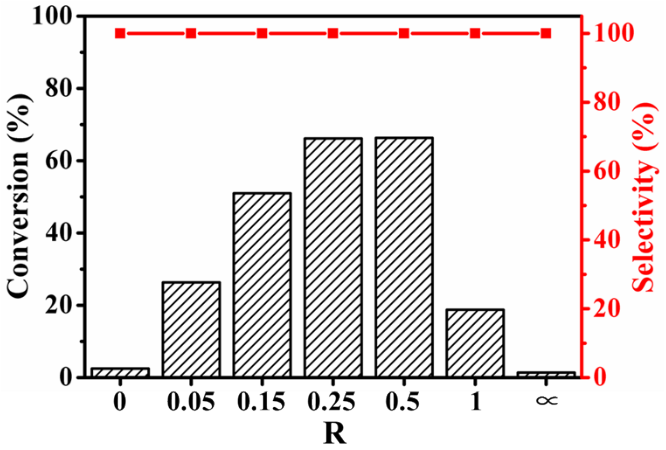

Figure S11. Comparison of the catalytic conversion and selectivity to veratraldehyde of Au/GQDs composites synthesized with different weight ratios of GQDs and $HAuCl_4$, the ratio of Au alone equals 0, while the ratio of GQDs alone equals ∝. The VA catalytic experiments were carried out in H_2O (pH = 8.5) with 15 μg of different Au/GQDs, 3 mM of H_2O_2, and 0.3 mM of VA at 50 ℃ for 1 h.

Table S1. Comparison of the catalytic activities with different catalysts. Reaction conditions: 15 μg of catalyst, 3 mM of H_2O_2, 0.3 mM of VA, 50 °C, pH 8.5.

Catalyst	**Conversion (%)**	**Selectivity to Veratraldehyde (%)**	**Time (h)**
Au	6	>99	2
GQDs	1	>99	2
Au+GQDs	9	>99	2

Au/GQDs	97	>99	2

Table S2. Results of VA oxidation using Au/GQDs composites. Reaction conditions: 15 μg of Au/GQDs, 3 mM of H_2O_2, 0.3 mM of VA under 50 °C.

Time (h)	**Conversion (%)**	**Product selectivity**	
	pH 5	Veratraldehyde (%)	Veratric acid (%)
0.25	75	>99	-
0.5	96	>99	-
1	>99	86	14
1.25	>99	78	22
1.5	>99	71	29
1.75	>99	64	36
2	>99	51	49
4	>99	14	86
6.5	>99	-	>99

Time (h)	**Conversion (%)**	**Product selectivity**	
	pH 11	Veratraldehyde (%)	Veratric acid (%)
0	0	>99	-
1	29	>99	-
2	49	>99	-
4	70	>99	-
7	83	>99	-
9	91	>99	-
13	>99	84	16
21	>99	71	29

Table S3. Oxidation of alcohols using Au/GQDs composites as catalysts. Conditions: 15 μg of Au/GQDs, 3 mM of H_2O_2, 0.3 mM of alcohols at 50 °C, pH 8.5 for 2 h.

Substrate	**Product**	**Conversion (%)**	**Selectivity**	
			aldehyde (%)	acid (%)
1-hexanol	1- hexaldehyde	trace	trace	-
1-pentanol	1-pentanal	trace	trace	-
cyclohexanemethanol	cyclohexanaldehyde	trace	trace	-
4-methylcyclohexanemethanol	4-methylcyclohexanaldehyde	trace	trace	-
PhCH$_2$OH	PhCHO	>99	18	82
4-MePhCH$_2$OH	4-MePhCHO	>99	59	41

4-$MeOPhCH_2OH$	4-MeOPhCHO	>99	68	32
$PhCH=CHCH_2OH$	PhCH=CHCHO	>99	74	26

EXPERIMENTAL METHODS

Materials. Veratryl alcohol was purchased from J&K Scientific Ltd., China. Graphene quantum dots (GQDs) were prepared as described in our previous work.[30,31,50,51] 5,5′-Dimethylpyrroline N-oxide (DMPO) and 2,2,6,6-Tetramethylpiperidine (TEMP) were ordered from Sigma-Aldrich, USA. DMPO was treated with activated carbon prior to use. Other reagents were obtained from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China and used as-received.

