

## **Supporting information:**

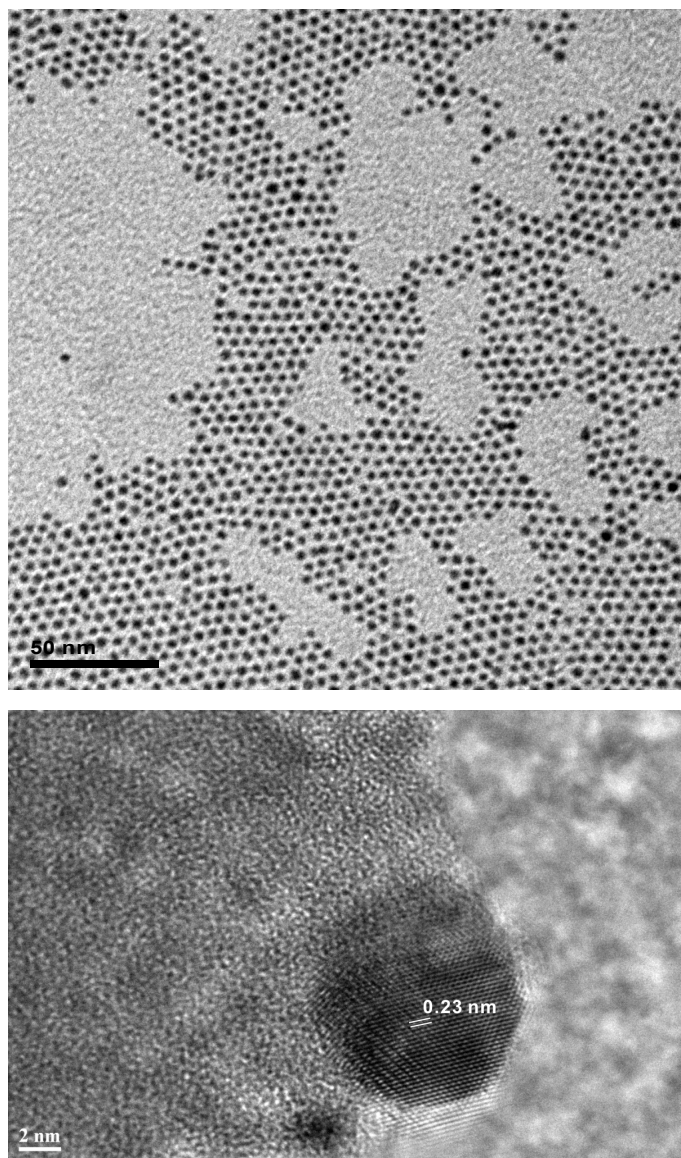
### **Radical-Involved Photosynthesis of AuCN Oligomers from Au Nanoparticles and Acetonitrile**

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**Figure S1.** Representative TEM image of as-prepared AuNPs with uniform size of  $3.3 \pm 0.5$  nm (above), and HR-TEM image of AuNPs loaded on silica support (below), where the distance of the crystal plane is 0.23 nm corresponding to the Au(111) facet.

### ***Silica Supports:***

#### **1) *Mesoporous EP-FDU-12:***

0.50 g of Pluronic F127, 0.60 g of TMB and 1.25 g of KCl were dissolved in 50 ml of 1.0 M HCl at  $14 \pm 0.1$  °C ( see reference: Ma, G. et. al.J. Am. Chem. Soc. **2010**, 132, 9596-9507.). After 1h stirring, 2.08g of TEOS was added to this solution. The synthesis composition (in molar) F127/KCl/TEOS/TMB/HCl/H<sub>2</sub>O was 0.00147/0.62/0.37/0.185/1.85/100. After stirring for 24 h at 14 °C, the mixture was transferred into an autoclave and heated at 140 °C

for 24h. Then the products were obtained by filtration and dried at room temperature in air. The organic templates were removed by microwave digestion. The organic templates were removed by microwave digestion as described by Tian et. al. (Tian; B. Z. et al. *Chem. Commun.*, 2002, 1186). The detailed process was conducted as follows: 0.3 g of as-made FDU-12 sample was mixed with 2 mL 30% H<sub>2</sub>O<sub>2</sub> and 5 mL 15 M HNO<sub>3</sub> in a 30 mL Teflon sample vessel. The system was operated at approximately 800 W. The operation pressure of the digestion process was maintained at 1.0 MPa for 10 minutes. The sample after microwave digestion was washed by water for three times and dried for use.

