Carbon Quantum Dot/Silver Nanoparticle/Polyoxometalate Composites as Photocatalysts for Overall Water Splitting in Visible Light


The design of photocatalysts for overall water splitting in visible light remains a huge challenge. Carbon quantum dots (CQDs)/Ag/Ag$_3$PW$_{12}$O$_{40}$ nanocomposites have high photocatalytic activities for overall water splitting in visible light without electron acceptors or hole scavengers. In the present system, H$_2$ evolution was performed on Ag particles. O$_2$ evolution appears to be a result of the oxidation of H$_2$O on the valence band of Ag$_x$PW$_{12}$O$_{40}$, which is enhanced by promoted electron-transfer events at hybrid interfaces of the polyoxometalates and CQDs. The synergistic effects of CQDs, Ag, and Ag$_3$PW$_{12}$O$_{40}$ enable the design of a water-splitting catalyst with a remarkably improved efficiency (with an active region of $\lambda < 650$ nm; apparent quantum yield $\approx 4.9\%$ at 480 nm) and operational stability.

Introduction

Solar water splitting into hydrogen and oxygen is a potentially ideal, clean, and renewable source of hydrogen fuel. The solar water splitting into hydrogen and oxygen is a potentially ideal, clean, and renewable source of hydrogen fuel. The traditional strategy to design photocatalysts for overall water splitting is based on metal oxide systems with activities that are related to the band gap and photogenerated electron–hole pairs. Typically, photocatalysts are divided into three groups according to the electronic configuration of their core metal ions. (1) Transition metal ions with d$^0$ configurations such as Ti$^{4+}$, Zr$^{4+}$, Ta$^{5+}$, Nb$^{5+}$, V$^{4+}$, and W$^{6+}$. (2) A rare-earth metal ion with f$^0$ configuration such as Ce$^{3+}$. (3) Typical metal ions with d$^{10}$ configurations such as Ga$^{3+}$, In$^{3+}$, Ge$^{4+}$, Sn$^{4+}$, and Sb$^{5+}$.[14–22] Unfortunately, the majority of photocatalysts are complex and expensive or function only with UV irradiation and need an appropriate electron acceptor or hole scavenger. Although some semiconductors, such as La-doped NaTaO$_x$, Ni-doped InTaO$_x$, and (Ga$_x$Zn$_{1-x}$)-(N$_x$I$_{1-x}$) solid solution (or in a Z-Scheme structure), are employed to realize overall water splitting, these catalyst systems still suffer from low light absorption (< 510 nm), poor separation efficiency of electron–hole pairs, and the formidable complexity of the oxidative half-reaction.[23–28] Systems that are sufficiently stable and efficient for practical use have not yet been identified. Therefore, the design of new, simple, and inexpensive high-performance photocatalysts for solar water splitting without an electron acceptor or hole scavenger remains a great challenge.