Fabrications of Au/GQDs composites. In a typical experiment, 5 mg of GQDs was dissolved in 50 mL of $HAuCl_4$ (1 mM) solution by sonication and then stirred vigorously for 30 min. The mixture then was heated to boiling under stirring, 5 mL of trisodium citrate (40 mM) was then added to the boiling mixture quickly. The solution was refluxed for 60 min, with a final color of deep red. After cooling down to room temperature, the solution was centrifuged to remove the extra free GQDs and trisodium citrate, and re-dispersed in distilled water. For comparison, bare Au NPs were also prepared through a similar way.

Characterization. Atomic force microscopic (AFM) images were taken on a MultiMode Nanoscope V scanning probe microscopy system (Veeco, USA). AFM cantilever tips with a force constant of ~ 48 N/m and resonance vibration frequency of ~ 330 kHz were used and the scanning rate was set at 1 Hz. Transmission electron microscope (TEM) images were obtained using a JEM-2010 transmission electron microscope (JEOL, Japan). X-ray photoelectron spectroscopy (XPS) measurements were performed on an Axis Ultra DLD spectrometer (Kratos Analytical, UK) using a monochromated Al Kα source at 15 kV. The FT-IR spectra were acquired on a Nicolet 6700 FT-IR (Thermo Electron, USA) in the range of 4000-400 cm^{-1}. The specimens for FT-IR measurements were prepared by grinding the dried powder with KBr together and then compressed into thin pellets. Raman spectroscopy measurements were performed on an Ar ion laser Micro-Raman spectroscope (Jobin Yvon LabRam HR 800 UV, France) with an excitation laser beam wavelength of 514.5 nm. UV-visible absorption spectra were recorded using a Shimadzu UV-2550 (Shimadzu, Japan). Electron Paramagnetic Resonance (EPR) spectra were recorded at room temperature in a quartz capillary on a Bruker BioSpin EMX-8 at 9.856 GHz, with 100 kHz modulation frequency and 1.0 G modulation amplitude. For spin trapping experiments, DMPO, Trion, or TEMP were added to the mixtures before the measurements.

Catalytic activity assay. The oxidation reaction of VA was carried out in a tube containing 15 μg of Au/GQDs composites, 0.3 mM of VA and 3 mM of H_2O_2 in 20 mM phosphate buffer. The reactions in different pH solutions were carried out with phosphate buffer adjusted by NaOH/H_3PO_4. The solutions with pH below 5.0 and above 8.0 were not buffer solutions, but for comparison, they were not replaced with other buffer systems. The reaction mixture was maintained in water bath at 50 ℃ for 2 h, then the reaction solution was acidified with HCl and extracted with ethyl acetate for 3 times. The extracted solution was dried with Na_2SO_4, and analyzed by GC-MS. GC-MS analysis was performed with a 7890A gas chromatograph coupled with a 5975C mass spectrometer (Agilent Inc., CA, USA). A DB-5ms capillary column (30 m × 0.25 mm × 0.25 μm) from Agilent was used to separate compounds. The injector port was heated to 270°C and injections (1 μL) were performed in splitless mode. Helium (purity＞99.999%) was used as the carrier gas at a constant flow of 1 mL/min. The reaction products were identified by comparing mass spectra (SCAN mode) from the data base NIST 11. Quantification of the reactant products was done by the external calibration method with the standard compounds.

The durability of Au/GQDs composites. The reaction mixture containing 15 μg of Au/GQDs composites, 0.3 mM of VA and 3 mM of H_2O_2 , 1 mL of phosphate buffer (20 mM, pH = 8.5) was incubated in water bath at 50 ℃ for 2 h of reaction. The catalysts Au/GQDs composites were then separated from the reaction mixture by centrifugation (10000 r/min, 15 min). The supernatant was analyzed to calculate the conversion of VA, while the Au/GQDs composites was re-dispersed in 1 mL of phosphate buffer (20 mM, pH = 8.5) containing 0.3 mM of VA and 3 mM of H_2O_2 to catalyze the second cycle of the reaction. The same performance was done 6 times. The conversion of VA in the first run was used as 100 % to calculate the relative catalytic activity in the following cycles.