## **2) SiO<sub>2</sub> Sub-Microsphere:**

4 mL aqueous ammonia was added into a mixed solution of ethanol (80 mL) and distilled water (5 mL). After 15 min stirring, 4 mL of tetraethyl orthosilicate (TEOS) was added to the above solution under magnetic stirring at 25 °C. After continuous stirring for 3 h, the white solid products were obtained by filtration and repeatedly washed with water and ethanol, and then dried in a vacuum oven at 60 °C for 4 h (Stober, W.; Fink, A.; Bohn, E., *J. Colloid Interface Sci.* 1968, 26, 62.).

## **AuNPs/support:**

AuNPs were loaded into various supports by a colloid deposition method as previously reported (*J. Am. Chem. Soc.* 2006, 128, 14278.). Desired amount of AuNPs were dissolved in 25 mL chloroform. To this solution, desired amount of supports (e.g., FDU-12 and SiO<sub>2</sub> sub-microspheres) was added. After 30 min stirring, the solid product was centrifuged and dried in air. The AuNPs/SiO<sub>2</sub> was calcined at 550 °C for 5 h (in air) to eliminate undesired ligands.

## **AuCN/support:**

Photocatalysis of AuCN was carried out with 40 mg of 5wt% AuNPs/support suspended in 4 mL of acetonitrile solution with 100 μmol benzaldehyde (or benzyl alcohol) in air under stirring. Side-irradiation by a 300 W high-pressure mercury lamp was used to initiate the photoreaction. After 1 ~ 4 h reaction, the solid product was obtained by centrifuging and drying in air at 90 °C (which exceeds the boiling point of acetonitrile (81.1 °C) overnight, ensuring the total elimination of the precursors.

### ***In situ* EPR and Spinning Trapping Experiments:**

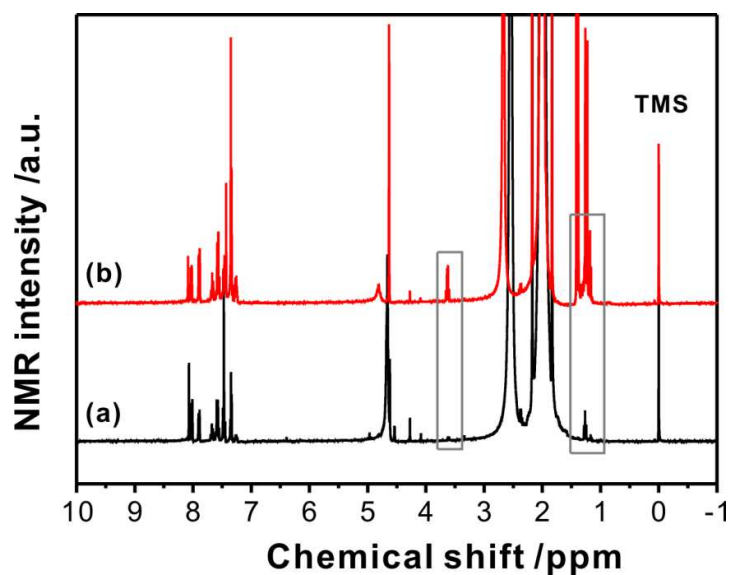
X-band EPR signals were recorded at ambient temperature on a Bruker EPR A-300 spectrometer. The settings for the EPR spectrometer were as follows: center field, 3511.39 G; sweep width, 100 G; microwave frequency, 9.86 G; modulation frequency, 100 kHz; power, 101 mW; conversion time, 10msec. The spin trapping experiments were performed as follows: 5,5-Dimethyl-pyrroline-N-oxide (DMPO) and *N*-*t*-butyl- $\alpha$ -nitrone (PBN) spin-trapping reagents and other chemicals were purchased from Sigma-Aldrich Chemical Co. and used without further purification. Stock solutions of DMPO (0.8 M) in deaerated water were prepared under argon and stored in the dark at -20 °C. The stock DMPO solution was first diluted to 0.08 M with phosphate buffer solution (pH = 7.6) prior to the reaction with any solid substrate. The acetonitrile solution containing calculated benzaldehyde and ice-cooled DMPO solution (0.08 M) was quickly transferred into a glass capillary tube and tested by EPR spectroscopy at room temperature upon UV-light irradiation. A 100 W Hg lamp (LOT Oriel) was used to provide UV-light with  $\lambda > 300$  nm. The same experiments were performed when PBN was used as the spin reagent. In addition, the solid AuNPs/support (~ 5.0 mg) was also mixed with the above solution to obtain EPR signals.