Polyoxometalates (POMs; e.g., polyoxotungstates, polyoxoniobates, and polyoxotantalates), which have unique photophysical properties, are potentially useful for photocatalytic H$_2$ and O$_2$ generation.[29–34] The utilization of surface plasmon resonance (SPR) has offered a new opportunity to overcome the limited efficiency of photocatalysts. It can enhance the photocatalytic activity toward organic-compound decomposition[35–37] and water splitting.[38,39] Currently, visible-light-triggered plasmonic photocatalysts have been recognized as one of the most promising alternatives to traditional photocatalysts.[40–42] SPR improves the solar-energy conversion efficiency by (i) extending light absorption to longer wavelengths, (ii) increasing light scattering, and (iii) exciting electron–hole pairs in the semiconductor by transferring the plasmonic energy from the metal to the semiconductor.[43] As one of the most efficient plasmonic metals, Ag has always performed catalysis by providing chemically active sites upon which the relevant chemical transformations can take place with lower activation barriers than on the semiconductor. Furthermore, Ag can act to extend the lifetime of energetic charge carriers that reach the surface of the semiconductor by enhancing the rates of electron–hole separation at the cocatalyst–semiconductor interface.[44,45] Strong evidence proves that Ag nanoparticles can cause a notable photoresponse in the visible range as a result of SPR effects.[46–48] Carbon quantum dots (CQDs) are a class of nanocarbons discovered recently that display abundant unique photophysical properties.[49] CQDs exhibit photo-induced electron-transfer, photoluminescence (PL), and ele-
tron reservoir properties. Based on the photoinduced electron-transfer, PL, and electron reservoir properties of CQDs, CQDs/semiconductor composites (CQDs/TiO₂, CQDs/SiO₂, CQDs/Fe₂O₃, CQDs/Cu₂O, CQDs/Ag₃PO₄) that have enhanced photocatalytic activity and stability under visible light have been achieved.\textsuperscript{[30–35]} In light of the remarkable photocatalytic properties of CQDs, the SPR effect of Ag, and the photocatalytic hydrogen generation of POMs, we consider that the combination of CQDs, Ag, and POMs may be a unique approach to construct a stable and efficient complex photocatalyst for solar water splitting. In this work, we present the design and fabrication of CQDs/Ag/Ag₃PW₁₂O₄₀ nanocomposites that served as photocatalysts for overall water splitting in visible light (light absorption extend to 650 nm) without any electron acceptors or hole scavengers. The estimated apparent quantum yield (AQY) was 4.9% at 480 nm.\textsuperscript{[19, 54]} We also propose mechanisms for visible-light-driven overall water splitting on CQDs/Ag/Ag₃PW₁₂O₄₀ nanocomposites.

Results and Discussion

In our experiments, the CQDs/Ag₃PW₁₂O₄₀ nanocomposites were synthesized by solid-state grinding of a mixture of 0.7 g AgNO₃, 2.88 g H₃PW₁₂O₄₀, and 4 mL CQDs aqueous solution for 20 min at room temperature, followed by the addition of 100 mL pure water and stirring for 24 h under visible light to form CQDs/Ag/Ag₃PW₁₂O₄₀ nanocomposites (Figure 1a, more details are given in the Experimental Section). An SEM image of the CQDs/Ag/Ag₃PW₁₂O₄₀ complex photocatalysts is shown in Figure 1b. The images revealed the spherical morphology of the complex, which had an average diameter of 300–400 nm. This is different from the rhombic dodecahedral morphology of the CQDs/Ag₃PW₁₂O₄₀ nanocomposite of 500–600 nm in size (Figure S1). The morphology difference is primarily because of the partial dissolution of the CQDs/Ag₃PW₁₂O₄₀ complex. The inset in Figure 1c shows the TEM image of a typical single CQDs/Ag/Ag₃PW₁₂O₄₀ nanoparticle. The distinct contrast between the Ag₃PW₁₂O₄₀ particles and the CQDs surface layer confirmed the introduction of CQDs. High-resolution transmission electron microscopy (HRTEM) was performed to further confirm the formation of CQDs/Ag/Ag₃PW₁₂O₄₀ complex (Figure 1c). Alongside the Ag₃PW₁₂O₄₀ particles, the lattice spacing of approximately 0.32 nm caused by the (0 0 2) plane of graphitic carbon and the lattice spacing of 0.21 nm caused by the (2 0 0) plane of crystalline Ag, provide convincing evidence for the formation of CQDs/Ag₃PW₁₂O₄₀ nanocomposites (Figure 1c). The energy dispersive spectroscopy (EDS) patterns of Ag₃PW₁₂O₄₀, CQDs/Ag₃PW₁₂O₄₀, and CQDs/Ag/Ag₃PW₁₂O₄₀ are displayed in Figure S2. Along with the Ag, P, W, and O peaks from Ag₃PW₁₂O₄₀ and Ag, C diffraction peaks that correspond to the CQDs (CQDs content: ~5%) were observed clearly (Figure S3).