Some results of the EPR control experiments are summarized as follows: (1) no signals are observed in the system containing benzaldehyde and MeCN under UV light irradiation in the absence of spin trapping reagents, (2) no signals are observed in the system containing DMPO (or PBN) spin trapping reagents and MeCN even under UV light irradiation, (3) no signals are observed in the system containing DMPO (or PBN), MeCN and AuNPs in open air even under UV light irradiation, and (4) the DMPO adducts recorded in the AuNPs/MeCN/benzaldehyde ternary system at room-temperature with UV light irradiation ( $\lambda > 300$  nm) are shown below.

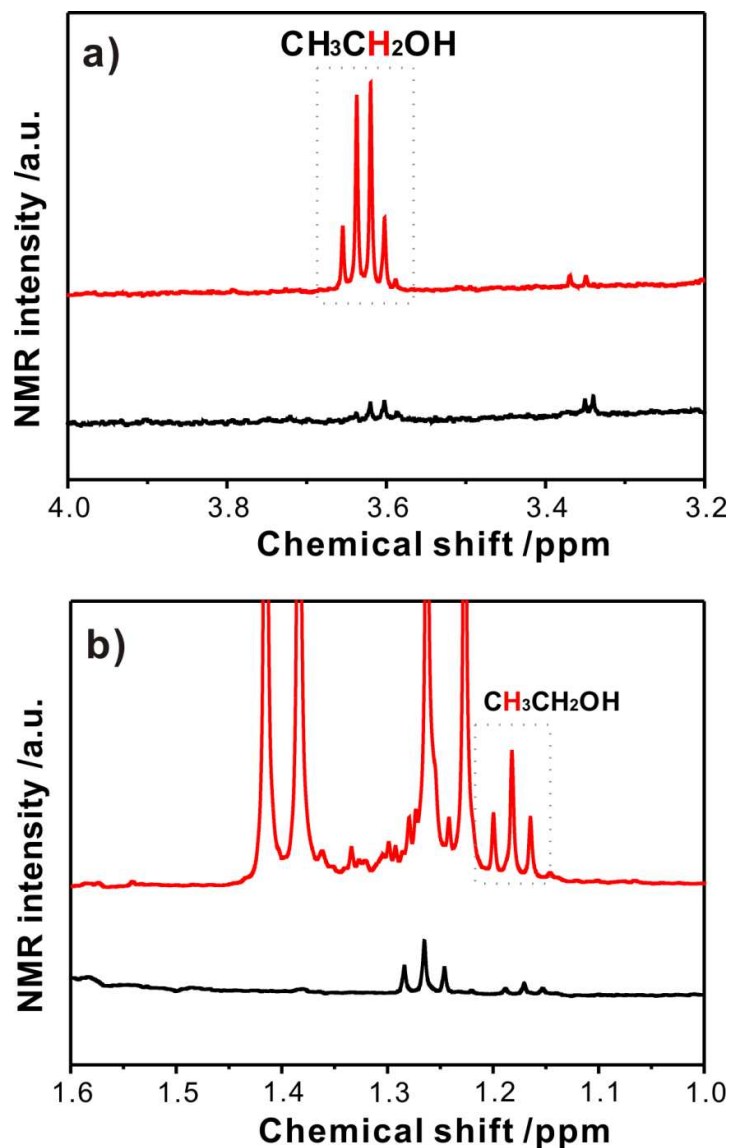
**Control Experiments:**

We also performed the control experiments to determine the exact mechanism of AuCN photo-formation. It is described in the main manuscript that AuCN is formed in the suspension containing AuNPs, MeCN and benzaldehyde (or benzyl alcohol) in open air under UV light irradiation for several hours. The control experiments showed that (1) no AuCN is formed in the suspension containing AuNPs, MeCN and benzaldehyde (or benzyl alcohol) in open air **under dark conditions** even after 24 h reaction, (2) no AuCN is formed in the suspension containing AuNPs, MeCN and benzaldehyde (or benzyl alcohol) under UV light irradiation for 10 h but **in the absence of molecular oxygen**, and (3) no AuCN is obtained in the suspension containing AuNPs and MeCN in open air under UV light irradiation for 10 h. Therefore, it is concluded that UV-light, benzaldehyde (or benzyl alcohol), and molecular oxygen are all key factors to the success of the photosynthesis; lack any of them is impossible for making AuCN from AuNPs/MeCN suspension.