The XRD patterns shown in Figure 1d provide further support for the different crystalline structures of Ag₃PW₁₂O₄₀, CQDs/Ag₃PW₁₂O₄₀, and CQDs/Ag/Ag₃PW₁₂O₄₀. The patterns of the samples with the cubic structure of H₃PW₁₂O₄₀·6H₂O are consistent with previous results.\textsuperscript{[40]} The characteristic peak for carbon at 2θ = 26° was too weak to be observed because of the small quantities of CQDs in the composites. Compared to Ag₃PW₁₂O₄₀ and CQDs/Ag₃PW₁₂O₄₀, other common peaks for CQDs/Ag/Ag₃PW₁₂O₄₀ were indexed readily as (111) (Figure 1e) and (2 0 0) (Figure S4). The remaining diffraction peaks for CQDs/Ag/Ag₃PW₁₂O₄₀ were indexed readily as the (111) planes of Ag (JCPDS No. 04-0783; Figure 1e), which confirms the formation of Ag nanoparticles.\textsuperscript{[52]} Raman spectra were recorded to further confirm the presence of C in the complex structures of CQDs/Ag₃PW₁₂O₄₀ and CQDs/Ag/Ag₃PW₁₂O₄₀. In addition to the peaks from Ag₃PW₁₂O₄₀, two characteristic D and G band peaks of C located at ~1336 and 1610 cm⁻¹ were observed in the Raman spectra of CQDs/Ag₃PW₁₂O₄₀ and CQDs/Ag/Ag₃PW₁₂O₄₀. In Figure 1f, the Raman scattering activity (SERS) of Ag nanoparticles, which can be attributed to the surface-enhanced Raman scattering activity (SERS) of Ag nanoparticles,\textsuperscript{[55, 56]} The UV/Vis diffuse reflectance spectra of Ag₃PW₁₂O₄₀, CQDs/Ag₃PW₁₂O₄₀, CQDs/Ag/Ag₃PW₁₂O₄₀, and CQDs/Ag/Ag₃PW₁₂O₄₀ are shown in Figure S5. Clearly, pure Ag₃PW₁₂O₄₀ absorbs solar energy at wavelengths shorter than 400 nm. CQDs/Ag₃PW₁₂O₄₀ exhibited intense surface plasma resonance (SPR) in the region of λ = 400–550 nm as a result of the introduction of Ag nanoparticles. In comparison to pure Ag₃PW₁₂O₄₀, CQDs/Ag₃PW₁₂O₄₀ and CQDs/Ag/Ag₃PW₁₂O₄₀ displayed consistently strong absorption in the range of λ = 420–800 nm. These data suggest that these two
complex photocatalysts will absorb more solar light for the CQDs to use.

The quantum efficiency of overall water splitting by the photocatalyst as a function of wavelength of the incident light is shown in Figure 2a. The quantum efficiency decreases with increasing wavelength, and the longest wavelength suitable for overall water splitting coincides with the absorption edge of the CQDs/Ag/Ag₃PW₁₂O₄₀ nanocomposites. This indicates that the reaction proceeds by light absorption by the solid solution. The quantum efficiency of overall water splitting on this catalyst system is caused by the interaction between Ag₃PW₁₂O₄₀ and Ag nanoparticles in visible light. If CQDs/Ag/TiO₂ nanocomposite (Figure S10) was used as the photocatalyst, little or no H₂ or O₂ was evolved under visible-light irradiation (Figure S11) as TiO₂ cannot be excited by visible light. Furthermore, no H₂ evolution occurred if CQDs/Ag/AgNO₃ nanocomposite was used as the photocatalyst for water splitting (Figure 3b). At the same time, this reaction system produces ≈300 μmol O₂ after 24 h in the first run, but less O₂ evolution was observed in the second run (Figure 3b). This phenomenon was a result of the slight decomposition of AgNO₃ (Ag⁺ to Ag⁰) during water oxidation in visible light even though CQDs reduce the photocorrosion of AgNO₃ substantially. Thus, in the CQDs/Ag/Ag₃PW₁₂O₄₀ system, O₂ evolution can be attributed to water oxidation by Ag₃PW₁₂O₄₀ excited by visible light. The experiments suggest that H₂ evolution in the CQDs/Ag/Ag₃PW₁₂O₄₀ catalyst system is caused by the interaction between Ag₃PW₁₂O₄₀ and Ag nanoparticles in visible light. If a Ag₃PW₁₂O₄₀/SiO₂/Ag (Ag₃PW₁₂O₄₀ as core, SiO₂ as shell, and Ag nanoparticles on the surface of SiO₂; Figure S12) nanocomposite was used as the photocatalyst, there was no H₂ (or O₂) evolution (Figure S13).

In subsequent experiments, the photoinduced electron-transfer properties of CQDs irradiated under visible light were investigated. The PL of CQDs excited by λ = 450 nm with an emission located at λ = 509 nm could be quenched by either electron acceptor or electron donor molecules in solution, which confirms that CQDs are excellent as both electron donors and acceptors under visible light. CQDs exhibit a broad luminescence peak at approximately λ = 509 nm with excitation at λ = 450 nm, and the emission intensities were thermore, a similar photocatalytic experiment was performed under 450 W high-pressure Hg lamp irradiation. The corresponding hydrogen evolution rate was up to 650 μmol h⁻¹ (Figure S7). These results demonstrate clearly that CQDs/Ag/Ag₃PW₁₂O₄₀ nanocomposites can serve as photocatalysts for solar water splitting.

CQDs, Ag₃PW₁₂O₄₀, and CQDs/Ag₃PW₁₂O₄₀ nanocomposites, respectively, were used as photocatalysts with visible-light irradiation for water splitting in control experiments. There is little or no gas evolution for the reaction in which CQDs served as the photocatalyst (Figure S8). There was trace O₂ evolution but no H₂ evolution in the first run of the reaction in which Ag₃PW₁₂O₄₀ was used as the catalyst (Figure S9). In the next run, there was no gas (O₂ and H₂) evolution. In the reaction in which CQDs/Ag₃PW₁₂O₄₀ nanocomposites were used as catalysts, the rate of O₂ evolution in the first run was ≈1.86 μmol h⁻¹, whereas H₂ evolved more slowly (only ≈1.90 μmol h⁻¹) as the reaction proceeded (Figure 3a). Ag nanoparticles were formed under visible light from the excess AgNO₃ in CQDs/Ag₃PW₁₂O₄₀ nanocomposites. Thus, the rates of H₂ and O₂ evolution in the second run were ≈3.66 and 1.92 μmol h⁻¹, respectively. Both H₂ and O₂ evolved steadily and stoichiometrically as the reaction proceeded. These results demonstrate that the synergistic reaction of CQDs, Ag, and Ag₃PW₁₂O₄₀ plays a key role in overall water splitting.

Serial control experiments were performed to further investigate the mechanism of water splitting on the CQDs/Ag/Ag₃PW₁₂O₄₀ photocatalyst. If CQDs/Ag/TiO₂ nanocomposite was used as the photocatalyst, little or no H₂ or O₂ was evolved under visible-light irradiation (Figure S11) as TiO₂ cannot be excited by visible light. Furthermore, no H₂ evolution occurred if CQDs/Ag/AgNO₃ nanocomposite was used as the photocatalyst for water splitting (Figure 3b). At the same time, this reaction system produces ≈300 μmol O₂ after 24 h in the first run, but less O₂ evolution was observed in the second run (Figure 3b). This phenomenon was a result of the slight decomposition of AgNO₃ (Ag⁺ to Ag⁰) during water oxidation in visible light even though CQDs reduce the photocorrosion of AgNO₃ substantially. Thus, in the CQDs/Ag/Ag₃PW₁₂O₄₀ system, O₂ evolution can be attributed to water oxidation by Ag₃PW₁₂O₄₀ excited by visible light. The experiments suggest that H₂ evolution in the CQDs/Ag/Ag₃PW₁₂O₄₀ catalyst system is caused by the interaction between Ag₃PW₁₂O₄₀ and Ag nanoparticles in visible light. If a Ag₃PW₁₂O₄₀/SiO₂/Ag (Ag₃PW₁₂O₄₀ as core, SiO₂ as shell, and Ag nanoparticles on the surface of SiO₂; Figure S12) nanocomposite was used as the photocatalyst, there was no H₂ (or O₂) evolution (Figure S13).
Figure 3. Evolution of H₂ (solid squares, black) and O₂ (solid circles, red) from 100 mL pure water using a) 0.5 g CQDs/Ag₃PW₁₂O₄₀ and b) 0.5 g CQDs/Ag₃PO₄ nanocomposites as photocatalysts in a glass cell under visible-light irradiation (cutoff filters were used to remove light of λ < 420 nm from a 300 W Xe lamp). The gases evolved were determined by GC. c) (aνhν)² vs. hν curve of Ag₃PW₁₂O₄₀. d) UPS spectra of Ag₃PW₁₂O₄₀.