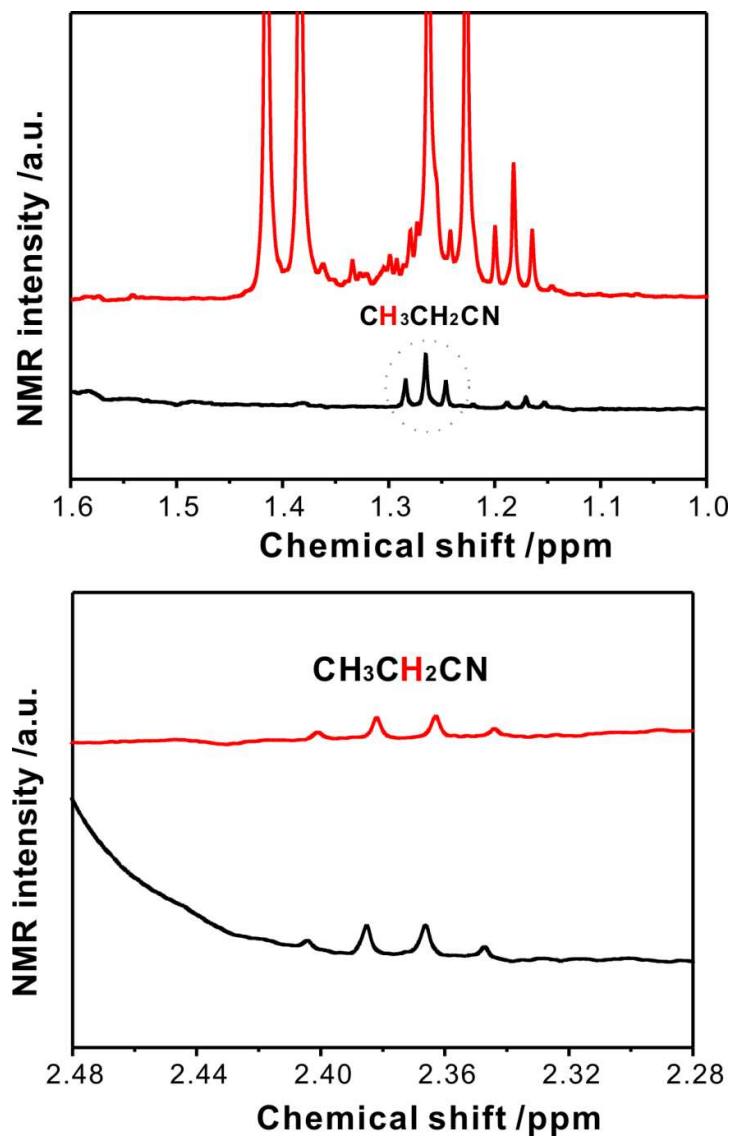
<sup>1</sup>H-NMR results (Figure S2-S4):



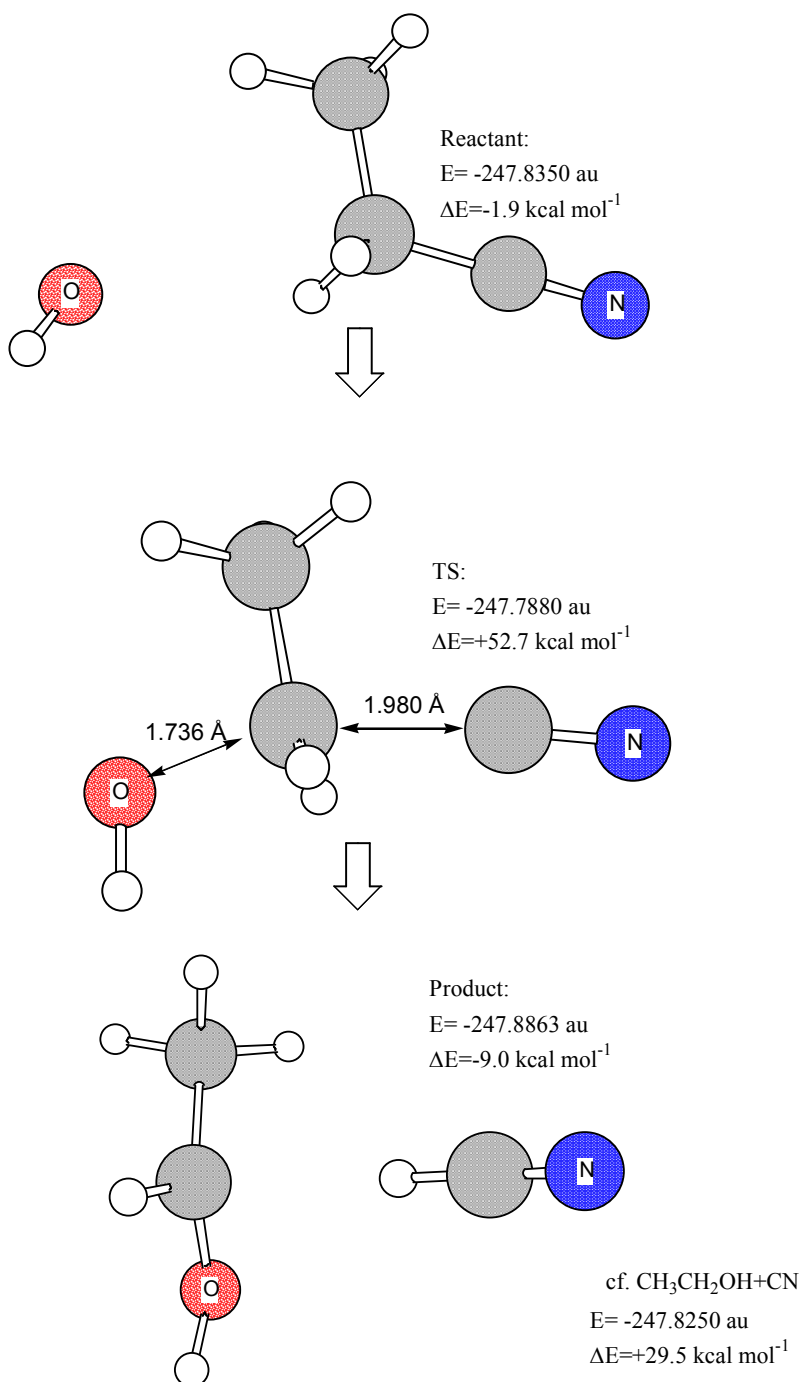
**Figure S2.** The red line (b) represents the reaction solution containing AuNPs, MeCN and benzaldehyde after photoreaction, while the black line (a) represents the blank sample, i.e., without AuNPs. The signals observed at  $\delta = 10.03$  ppm (not shown) and in the range of  $\delta = 7.20 - 8.10$  ppm are attributed to benzaldehyde and its derivatives, such as benzophenone, the signals observed at  $\delta = 1.99$  ppm are attributed to acetonitrile, and the signals observed at  $\delta = 4.63$  ppm are attributed to water. Importantly, the two spectra are almost the same except two regions indicated by black rectangles. Detailed results are shown below.