The optical band gap of a crystalline semiconductor can be estimated from the curve of converted (aνhν)² versus hν (Figure 3 c) from the UV/Vis spectrum, in which a, h, and ν are the absorption coefficient, the Plank constant, and light frequency, respectively. The direct band gap energy (Eᵥ) of the POMs was determined to be 3.2 eV by measuring the x axis intercept of an extrapolated line from the maximum slope of the curve. In addition, ultraviolet photoelectron spectroscopy (UPS) was used to determine the absolute value of the work function (Fermi level, Eᵥ) and ionization potential, which is approximately equivalent to the valence band energy (Eᵢ). The work function of POMs was calculated to be 4.8 eV by subtracting the secondary electron onset position of the He I UPS spectra (Figure 3 d) from the excitation energy (21.22 eV). The Eᵢ with respect to Eᵥ was extrapolated by the linear portion of the low binding energy side of the appropriate emission peak to the energy axis. Then, Eᵢ was estimated to be 2.6 eV below the Fermi level. The Eᵦ and Eᵢ (conduction band energy) of POMs [eV] can be converted to the electrochemical energy potential [V] based on the reference standard for which 0 V versus the normal hydrogen electrode (NHE) is 4.4 eV versus Eᵥ (vacuum level).

In general, a POM with a band gap of 3.2 eV cannot be excited by visible light to form photoelectrons and photoholes in visible light, but POMs can be transferred into heteropoly blue (PB, a reduced state of POMs) under visible light (Figure S20). PB is a reduced state of a POM that has a mixed valence. \[57, 58\] This result confirms the successful hybridization between Ag/Ag₃PW₁₂O₄₀ nanospheres and CQDs nanosheets.

The CQDs can also stabilize the present complex catalyst. Further control experiments indicated that after 12 h, the solid Ag/Ag₃PW₁₂O₄₀ catalyst without CQDs will dissolve into water and give a clear solution (Figures S17–S19). However, the CQDs/Ag₃PW₁₂O₄₀ catalysts are very stable in solution, which suggests that the insoluble CQDs layer on the surface of Ag₃PW₁₂O₄₀ protects Ag₃PW₁₂O₄₀ effectively from dissolution in aqueous solution.

is that the C=O stretching mode of the carboxylic acid groups shifts from ν = 1639 to 1622 cm⁻¹. A peak shift of approximately 17 cm⁻¹ to lower frequency is observed. The reason is that the length of the covalent –C=O bond of the CQDs has stretched, which indicates evident interactions between the Ag/Ag₃PW₁₂O₄₀ nanoparticles and CQDs. \[57, 58\] This result confirms the successful hybridization between Ag/Ag₃PW₁₂O₄₀ nanospheres and CQDs nanosheets.

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The production of PB as an intermediate energy level may lead to the excitation of POMs by visible light. To confirm the existence of the intermediate states, the UV/Vis absorption spectra of the PB sample (PW$_{12}$O$_{40}$$^{3-}$) were measured under N$_2$ protection. The PB sample had clear absorption peaks at $\lambda = 466$ and 738 nm (Figure S21). The PB sample was further investigated by cyclic voltammetry (CV) measurements (Figure S22).

The electrochemical behavior of the carbon paste electrode modified by the catalyst (CQDs/Ag/Ag$_3$PW$_{12}$O$_{40}$) was investigated in water with a scan rate of 0.005 V s$^{-1}$. In the potential range of $-0.74$ to 0.30 V, the reversible redox peaks exist at $-0.072$ and 0.005 V, respectively, attributable to the redox process of W VI/V.