**Figure S3.** By analysis of the above Figure S3 a) and b), a quartet ( $J = 8.0$  Hz) is observed in the  $^1\text{H}$  NMR spectrum at  $\delta = 3.64$  ppm for the two hydrogen atoms, and a triplet ( $J = 8.0$  Hz) is observed at  $\delta = 1.28$  ppm for the three hydrogen atom. Thus we conclude that  $\text{CH}_3\text{CH}_2\text{OH}$  is generated as a by-product in the reaction solution. In addition, the other four strong peaks in Figure S3b are designated to amine derivatives, which indicate acetonitrile may undergo hydrolysis in the presence of gold or gold cyanide.

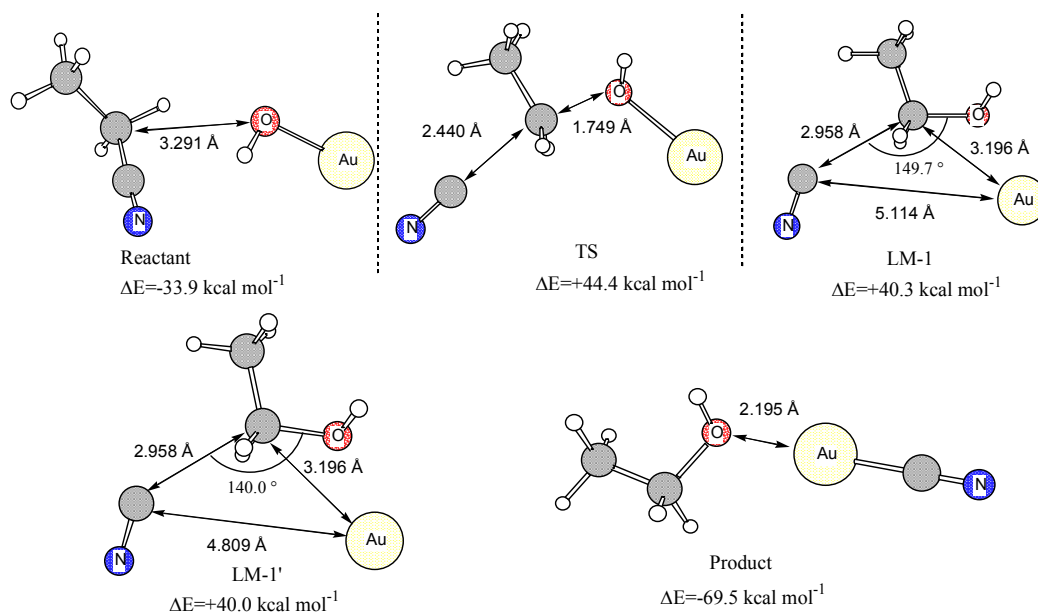


**Figure S4.** By analysis of the above Figure, we found that  $\text{CH}_3\text{CH}_2\text{CN}$  is also formed as a by-product (the presence of  $\text{CH}_3\text{CH}_2\text{CN}$  molecules are further evidenced by GC-MS). The signals in the sample containing AuNPs are overlapped by stronger amine signals, but they can still be recognized.



**Figure S5.** Structure and energy change for  $\text{CH}_3\text{CH}_2\text{CN} + \cdot\text{OH} \rightarrow \text{CH}_3\text{CHOH} + \text{HCN}$

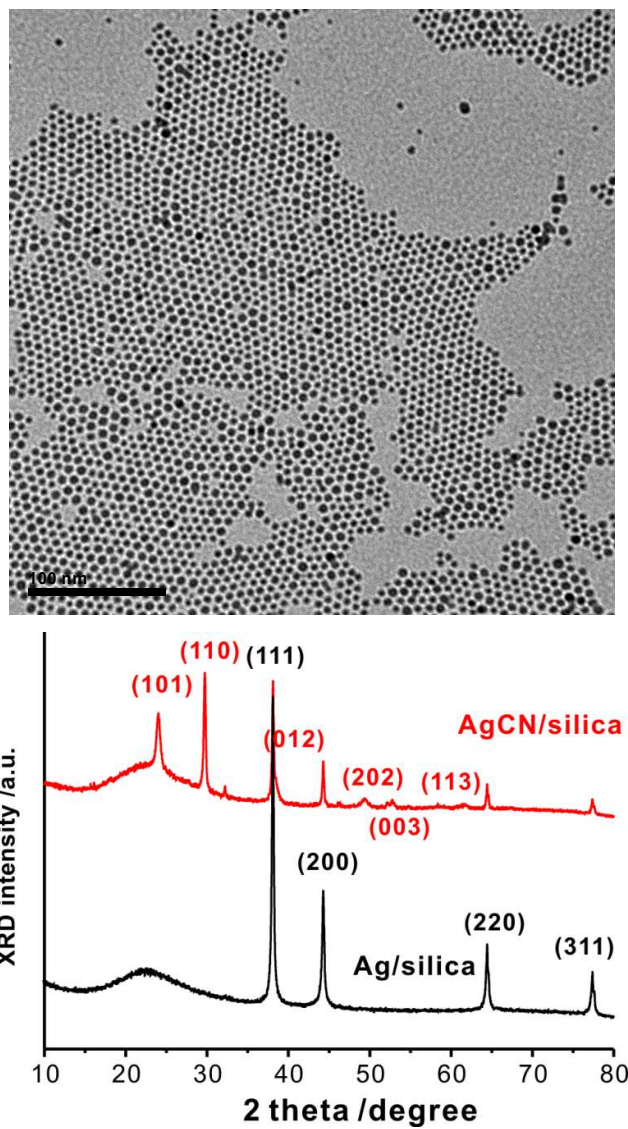
Considering the production of  $\text{CH}_3\text{CH}_2\text{OH}$ , we proposed that it may be formed by the reaction of  $\text{CH}_3\text{CH}_2\text{CN} + \cdot\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \cdot\text{CN}$ , however, DFT calculations show that the reaction leads to a different product including HCN which is not detected by  $^1\text{H}$ -NMR and GC-MS. It is noticed that the product consisting of  $\text{CH}_3\text{CH}_2\text{OH}$  and  $\cdot\text{CN}$  is more unstable by 38 kcal than the system consisting of  $\text{CH}_3\text{CHOH} + \text{HCN}$ , therefore  $\text{CH}_3\text{CH}_2\text{OH}$  cannot be obtained by the reaction between  $\text{CH}_3\text{CH}_2\text{CN}$  and  $\cdot\text{OH}$  (See also Figure S6).



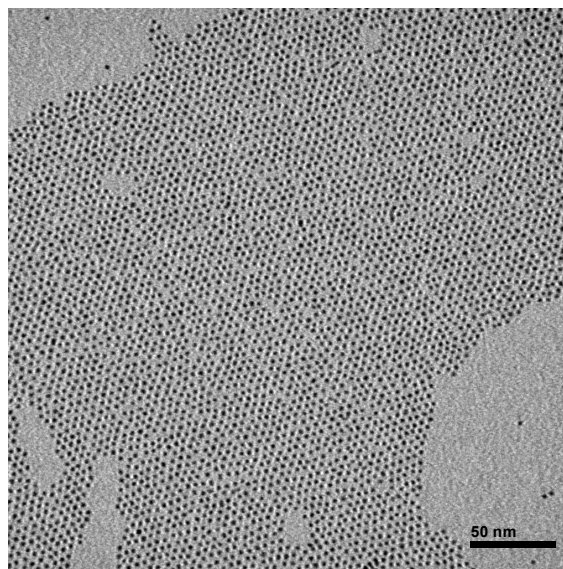
Reference to  $\text{CH}_3\text{CH}_2\text{CN}$  ( $E = -172.1175 \text{ au}$ ) +  $\text{AuOH}$  ( $E = -211.2211 \text{ au}$ )  
 B3LYP/LanL2DZ for Au and 6-311G(d,p) for others.