The frontier molecular orbital energy levels of [PW$_{12}$O$_{40}$]$^{3-}$, [PW$_{12}$O$_{40}$]$^{4-}$ and [PW$_{12}$O$_{40}$]$^{5-}$ were calculated by DFT methods (Figure S23). The HOMO and LUMO energies of oxidized [PW$_{12}$O$_{40}$]$^{3-}$ are $-7.143$ and $-4.411$ eV, respectively. Compared with [PW$_{12}$O$_{40}$]$^{3-}$, the energy of the $\alpha$-HOMO is increased to $-4.143$ eV for the one-electron-reduced polyanion [PW$_{12}$O$_{40}$]$^{4-}$ and $-3.882$ eV for the two-electron-reduced polyanion [PW$_{12}$O$_{40}$]$^{5-}$ . The energy of the $\beta$-HOMO is also increased to $-6.837$ eV for [PW$_{12}$O$_{40}$]$^{4-}$ and $-6.540$ eV for [PW$_{12}$O$_{40}$]$^{5-}$ . The LUMO energy levels are also increased significantly from oxidized [PW$_{12}$O$_{40}$]$^{3-}$ to one- and two-electron-reduced polyanions. In addition, the HOMO of [PW$_{12}$O$_{40}$]$^{3-}$ is composed of $p$ orbitals of O atoms, whereas the LUMO is formed mainly by $d$ orbitals of W atoms with some contributions from the $p$ orbitals of the O atoms. For the reduced polyanions [PW$_{12}$O$_{40}$]$^{4-}$ and [PW$_{12}$O$_{40}$]$^{5-}$, the $\alpha$-HOMOs are localized on W and O atoms, whereas the $\beta$-HOMOs are similar to that of [PW$_{12}$O$_{40}$]$^{3-}$.

Even if the present simple DFT calculations only give a rough result, we still can confirm that the positions of the energy levels of PB are located between the conduction and valence bands.

The catalytic activity of the modified glassy carbon electrodes was further studied initially by CV in a standard three-electrode cell equipped with a Ag/AgCl reference electrode and a Pt wire counter electrode that contained a phosphate buffer (PBS) in air at room temperature (Figure 4). As expected, the bare glassy carbon electrode was catalytically inert (red line in Figure 4a). In contrast, the glassy carbon electrode modified with CQDs/Ag/Ag$_3$PW$_{12}$O$_{40}$ exhibited an oxidation wave at 1.0 V followed by the onset of a catalytic current at applied voltages greater than 1.20 V caused by water oxidation. The oxygen-evolving activity of a catalytic current at applied voltages greater than 1.20 V is totally inactive towards O$_2$ production (Figure 4b, red trace).

Based on our experimental results, a rough energy-level diagram of each part of this complex system is shown in Scheme S1. A reaction mechanism is proposed to explain the photocatalytic water splitting by this composite photocatalyst in visible light (Scheme 1). In our system, POMs play a key role in water splitting. PB could be formed under visible-light irradiation in a complex system. The absorption of visible light to be addressed on an electrode device engineered appropriately. Under the same conditions, bare glassy carbon electrode is totally inactive towards O$_2$ production (Figure 4b, red trace).
happens at the Ag nanoparticle surface because of the SPR effect, and the absorbed photons are separated efficiently into electrons and holes. Given the dipolar character of the surface plasmonic state of Ag nanoparticles, these electrons effect the one- or two-electron reduction of POM into PB, and the holes will act as positive charge centers on the Ag₃PW₁₂O₄₀ surface.⁶⁴–⁶⁵ Also, PB could be further excited by visible-light irradiation and transfer electrons to the conduction band of POM as reported previously.⁶⁶–⁶⁸ These loosely bound electrons in the intermediate energy levels act as a “color center” in Ag₃PW₁₂O₄₀ which can be stabilized transiently and further photoexcited to the conduction band of Ag₃PW₁₂O₄₀ by photons in visible regions. However, the photoexcited electrons in the conduction band of Ag₃PW₁₂O₄₀ are thermodynamically feasible for water splitting. The Ag nanoparticles here play two vital roles for the enhanced photocatalytic water splitting efficiency: (1) the strong SPR-induced electric fields are localized near the Ag/Ag₃PW₁₂O₄₀ interfaces, which can cause electron generation and enhance the separation efficiencies of electron–hole pairs in Ag₃PW₁₂O₄₀²⁵ and (2) the electrons in the conduction band of Ag₃PW₁₂O₄₀ can inject into the contractile Ag nanoparticles, which act as an electron buffer and catalytic site for hydrogen generation. The insoluble CQDs layer on the surface of Ag₃PW₁₂O₄₀ protects it effectively from dissolution in aqueous solution, which thus enhances the structural stability of CQDs/Ag₃PW₁₂O₄₀ during the photocatalytic processes. Also, the CQDs (a schematic energy-level model is shown on the right in Scheme 1), which have an excellent charge-storing ability, can also act as an electron buffer to promote the electron extraction from the conduction band of Ag₃PW₁₂O₄₀ and subsequently decrease the electron–hole recombination rate in Ag₃PW₁₂O₄₀ and increase the optical absorption of Ag₃PW₁₂O₄₀ for the increased unoccupied occupied states in the conduction band of Ag₃PW₁₂O₄₀.²⁵,²⁶ Finally, CQDs can enhance electron transport because of their photoinduced electron-transfer properties.²⁵,²⁶ All of these positive roles of Ag, CQDs, and Ag₃PW₁₂O₄₀ are responsible for the excellent photocatalytic water-splitting properties of our composite CQDs/Ag/Ag₃PW₁₂O₄₀ photocatalysts in visible light.

Conclusions

We have developed a facile approach to synthesize CQDs/Ag/Ag₃PW₁₂O₄₀ complex photocatalysts. Significantly, these noble photocatalysts promote overall water splitting without electron acceptors or hole scavengers in visible light. The synergistic effects of CQDs, Ag, and Ag₃PW₁₂O₄₀ lead to the overall water splitting on CQDs/Ag/Ag₃PW₁₂O₄₀ nanocomposites. In the present system, the photoelectron on Ag₃PW₁₂O₄₀ can transfer easily to the surface of Ag particles and then react with H₂O to generate H₂. In contrast, the evolution of O₂ should arise from the oxidation of H₂O on the valence band of Ag₃PW₁₂O₄₀. CQDs can enhance electron transport and protect Ag₃PW₁₂O₄₀ from dissolution into water, which allows the full solar spectrum to enhance the photocatalytic activities of CQDs/Ag/Ag₃PW₁₂O₄₀. Here, the overall water-splitting performance of CQDs/Ag/Ag₃PW₁₂O₄₀ may provide a new strategy to design new photocatalysts for energy sources and environmental issues.

Experimental Section

Photocatalyst characterization

All chemicals were purchased from Sigma–Aldrich. SEM images and EDS were recorded by using an FEI-quantu 200 scanning electron microscope with an acceleration voltage of 20 kV. TEM and HRTEM images were obtained by using an FEI/Philips Tecnai 12 BioTWIN transmission electron microscope and a CM200 FEG transmission electron microscope, respectively. The normal TEM samples were prepared by dropping the solution onto a copper grid with a polyvinyl formal support film and dried in air. The crystal structure of the resultant products was characterized by powder XRD by using an X’Pert-ProMPD (Holand) D/max-γA X-ray diffractometer with CuKα radiation (λ = 0.154178 nm). Raman spectra were collected on an HR 800 Raman spectroscope (J Y , France) equipped with a synapse CCD detector and a confocal Olympus microscope. The spectrograph uses 600 g mm⁻¹ gratings and a 633 nm He-Ne laser. RT UV/Vis absorption spectra were recorded by using a Lambda 750 (PerkinElmer) spectrophotometer in the wavelength range of 200–1000 nm. Gases (H₂ and O₂) evolution were analyzed by GC (Shimadzu GC-14C), with nitrogen as a carrier gas) equipped with a 5 Å molecular-sieve column and a thermal-conductivity detector. The samples used for UPS measurement were powders. UPS samples were prepared by pressing CQDs/Ag/Ag₃PW₁₂O₄₀ powder on a piece of indium wafer. UPS measurements were performed with an unfiltered Hel (21.22 eV) gas discharge lamp and a total instrumental energy resolution of 100 meV.