**Figure S6.** Structure and energy change for  $\text{CH}_3\text{CH}_2\text{CN} + \text{AuOH} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{AuCN}$ .

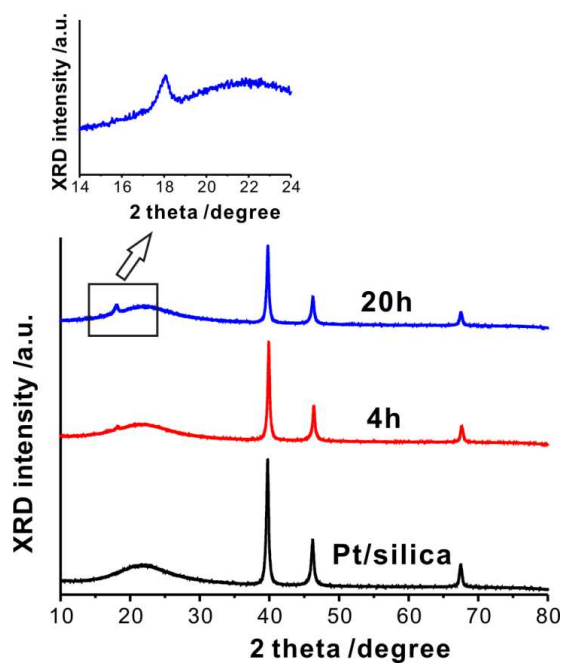
Scholz and coworkers have reported that  $\text{OH}\cdot$  radicals in Fenton's reagent preferentially oxidize asperities on the gold surface (*Angew. Chem. Int. Ed.*, 49, 1061-1063). Therefore, we supposed that  $\text{AuOH}$  intermediate may be generated on the surface of AuNPs after  $\text{OH}\cdot$  attacking. Indeed,  $\text{CH}_3\text{CH}_2\text{OH}$  is obtained energetically favourable by the reaction between  $\text{CH}_3\text{CH}_2\text{CN}$  and  $\text{AuOH}$ . As shown in Figure S6,  $\text{CH}_3\text{CH}_2\text{CN}$  and  $\text{AuOH}$  passes the TS, but trapped by a local minimum (LM-1). The second TS cannot be characterized because it may be close to LM-1 and the barrier is low. Then in LM-1 structure, the O-C-C angle is 149.7 deg, and this angle is changed to 140 deg. The successive optimization leads to the product.



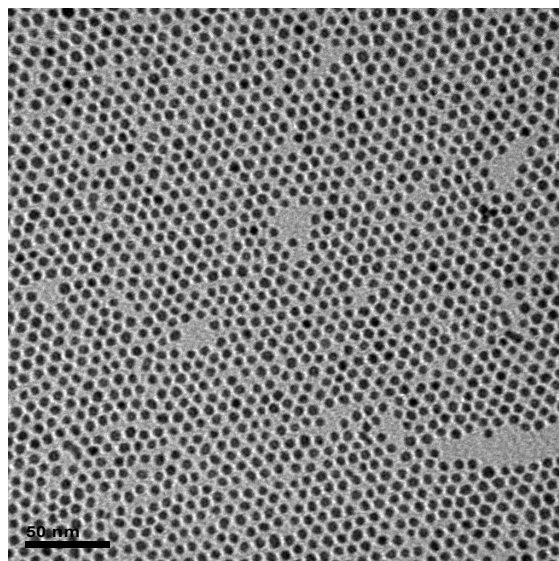
**Figure S7.** We synthesized AgNPs (as shown in the TEM image) and loaded them onto silica support. By using the same photochemical method, we also obtained AgCN, as shown in the XRD spectrum. The reaction condition is not optimized so that residual AgNPs are still present in the AgCN/silica samples.