Photocatalyst preparation

CQDs were synthesized by the typical electrochemical method.⁵⁰ Two graphite rods (99.99 %, Alfa Aesar Co. Ltd.) were inserted into the ultrapure water as the anode and cathode. Static potentials of 30 V were applied to the two electrodes by using a direct current power supply. After 120 h of continuous stirring, a dark yellow solution formed in the reaction cell. After filtration, CQDs with an electrospray were dried on an HR 800 Raman spectroscope (J Y , France) equipped with a synapse CCD detector and a confocal Olympus microscope. The spectrograph uses 600 g mm⁻¹ gratings and a 633 nm He-Ne laser. RT UV/Vis absorption spectra were recorded by using a Lambda 750 (PerkinElmer) spectrophotometer in the wavelength range of 200–1000 nm. Gases (H₂ and O₂) evolution were analyzed by GC (Shimadzu GC-14C), with nitrogen as a carrier gas) equipped with a 5 Å molecular-sieve column and a thermal-conductivity detector. The samples used for UPS measurement were powders. UPS samples were prepared by pressing CQDs/Ag/Ag₃PW₁₂O₄₀ powder on a piece of indium wafer. UPS measurements were performed with an unfiltered Hel (21.22 eV) gas discharge lamp and a total instrumental energy resolution of 100 meV.

CQDs/Ag/Ag₃PO₄ was prepared by the addition of CH₃COOAg (0.25 g) and polyvinylpyrrolidone (0.5 g, PVP, MW = 50 000) to a flask that contained CQDs aqueous solution (25 mL), and the mixture was heated to reflux at 90 °C. Na₂HPO₄ aqueous solution (0.075 M) was added dropwise to the above solution. After reaction for 3 h, the obtained samples were washed with water to remove the CH₃COO⁻ and PVP, and finally dried in an oven at 50 °C for 12 h.

The CQDs/Ag composite was obtained by the dropwise addition of AgNO₃ solution (500 μL, 10 mm) to CQDs solution (20 mL) with vigorous magnetic stirring in the dark at RT. The resultant mixture was irradiated under a Xe lamp with constant magnetic stirring at RT for 6 h. Then, the CQDs/Ag composite was centrifuged at 12,000 rpm for 15 min, washed three times with deionized water and ethanol, respectively, and the obtained sample was dried 6 h at 60 °C.

Photocatalyst activity
A reactant solution that consisted of catalyst (0.5 g) and pure water (100 mL) was evaporated several times prior to the reaction to ensure that no air remained in the reaction vessel. During the visible-light irradiation, the evolved gases were analyzed by a gas chromatograph connected directly to the closed gas-circulation system. Visible light was obtained by using cutoff filters to remove light (300 W, Xe lamp) of λ < 420 nm.

The AQE for H₂ evolution was measured by using several cutoff filters modified with 10 mm modified with 10 μm (Figure S21).

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The CV tests were performed by using a Model CHI 660C workstation. Visible light was obtained by using cutoff filters to remove light (300 W, Xe lamp) of λ < 420 nm.

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The number of incident photons (Nₐₐₐ) is 9.89×10¹⁸ calculated by Equation (2). The produced H₂ molecules reach to CQDs solution (20 mL) with vigorous magnetic stirring in the dark at RT. The resultant mixture was irradiated under a Xe lamp with constant magnetic stirring at RT for 6 h. Then, the CQDs/Ag composite was centrifuged at 12,000 rpm for 15 min, washed three times with deionized water and ethanol, respectively, and the obtained sample was dried 6 h at 60 °C.

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Electrochemical tests
The CV test shown in Figure 4, the electrolyte was ultrapure water (pH 7), and a Ag/AgCl electrode was used as the reference electrode. The scan rate was 0.02 V s⁻¹. A test was performed in 0.5 M H₂SO₄ solution with a saturated calomel electrode (SCE) as the reference electrode at the speed of 0.005 V s⁻¹ (Figure S21).

Acknowledgements
This work is supported by the National Basic Research Program of China (973 Program) (2012CB825800, 2013CB932702), the National Natural Science Foundation of China (51132006), a Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), a Suzhou Planning Project of Science and Technology (ZXG2012028), and a project funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions.

Keywords: photochemistry · polycrystallates · quantum dots · silver · water splitting