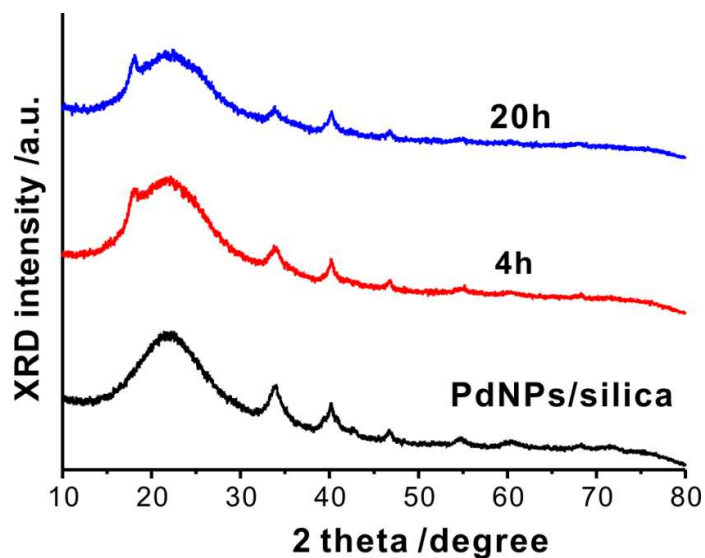
**Figure S8.** representative TEM image of as-prepared PtNPs with uniform size of ~2.5 nm.



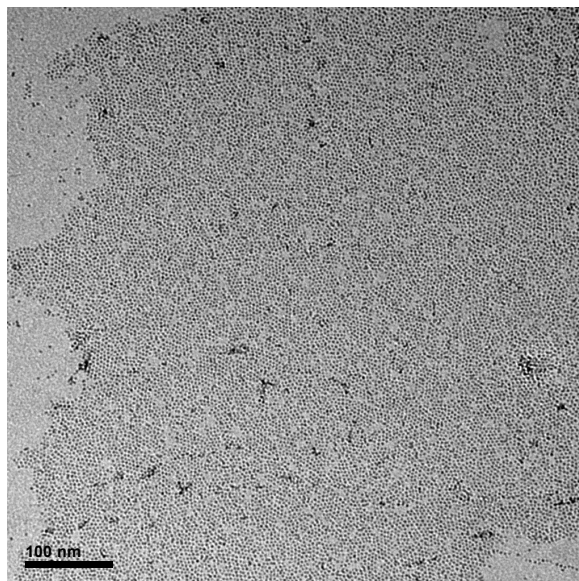
**Figure S9.** XRD spectrum of PtNPs/silica (black line) and after 4 h (red line) and 20 h photoreaction (blue line). The inset enlarges the region of 14 to 24 degree. It is seen that a new peak around 18 degree appears after photoreaction with the degradation of the other three peaks corresponding to PtNPs. The new peak is tentatively ascribed to the (101) facet of Pt cyanide derivatives, possibly  $\text{Pt}(\text{CN})_2$ . It should be note that the reaction optimization and detailed analysis are needed to obtain Pt cyanide as well as examine its crystal structure. In addition to PtNPs, PdNPs and RuNPs are synthesized and supported onto silica. The resulting samples are also for cyanidation using the same photochemical method. The TEM images of PdNPs and RuNPs and their XRD spectrum are shown below. The similar peak around 18 degree is found for both Pd and Ru cyanide derivatives.



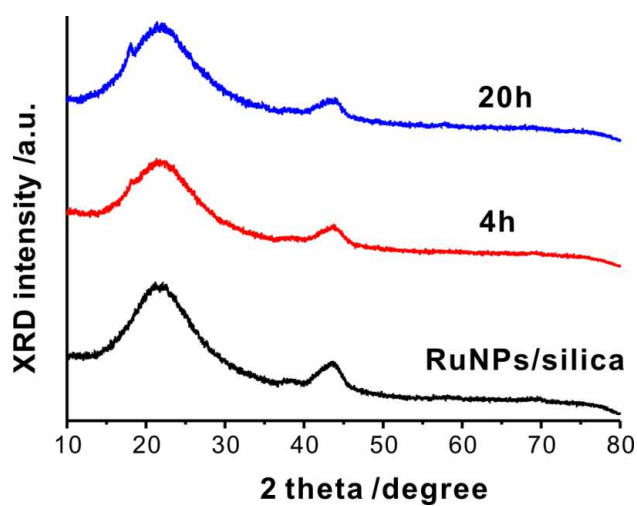
**Figure S10.** representative TEM image of as-prepared PdNPs with uniform size of ~5 nm.



**Figure S11.** XRD spectrum of PdNPs/silica (black line) and after photochemical cyanidation for 4 h (red line) and 20 h (blue line)



**Figure S12.** Representative TEM image of as-prepared RuNPs with uniform size of ~2 nm.



**Figure S13.** XRD spectrum of RuNPs/silica (black line) and after photochemical cyanidation for 4 h (red line) and 20 h (blue line)